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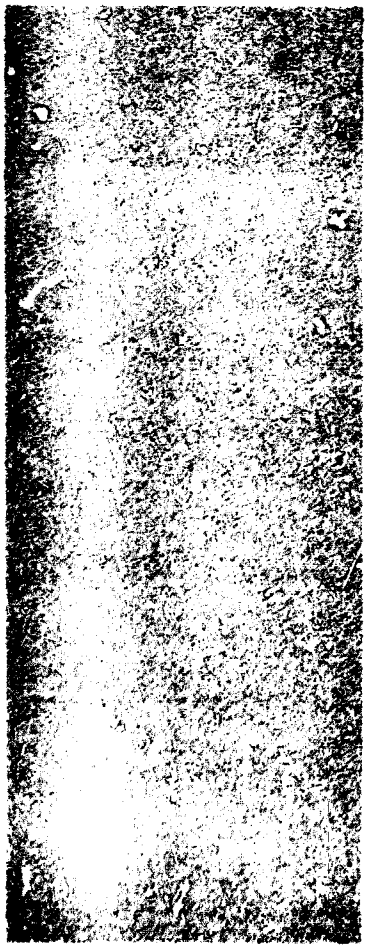
ORNL-5100

ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

Period Ending November 30, 1975



OAK RIDGE NATIONAL LABORATORY

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ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
For Period Ending November 30, 1975

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FEBRUARY 1976

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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Preface

We concluded the Preface to last year's annual report with the statement that we anticipated an increasing involvement in coal conversion technology programs in 1975. This expectation has turned out to be well founded. The Division's strong program in the characterization and measurement of complex mixtures of organic compounds found in tobacco smokes and condensates has been extended to equally complex mixtures of organic compounds from coal conversion processes, with particular emphasis on environmental and health considerations. As a consequence of this extension, we have established collaborative working relationships with several of the ERDA research centers, such as those at Pittsburgh, Laramie, and Bartlesville, and also with private industrial organizations, through exchange of samples and methodologies. A new program was started to investigate instrumentation and methods for characterizing products from oil shale processing, oil refining, and geothermal energy sources for environmental considerations; this study is funded by EPA pass-through funds and by the Division of Biomedical and Environmental Research, ERDA. Much of our research and development continues to be collaborative in nature, a characteristic of productive and efficient analytical chemistry. For example, we maintain close ties with the Chemical Technology and Metals and Ceramics Divisions in their reactor programs; our environmental and health program contributions are mainly to the Environmental Sciences Division; and we have a developing involvement with the Biology Division in their carcinogenic and bioassay testing programs.

The main objective of our analytical chemistry research remains the same — to investigate those techniques that provide multianalyses with accompanying high reproducibility. This goal is not likely to change, since the need for analytical data in both quantity and quality continues to be of highest priority in ERDA's programs. In this report, the accounts of our many programmatic activities reflect our continuing efforts to keep pace with this requirement.

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Part A. Analytical Research and Development

I. Advanced Methodology and Instrumentation

H. H. Ross, Head

The present programs of the Advanced Methodology and Instrumentation Group are best described as ambitious, innovative, and responsive. In no recent reporting period have we been able to discuss as many new and significant research directions. We are especially pleased to note that a number of our current tasks were generated in response to problem or technology areas that were only recently recognized as being fundamental in both application and scope. For example, our previous work in instrumentation suggested that large-scale integrated (LSI) circuits would play an important role in the future development of sophisticated "smart" analytical systems. Thus we initiated a program to demonstrate the potential of such LSI devices in chemical applications. Significant progress has been made in this pursuit, and our leadership has already been recognized. A closely related task, the development of "experimental language programming," appears to be unique and promises to greatly simplify scientist machine interaction. Our work on multielement analysis has been pushed on several fronts. We have completed an evaluation of the design of an echelle-crossed dispersion spectrograph for use with a solid-state array detector. Testing of various types of detectors has also begun. We are now considering the feasibility and methodology of interfacing these two optical components. A high-power microwave generator, a truly impressive piece of equipment, has been acquired by the group this year. This unit is capable of generating a 2.5-kW plasma that promises to have important applications as an in-line spectroscopic source. The injection of aerosols into the plasma is under investigation. Other new projects include the development of a computer-based data management system for use within the service groups of the Division, an investigation of new separation and detection techniques in liquid chromatography, and several approaches to the determination of sulfate in the atmosphere.

Although we tend to experience a special excitement associated with new research challenges, we do not forget that these challenges can also arise in our more mature, continuing programs. The extensive methodology developed for low-level determination of arsenic is finding application in a new program in the Environmental Sciences Division, and a cooperative effort between the divisions has been established. The implementation of our pattern recognition effort has also come to fruition; actual data from the Tobacco Smoke Program are being processed with interesting and potentially valuable results. Our gas chromatograph microwave-excited spectrometer has again demonstrated its ability to yield analytical results difficult to obtain in any other way, and our fluorometric instrument for the analysis of uranium is being implemented throughout the country as the "system of choice." Finally, we continue to carry out an active effort on the forefront of electrochemical research. In the past year, new procedures were studied for the determination of lead (at the 10^{-11} level!) and for the predictive coulometry of uranium. An investigation of heterogeneous electron transfer reactions was also completed that suggests that an established theory on transfer mechanisms may not always be valid.

ADVANCED SYSTEMS DEVELOPMENT

Applications of large-scale integrated circuits. Work has begun on a program to assess the usefulness of various LSI circuits in the construction of analytical instruments to be used in support of programmatic research work as well as for routine analyses. Utilizing capabilities inherent in LSI circuits, our concept is to permit a researcher to sit at his teletypewriter and describe his measurement and control requirements by actually configuring an instrument. His vocabulary would be composed of control-oriented statements. This approach differs from computer-researcher dialog design in that, when finished with the program, the researcher has "built" an instrument that will actually perform, rather than having generated only a piece of paper. Various functions of the "instrument" can be tested while "construction" proceeds. Armed with a knowledge of the primitive instrument's adequacies and deficiencies, the instrument designer can then proceed to optimize performance if a stand-alone device is required.

Initial efforts toward accomplishment of our long-range goal involve the production of a demonstration instrument. The Environmental Analyses Laboratory receives a large number of water samples for which phosphate analyses are required. We are in the construction stage of a project to develop a "smart" photometer. This photometer will be self-calibrating to the range of sample concentrations it has received and self-diagnostic of the quality of results or outright failure to achieve acceptable calibration limits. The results will be printed, in conjunction with an identifying sample code. The photometric analysis is relatively simple. We can, therefore, focus our attention on instrument development.

Calculations will be performed using an MOS Technology, Inc., model MPS 2529-103 calculator chip. This chip provides up to 40 functions, most of which execute with a single entry. For the present design we will need only a small fraction of the total calculation capability. The use of the chip introduces both powerful computational capability and circuit complexity. The calculator chip was, of course, developed for the hand-held calculator, where speed was sacrificed for accuracy of data entry via keyboard. To assure adequate throughput for the present instrument, the chip had to be buffered on its input and output with fast-entry shift registers. The circuitry to accomplish the automatic entry of data required 46 additional integrated circuit packages. One of our goals is to ascertain how much of the added circuitry could best be incorporated in the same package as that with the calculator chip.

Most of the subassemblies for the instrument have been constructed. Design is essentially complete, and testing will begin within the next quarter. Our work to this point was presented at the 170th ACS Annual Meeting in Chicago, April 25–29, 1975.

Although the overall project is a rather ambitious one, we believe that it will not only teach us how to apply the new capability proffered by LSI circuits, but will give us a valuable assessment of their place in the design of new instruments. As we acquire experience with the concept of instrument synthesis by the experimenter via software, we will further our ability to assess and apply advances of this new electronic technology to a variety of challenging analytical problems. (T. R. Mueller)

Multielement spectroscopy. Our previously reported work on the development of Hadamard transform spectroscopy[1] suggested that, for multielement analysis in the ultraviolet and visible regions, no real experimental advantage exists over conventional scanning spectrometry. This conclusion, however, did not dampen our enthusiasm for the development of multielement techniques, because of the enormous potential application of such methodology. An alternate approach to the problem, which we also had under consideration, immediately became more attractive -- the coupling of an echelle-crossed dispersion spectrograph with one variety of the new solid-state array detectors.[2,3] Unfortunately, neither of these optical subsystems existed in a form suitable for spectroscopic interfacing. Thus we redirected our multi-

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[1] N. M. Larson, Y. Talmi, and R. V. Crosmun, "Theoretical Comparison of Singly Multiplexed Hadamard Transform Spectrometers and Scanning Spectrometers," *Appl. Opt.* 13, 2662 (1974).

[2] Y. Talmi, "Applicability of TV-Type Multichannel Detectors to Spectroscopy," *Anal. Chem.* 47, 658A (1975).

[3] Y. Talmi, "TV-Type Multichannel Detectors," *Anal. Chem.* 47, 697A (1975).

element effort toward the practical realization of both of these subunits.

The proposed research program was both ambitious and expensive. However, we felt that if we could demonstrate real progress toward the objective, external sources of funding for development and application could be obtained. Thus a "seed-money" proposal that outlined the project was prepared; the proposal was accepted and seed-money funding was granted.

The overall project was broken down into two main development objectives – the optical design and construction of a crossed dispersion echelle spectrometer and a spectroscopic evaluation of various solid-state imaging devices. We elected to work on both areas simultaneously so that advances in one component could be evaluated in terms of the other. An extensive theoretical design of the echelle system has been completed and is being prepared for publication. The design was optimized for use with a solid-state charge injection device having about 46K photodiodes in an array measuring 11.45 by 8.75 mm. Some of the design parameters considered include blaze angle of the echelle grating, spectral range, detector size, resolution, aberrations, and cross dispersion mechanics. At present, we are not sure of the need to continue this phase of the project by actual fabrication of the spectrometer; a new echelle system has recently become commercially available that may satisfy experimental demands.

The second phase of the project, the evaluation of array detectors, is in a very preliminary stage of development. A number of screening tests have been carried out with various solid-state devices to gain familiarity with their operating characteristics and instrumental demands. We have succeeded in producing optical spectra with the devices and in measuring some of the signal and noise parameters. This work will be expanded in the coming year with particular emphasis on applications development. (Y. Talmi, V. E. Norvell)

Microwave-excited plasmas for in-line monitoring. As an extension of the work on the microwave excitation source for analytical in-line spectroscopy,[4] a high-powered microwave generator (2.5 kW at a frequency of 2.45 GHz) was purchased. This generator is being used to investigate the possibility of direct injection of liquid or solid samples into an argon plasma. The success of this investigation will make possible the direct in-line analysis of process streams.

It was found previously that with low-power (30- to 160-W) generators *the amount of water that could be introduced in the plasma without quenching the* plasma was directly related to the power available; only 5 μg of water could be introduced at the 160-W level. We also determined that the emission lines from an element or molecule in the plasma were reduced in intensity by a factor of 3 upon introduction of water vapor. This reduction of intensity can be eliminated by the incorporation of HCl into the samples. The enhancement effect is now being investigated with the high-powered generator. The stability of the plasma at low pressure (5 to 30 mm Hg) is much greater than at atmospheric pressure for both the low- and high-power generators, so all future work will be carried out at subatmospheric pressures. The current research effort is concerned with six major areas: (1) radiation leakage and shielding, (2) antenna design for the maximum coupling with the plasma and minimum radiation leakage, (3) development of a method of injecting solid and liquid samples into the plasma (we are currently investigating the use of an ultrasonic aerosol generator to reduce dissolved solids to micron-size particles), (4) effect of chloride ions on the emission intensity and other common-ion effects, (5) selection of the optimum plasma containment vessel diameter and operating pressure, and (6) measurement of plasma temperature.

Our first attempts to measure the temperature of a 400-W discharge in argon at atmospheric pressure was by use of the O-H rotational band emission method and by the argon atomic line emission method.[5] It was found that the temperature measured by the former method (1976°K) was much lower than that measured by the latter method (4628°K). This difference is presumably due to the failure of the discharge to attain complete thermodynamic equilibrium. In previous temperature measurements of porous-cup discharges,[6] where complete thermodynamic equilibrium is attained, observed O-H band temperatures were in the 4000 to 4500°K range. To check the O-H band method, a similar technique was used to measure the temperature of an oxyhydrogen flame. The value obtained (2825°K) is typical of such flames.[7] Temperature measurement of the low-

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[4] 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).

[5] Y. Talmi and D. T. Bostick, "The Determination of Arsenic and Arsenicals," *J. Chromatogr. Sci.* 13, 231 (1975).

[6] C. Feldman, "Sample Transport and Temperature Studies in Porous-Cup Discharges," *Spectrochim. Acta* 9, 19 (1957).

[7] F. Pungor, *Flame Photometry Theory*, Van Nostrand, New York, 1967.

pressure plasma is now in progress. (J. E. Strain, C. Feldman, D. A. Batistoni)

Computer-based data management system. The Analytical Chemistry Division creates many records of the results of chemical-physical analyses on a wide variety of materials in support of research and development work at the Laboratory. During a 12-month period ending September 30, 1974, a total of 178,411 results were reported by the Division from its several service laboratories. The records must be kept accurately, they must be updated continuously, and they must be accessible readily. At the end of each month the records are summarized for cost accounting and distribution of charges. At present the records and reports are handled in the main by manual data methods.

Computerization of a data management system would reduce the large amount of manual data handling and would increase the effectiveness and efficiency of the Division considerably. As an initial step toward development of a data management system for the divisional service laboratories, we are acquiring a programmable ("intelligent") remote terminal for accessing one of the time-sharing computer services available at ORNL – either the DEC system 10 computer or the time-sharing option on the IBM 360 computer. An intelligent remote terminal is one containing an integral microprocessor and some form of local bulk storage. The microprocessor allows off-line data entry and editing, reduces the amount of connect time, and eliminates some of the difficulties caused by nonaccessibility and malfunction of the main computer.

To get a head start with the design of computer programs for a data management system and to gain some experience with cassette digital data recording, we have set up an 8K PDP-8/I minicomputer and a Sykes Compu/Corder 100-cassette unit to simulate the remote terminal. We have successfully formatted audioquality cassette magnetic tapes and have found it possible to READ/WRITE with a high degree of reliability. The audioquality tapes are far less expensive than certified, digital-quality, cassette tapes. When complete, the data management system will enable the Division to offer better and faster customer service. (R. W. Stelzner)

Liquid chromatography. A liquid chromatography research and development effort was recently initiated which is proceeding along three lines: (1) development of new and improved detectors, (2) development and characterization of new stationary phases, and (3) application to particular problems determined by Divisional and Laboratory programs.

Separation and determination of polynuclear aromatic hydrocarbons (PAH's) is of importance in the analysis of liquid fuels, products of coal conversion processes, tobacco smoke and tobacco condensates, and for air, water, and soil pollution studies. We have found that PAH's can be separated by liquid chromatography using cross-linked polyvinylpyrrolidone (PVP) as a stationary phase and a polar solvent as an eluant. Elution parameters were established for some 25 compounds as a function of various experimental conditions. In contrast to other chromatographic applications of PVP, in which retention and separation are due to hydrogen bonding, retention of PAH's appears to depend on the degree of aromaticity of the compound. Compounds with one aromatic ring elute before those with two, etc., and partially hydrogenated compounds elute earlier than their completely unsaturated counterparts. Elution volume and resolution depend on the composition of the eluant, flow rate, and temperature. An unusual effect was observed using mixtures of isopropanol and water for elution. As the water content of the eluant was increased, the elution volumes decreased, reaching a minimum with 25% (V/V) water in isopropanol. When the water content was further increased, elution volumes also increased. This observation suggests several possibilities for gradient elution. At elevated column temperatures, we also note elution volumes becoming smaller along with a substantial decrease in plate height and system operating pressure, particularly when using isopropanol as eluant. Temperature programming to minimize separation time and sharpen peaks at the end of the chromatogram thus appears feasible. At low linear flow rates (0.1 to 1 mm/sec), plate heights for most compounds followed the well-known empirical relationship $H = Dv^n$, with values of n between 0.35 and 0.45. Appropriate PVP columns for analytical and preparative separations of complex PAH mixtures are inexpensive, easy to pack and maintain, and are stable for long periods of time. Efficient separations were obtained with a 350 × 6 mm column packed with 63- to 90-μm particles of commercial PVP (Polyclar AT). Isopropanol, a good solvent for most PAH's, was used as eluant at a flow rate of 0.3 ml/min. A typical chromatogram is shown in Fig. 1.1. Capacity factors (k') ranged from 0.5 to 10 for PAH's having from 1 to 5 aromatic rings, and theoretical plate heights were between 0.3 and 0.5 mm (2000 to 3500 plates per meter). We are now evaluating PVP columns for analysis of several kinds of materials. This work has been submitted for publication.

Detectors employed as effluent monitors of chromatographic columns are classified either as specific or

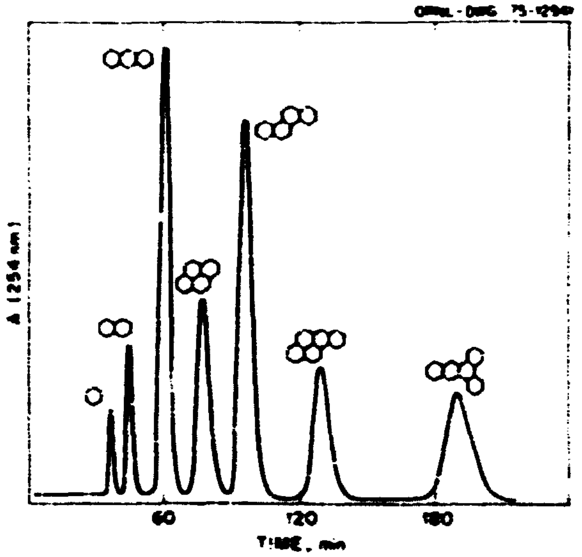

Fig. 1.1. Separation of polycyclic aromatic hydrocarbons by liquid chromatography on polyvinylpyrrolidone stationary phase. Column: 36 × 0.6 cm, packed with 65- to 90-μm PVP particles; eluent: isopropanol, 0.3 ml/min; temperature: 62°C.

universal. A specific detector is one that yields a response to those compounds possessing a unique property, for example, uv absorption at 254 nm. Conversely, a universal detector is based upon some property common to all compounds. The thermal conductivity detector is one example of a universal detector. In gas chromatography, several devices in both classifications are commercially available and are employed on a routine basis. In liquid chromatography, however, such a variety of monitors does not exist. The only detector in widespread use is the uv absorption detector. Because of the need to study materials in uv-absorbing matrices and the simultaneous need for liquid-chromatography monitors with different detection capabilities, we have begun a program to develop detectors that will satisfy this need.

Dielectric constant is a property possessed by all compounds that, with suitable instrumentation, can be translated into essentially a unique response. As the basis for a liquid-chromatography detector, changes in solution dielectric constant, $\Delta\epsilon$, must be measured. This can be accomplished by determining the shift in resonant frequency of an oscillator containing a capacitance cell, with the column effluent serving as the capacitor dielectric and the cell forming a part of the oscillator tank circuit.

A prototype instrument with the detector cell as the frequency-determining capacitor in a Colpitts oscillator was constructed. The frequency shift was converted to a dc signal with a phase-lock-loop integrated circuit. Successful operation with solvents possessing dielectric constants less than 10 was achieved. A detection limit of $0.001\Delta\epsilon$ with a signal-to-noise ratio of 2 was measured. This detection limit, expressed as weight-volume data, corresponds to 45 ppm naphthalene ($\epsilon = 2.5$) in $CHCl_3$ ($\epsilon = 4.8$), 0.16% naphthalene in hexane ($\epsilon = 1.9$), and 0.4% naphthalene in benzene ($\epsilon = 2.3$). Clearly, this detector concept has moderate sensitivity, but more importantly, it functions with sample matrices not amenable to study with the uv monitor.

Although the relationship between the change in dielectric constant and the observed frequency shift is nonlinear, the degree of nonlinearity for typical chromatographic conditions was predicted to be very small. This was verified experimentally. For example, using chloroform as the solvent and naphthalene as the solute (naphthalene ≤1%), statistical information obtained from a linear regression treatment of the frequency shift vs dielectric constant data indicated that a linear response model is valid at the 99% confidence level.

The prototype instrument has the capability of serving as a universal liquid-chromatography detector with low dielectric constant; however, for solvents with dielectric constant larger than 10, the oscillator energy dissipated within the sample increased to the point where regenerative feedback can no longer maintain oscillation. For the solvent-solute systems investigated, this dissipated energy is primarily due to dipole relaxation. Attempts to redesign the basic oscillator circuit in an effort to couple additional energy into the resonant network were unsuccessful. Consequently, development of an instrument based upon an alternate circuit concept was initiated.

The revised circuit consists of four basic elements: (1) a voltage-controlled oscillator–power amplifier, (2) a resonant network containing the detector cell, (3) a phase detector, low-pass filter, and dc gain amplifier, and (4) the frequency-shift readout circuitry. The system will operate via the following feedback mechanism. The sinusoidal output of the voltage-controlled oscillator–power amplifier unit drives a parallel inductive-capacitive resonant network containing the detector cell as the capacitive element. At resonance the phase angle between the current and voltage in this network is zero. A change in the dielectric constant of the solution flowing through the detector cell detunes this resonant network resulting in a nonzero phase angle, whose sign and magnitude are decoded by a phase-sensitive detector. After amplification of the filtered phase detector output, a dc voltage is applied to the tuning control of the voltage-controlled oscillator (VCO). This dc voltage changes the operating frequency of the VCO so as to restore the network containing the detector cell to the resonant condition, thereby completing the feedback process. The analytically useful information is the difference between the VCO operating frequency for the pure solvent and the sample. These frequency-shift data are displayed in a digital and analog format.

Theoretical circuit analysis, design, and construction of all four elements are complete. Successful operation of the high-frequency portion of the instrument with hexane (ϵ = 1.9), pyridine (ϵ = 12), methanol (ϵ = 33), and water (ϵ = 78) has been achieved. The signal amplitude applied to the cell does not vary with dielectric constant, and the resonant frequency observed for each solvent agrees with the a priori calculated values. Measurements of stability or sensitivity have not yet been attempted. Upon assembly of the entire electronic package into a completed instrument, a thorough characterization of this detector will be undertaken. Its application to the study of selected components of coal and/or shale oils will also be pursued.

A second detector concept being evaluated is based on oxidation or reduction of electroactive solutes at an electrode held at a controlled potential and measurement of the current flow. Electrochemical detectors have already been successfully employed to monitor trace quantities of electroactive organic compounds in liquid-chromatography effluents, but usually with an efficiency of only about 5%.[8] Efficiency refers to the fraction of the electroactive molecules in the eluant that are actually oxidized or reduced by the detector, and hence is directly related to sensitivity. We are attempting to develop an improved, small-volume, high-efficiency detector for quantitative analysis. Basically our detector consists of a carbon tubular flow cell packed with carbon microspheres, which is made the working electrode, in contact with a chamber containing the reference and auxiliary electrodes. There are a number of variable factors to be evaluated, including the kind of carbon to use; the length, diameter, and volume of the flow cell; the size, density, surface area, and porosity of the microspheres; and the concentration and flow rate of the electroactive species in the eluant. Although several problems remain to be resolved, we have thus far achieved over 50% efficiency for oxidation of ascorbic acid and over 90% for oxidation of ferrous ion, at reasonable concentrations and flow rates. Qualitatively, as little as 1 ng could be detected. (G. Goldstein, L. N. Klatt)

ANALYTICAL RESEARCH – NEW AND REVISITED

Determination of arsenic. The determination of traces (1 to 2 ppm) of arsenic in the slag from coal-fired power plants is complicated because acid leaching does not extract the arsenic from the slag, and HF attack or fusion introduces unacceptable amounts of contamination. A procedure has been developed which dissolves the slag without adding or removing arsenic. The sample and a 1:1 mixture of concentrated HF and HNO_3 are placed in separate small platinum or Teflon dishes. Both dishes are inserted into a Teflon jar. The jar is tightly capped and placed in an oven at 70 to 80°C for several hours. After cooling, the sample (now a mixture of fluosilicates) is heated to fumes with concentrated H_2SO_4 or $HClO_4$, cooled, and diluted to volume. Comparison analyses carried out on NBS SRM 1633 (fly ash) showed that this procedure does not result in either contamination or loss of arsenic (see Table 1.1).

Traces of nitro-compounds remaining after incomplete wet-ashing of organics with H_2SO_4 + HNO_3 interfere in the subsequent determination of arsenic, using $NaBH_4$, as described below. These nitro-compounds can be destroyed, once the wet-ashing is essentially complete, by adding a few drops of $HClO_4$ to the fuming mixture.

The basic methods used were those of Holak[9] and Braman[10] (volatilization of AsH_3, accumulation in a cold trap, liberation into a stream of helium, and detection of arsenic by arc emission spectroscopy). However, numerous changes and additions were made to improve the reliability and sensitivity of the procedure (see Fig. 1.2). Since constancy of helium flow rate was essential, a flow controller was installed to keep the flow rate constant to within ±0.5%, regardless of downstream fluctuations in back pressure. All

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[8] B. Fleet and C. J. Little, "Design and Evaluation of Electrochemical Detectors for HPLC," *J. Chromatogr. Sci.* **12**, 747 (1974).

[9] V. Holak, "Gas-Sampling Technique for Arsenic Determination by Atomic Absorption Spectrophotometry," *Anal. Chem.* 41, 1712 (1969).

[10] R. S. Braman, L. J. Justen, and C. C. Foreback, "Direct Volatilization-Spectral Emission Type Detection System for Nanogram Amounts of Arsenic and Antimony," *Anal. Chem.* 44, 2195 (1972).

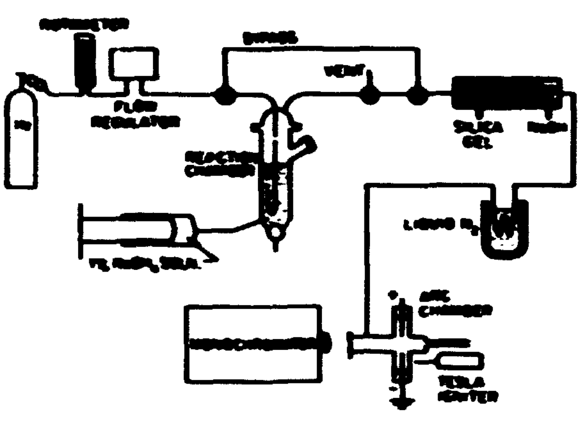

Fig. 1.2. System for determining nanogram quantities of arsenic.

joints were either Swagelok fittings, O-ring glass flanges, or shrinkable tubing. The reducing agent (1% $NaBH_4$ solution) was injected into the sample solution (1 *N* H_2SO_4) with an infusion pump. The reagent solution was delivered into the bottom of the reaction chamber near the gas disperser, to maximize mixing and to ensure the reproducibility of the kinetics of the reduction reaction. Since the helium arc excited arsenic emission most efficiently and reproducibly when H_2 (produced in the reduction) and H_2O vapor were absent, a pathway was provided to bypass the solution cell once accumulation of the AsH_3 in the liquid-nitrogen trap had been completed. Contrary to published experience,[11] "indicating" silica gel was found to give much more reproducible results than Drierite. We believe the presence or absence of impurities in the desiccant may have been the decisive factor in both cases. The trap was an empty W-shaped glass tube immersed in liquid nitrogen. When the accumulated AsH_3 was to be released from the trap, the Dewar flask was removed and the trap exposed to an air stream from a blower. Glass drainage tips, affixed to the lower extremities of the trap, ensured the immediate elimination of any hanging drops of liquid nitrogen after removal of the Dewar flask. The arc chamber was made from 6-mm-OD quartz tubing, narrowed to $\sim$2 mm ID where the helium stream crossed the arc. The helium was introduced near the window and flowed (along the projected optic axis of the monochromator) through the arc to the outlet. This flow pattern prevented clouding of the window by cathode sputtering or other impurities. The electrodes were 0.060-mm W–2% ThO_2 rods of the type used in helium arc welding. The arc was energized by a Jarrell-Ash hollow-cathode power supply. The arc was normally extinguished by the substantial flow of H_2 during the reduction step. Since the open-circuit voltage of the power source was not sufficient to reignite the arc, ignition was accomplished with a Tesla coil placed about 1½ in. from the arc chamber, set to produce a minimum-power silent corona discharge. The arsenic 228.8-nm radiation was observed in the second order with a Jarrell-Ash 0.5-m monochromator. A Hamamatsu R-166 solar-blind photomultiplier was used for detection, thus making it possible to operate at the blaze angle of the existing grating and to enjoy the benefits of second-order dispersion without the interference of visible radiation. Signals were amplified with a small operational amplifier and recorded with a Sanborn model 150 recorder.

At optimum values of the various operating parameters, and using analytical reagent-grade $NaBH_4$, we found the limit of detection to be 60 pg of arsenic. The blank level, found by the logarithmic standard additions procedure,[12] was 300 ± 30 pg. The limit of detection was thus taken to be twice the standard deviation (i.e., 60 pg) for this batch of reagent. Since the baseline was smooth enough to permit considerably greater electrical amplification, it appears probable that a lower detection limit would be possible if purer $NaBH_4$ were available. Peak heights were found to vary linearly with arsenic concentration when plotted on log-log paper. This eliminated the measuring of peak areas that was required by previous procedures.[10]

Day-to-day reproducibility of results at the 5- to 10-ng level (per aliquot) is ±4.3%. Accuracy was tested by comparison analyses with published results on NBS standard reference materials, as shown in Table 1.1. (C. Feldman)

Atmospheric sulfate analysis. A study was initiated recently to evaluate and develop new analytical methodology for the determination of water-soluble sulfate present in atmospheric filter samples. Sulfate analysis is conventionally based on the reaction of inorganic or organic barium salts. However, these methods suffer from lack of specificity and precision. Proposed methods of analysis include a direct kinetic sulfate analysis based on the catalytic effect of sulfate

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[11] D. J. Meier and C. S. Garner, "The Kinetics of the Europium(II)-Europium(III) Exchange Reaction," *J. Phys. Chem.* 56, 853 (1952).

[12] C. Feldman, "Spectrochemical Determination of Hafnium-Zirconium Ratios," *Anal. Chem.* 21, 1211 (1949).

Table 1.1. Determination of total As by AsH_3 evolution and detection of As by emission arc spectroscopy

Sample	ppm As		
	Present work	NBS value	Neutron activation[a]
NBS SRM 1633 (fly ash)	56 (HF-HNO_3 vapor-phase attack) 56 (H_2SO_4 leach)	61	58
NBS SRM 1632 (coal)	5.7	5.9	5.5[b]
NBS SRM 1571 (orchard leaves)	11.9	11 ± 2[c]	
NBS SRM 1577 (bovine liver)	0.055	0.055[d]	

[a] J. Ondov et al., "Elemental Concentrations in the National Bureau of Standards' Environmental Coal and Fly Ash Standard Reference Materials," *Anal. Chem.* 47, 1102 (1975).

[b] This average figure excludes one value withdrawn by the analyst since publication (R. H. Filby, private communication).

[c] Revised value as of July 1975.

[d] Provisional value.

ion on the slow reaction between methylthymol blue and aged zirconium solution. Because sulfate increases the depolymerization of the aged zirconyl species in acidic media, the rate of formation of the free zirconium ion–methylthymol blue couple is proportional to sulfate concentration. The kinetics of the reaction are followed spectroscopically, using the GeMSAEC minature centrifugal fast analyzer. At low concentrations of zirconium (1×10^{-4} *M*) the reaction rate was found to be psuedo first order with respect to sulfate ion concentration over the range 0 to 16 ppm. The precision of the reaction rate was typically 1 to 2%. Work is in progress to evaluate the method further, assess the effect of chemical interferents and procedures for their removal, and automate the analysis.

Because many anions present in air samples, including sulfite, also react under the conditions of most classical sulfate methods, efforts are under way to develop a procedure specific for sulfate. A spectroscopic method has been proposed that is based on the enzymatic transfer of sulfate to a chromogenic substrate. Sulfate concentration would be proportional to the decrease in absorbance of the sample due to the formation of a nonchromogenic sulfate product. In a possible second enzymatic method, sulfate is chemically reduced to sulfite which subsequently reacts, in the presence of an oxidase, to form hydrogen peroxide that may be assayed via a chemiluminescent reaction. Efforts are now under way to isolate and purify the enzymes required for the two proposed enzymatic procedures. Following this, reaction conditions will be determined for accurate and reproducible enzymatic analysis of sulfate. (D. A. Bostick)

Gas chromatograph–microwave-excited spectrometer (GC/MES). Because of its inherent sensitivity and selectivity, the GC/MES has proved to be a versatile tool in the analysis of volatile nonmetal and organometallic species. For the past three years the GC/MES has been routinely applied to the determination of volatile mercurial compounds. Using the MES detector system, levels from 0.002 to 0.0005 ng of mercury have been determined with a selectivity of greater than 10,000 in such complex matrices as biological tissues and sediment samples. The relative sensitivities obtained for CH_3HgCl are better than 10 ng/g for solid samples and 100 ng/g for water samples. Recently, we have attempted to improve the detection limit of CH_3HgCl in natural waters by preconcentrating the contaminant from large sample volumes.[13] Previous studies have demonstrated the excellent extractability of inorganic anionic complexes of mercury, from alkaline as well as acidic solutions, with quarternary amines dissolved in various organic solvents. We have continued these studies and found that tertiary amines are even more efficient in extracting CH_3HgCl. With 0.5% tertiary-amine benzene solutions, a quantitative extraction of CH_3HgCl (95 ± 3%) can

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[13] Y. Talmi and V. E. Norvell, "A Rapid Method for the Determination of CH_3HgCl at the Part Per Trillion Level in Water Samples Using the Gas Chromatograph–Microwave Emission Spectrometric Detector System," submitted to *Analytical Chemistry*, September 1975.

be achieved for aqueous/solvent volume ratios as high as 400. Following extraction, 1- to 10-µl aliquots of the benzene extract are injected into the gas chromatograph for analysis. In the injection port (200°C), the CH_3HgCl-amine complex is instantly cleaved to release the volatile CH_3HgCl, which is then separated by the gas chromatograph column in exactly the same manner as pure CH_3HgCl standards. Using this analytical technique, trace CH_3HgCl as low as 1 ng/liter can be determined in water samples with an accuracy and precision of 10 to 15%. The excellent sensitivity and relative simplicity of this analytical technique is of considerable interest to environmentalists who are concerned with the mechanisms of CH_3HgCl accumulation in various biological systems.

The GC/MES has also been applied to the analysis of alkylarsenic acids in industrial pesticide and environmental samples.[14,15] Previous analytical techniques have generally relied on the determination of total arsenic content to monitor the impact of arsenic in the environment. However, there is now evidence that the bioaccumulation of certain alkylarsenic herbicides also occurs in the environment. In addition, organoarsenic acids have been shown to undergo reduction by microorganisms to toxic and volatile arsines. Therefore, to study the true history of arsenic herbicides in the environment, an accurate and sensitive analytical technique is required that is capable of providing information concerning the chemical form of the arsenical. Our new procedure involves an $NaBH_4$ reduction of alkylarsenic acids, particularly mono- and dimethylarsenic acids, contained in acidic aqueous samples to their corresponding alkylarsines. The gaseous arsines are collected by either of two methods. In the first method the alkylarsines may be collected by extraction of gases with toluene or benzene concurrently with $NaBH_4$ reduction of the acids; in the second the alkylarsines may be flushed, through the effervescence of the $NaBH_4$ reduction reaction, into a cold toluene trap (5°C). The arsine collection procedure employed depends upon the volatility of the alkylarsine generated. Because of its high volatility, monomethylarsine was collected using the toluene cold trap. Dimethylarsine was collected using both procedures. However, because of their low volatility, alkylarsines possessing greater than a two-carbon organic moiety could only be collected efficiently by the extraction technique. Aliquots of the organic phase, collected from either procedure, were subsequently injected into and separated by a GC column. The separated alkylarsines were eluted into an argon plasma where they were detected by monitoring the 228.8-nm As emission line. Using the cold toluene trap procedure, linear working curves were obtained for both mono- and dimethylarsenic acid in the 0.03- to 100-ng range. This corresponds to a relative sensitivity of 0.01 µg/ml of alkylarsenic acids in water samples. By preconcentrating the alkylarsines evolved from large sample volumes into a minimum volume of toluene, the relative sensitivity can be reduced by at least a factor of 40. With this extended range, the present analytical method can be used to separate and individually determine alkylarsenic acids as either major, minor, or trace sample components.

In a further study, the GC/MES was adapted as a silicon selective detector that will be used to aid in the characterization of the numerous organic compounds eluted during the GC separation of coal-derived effluents. With this adaptation, those compounds containing active hydrogen atoms can be identified from various other volatile sample components as silylized derivatives. Silicon detection has been investigated using both a helium and an argon plasma. The spectral characteristics of silicon in a helium plasma were studied by measuring the emission intensity of the silylizing reagent, bis(trimethylsilyl)-trifluoroacetamide (BSTFA), in benzene. Monitoring the 251.6-nm Si emission line, BSTFA could be detected in the concentration range 10 to 1000 ppm. However, under optimum conditions the best selectivity for silicon, when compared with a non-silicon-containing compound, was 25. The reproducibility in analyzing a sample was very dependent upon the ability to control both the power of the plasma and the duration of the silicon-continining compound in the plasma. In an effort to reduce the influence of these factors on silicon determination, the less energetic argon plasma was used. The plasma was operated both in vacuum (5 to 10 torr) and at atmospheric pressure. Several silicon atomic emission lines were monitored, and the best silicon response was observed at the 251.6-nm Si line in vacuum. Silicon selectivity and sensitivity varied with the region of the plasma monitored, with both parameters showing a maximum when silicon response was detected in the extreme upstream portion of the plasma. In contrast to the helium plasma, sensitivity and reproducibility in argon were only slightly dependent upon microwave power. When the above parameters are optimized, the detec-

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14. Y. Talmi and D. T. Bostick, "Determination of Alkylarsenic Acids in Pesticide and Environmental Samples by Gas Chromatography with a Microwave Emission Detector System," *Analytical Chemistry*, 1975, in press.

15. Y. Talmi and D. T. Bostick, "The Determination of Arsenic and Arsenicals," *J. Chromatogr. Sci.* 13, 231 (1975).

tion limit of the silylizing reagent samples is 0.1 to 100 ppm, with a reproducibility of 2 to 3% and a selectivity greater than 250. In a final study, real samples of silylized compounds will be used to evaluate the usefulness of the GC/MES in the coal program. **(Y. Talmi, D. A. Bostick, V. E. Norvell)**

Pattern recognition. In cooperation with the Computer Sciences Division, we have continued the study of pattern recognition techniques for dealing with complex analytical problems. High-resolution gas chromatographic profiles consisting of ~150 peaks produced in the Tobacco Smoke Research Program are used to generate the data set. One program objective is to determine which of the GC peaks are correlated highly with biological activity and to select those peaks for which chemical compound identification would be worth the effort. A second objective is to determine if a model can be developed that would predict biological activity, using chemical information present in the gas phase of cigarette smoke. Since biological studies involving large colonies of experimental animals are expensive laboratory operations that require considerable time (up to two years) to achieve results, a chemical indicator of carcinogenesis, if it could be developed, would be a very valuable tool in cancer research work.

Gas chromatographic runs (in duplicate) for each of the 22 cigarettes in the set of 23 series I cigarettes obtained from the National Cancer Institute have been completed. The code 12 cigarette could not be analyzed because the supply was exhausted. Interspersed in the time period of the gas chromatographic runs was a set of ten GC runs on code 2 cigarettes. This set was used to assess the reliability and reproducibility of the GC procedure. Relative standard deviations for retention times on the column and for normalized (to total particulate matter) peak areas were calculated for each of the 36 GC peaks selected. The retention times had remarkable relative standard deviations (RSD's) in the range of 0.18 to 0.33%, while peak areas showed RSD's in the range of 5 to 25%.

Raw analog data from the gas chromatograph are digitized by a dedicated 8K PDP-8/E computer and stored sequentially on magnetic tape (DECTAPE). Since it would be costly and time consuming to rerun this experiment should the data be lost, backup copies of the GC raw data were produced on the DEC system 10 computer. Disk files were created from the PDP-8/E formatted DECTAPES and transferred to DEC 10 formatted DECTAPES.

The raw GC data file (consisting of 8447 double-precision members) was processed on the DEC system 10 computer to produce FORTRAN IV recognizable code, and was further processed and analyzed to eventually give a file containing peak area vs retention time. These latter DEC-10 files are stored on magnetic tape in sets and are in such form that they can be inputted to the FORTRAN pattern recognition program, RECOG, for running on the IBM 360/91 computer.

Our first plan for analyzing the data set utilized the computer to sort and index the GC peaks on the chromatogram. Because of a finite tolerance on retention times, classification errors occurred, and we decided to test a visually selected data set consisting of 36 of the larger GC peaks. This set of 36 members showed enough promise so that a set of 125 members (includes smaller peaks) was created for input to RECOG.

Least-squares fitting using 25 of these 125 GC peaks (selected on the basis of redundancy stripping) has allowed biological activity (T_{50} values) to be predicted to better than 5% for a nonmember of a training set for series I cigarettes. We plan to test this model on series II and series III cigarettes, for which the biological activity data are not known to us. **(R. W. Stelzner)**

Fluorometric analysis of uranium. The improved instrumentation[16] (fluorophotometer Q-5198 and automatic fusion train) used for the determination of uranium has improved the standard deviation of the analytical results by a factor of 2, but the variation (σ ≅ 6%) was still greater than expected. The source of this variation was identified as differences in the surface condition of the platinum dish in which the sample is fused. The light seen by the photomultiplier in the Q-5198 consists of 52% direct radiation from the sintered pellet and 48% radiation reflected from the platinum dish. At the 100-ng/pellet level, the relative standard deviation observed in ten pellets, in randomly selected dishes, was 7.3%. In polished and re-formed dishes the relative standard deviation was found to be 3.8%. When a single dish was used to read all ten pellets, the relative standard addition fell to 1.7%. This is about the same magnitude of instrumental error as expected from the fluorophotometer. Other factors investigated included: pellet size and

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[16] H. H. Ross et al., "Improved Fluorometric Analysis System," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 3.

homogeneity, sample size, distribution of uranium in the sintered pellet, pellet volume, chemical state of the uranium (U^{4+} vs U^{6+}), and effect of quenching agents. A report on the complete study is in preparation.

A second complete analysis system consisting of the model Q-5198 fluorophotometer and furnace train was constructed and placed in service during this report period. The new furnace was modified so as to uniformly sinter about 90 pellets per hour. (J. E. Strain)

GROUP COORDINATED VISITOR RESEARCH

Electron transfer reactions. Understanding the basic molecular processes that occur during an electron transfer reaction has implications ranging from energy conversion and corrosion to the mechanism of numerous enzyme-catalyzed reactions. Several theories of electron transfer reactions based upon quantum and statistical mechanics have been formulated and subjected to varying degrees of experimental verification. One of the more successful ones was developed by Marcus.[17] His theory predicts numerous correlations between various types of homogeneous electron transfer reactions, and numerous experimental studies have reported reasonable agreement between theory and experiment. Marcus' theory also predicts the existence of a correlation between the rates of homogeneous and heterogeneous electron transfer reactions. The theory implies that for a given chemical system, the mechanisms of the two types of reactions should be similar. The general question of a parallelism between heterogeneous and homogeneous electron transfer reactions has not received any significant experimental test. The objective of our research effort in electrochemical kinetics is to obtain kinetic data for the heterogeneous reduction of selected redox couples and correlate these data with the self-exchange reactions according to the predictions of Marcus.

In a previous investigation the standard heterogeneous rate constant of the Eu(III)-Eu(II) couple was found to be independent of hydroxide ion concentration.[18] This result agrees with the self-exchange reaction;[19] hence the two studies are in accord with the theoretical predictions. Because the self-exchange reaction rate of the europium couple is greatly enhanced by chloride ion, the influence of chloride ion upon the standard heterogeneous rate constant of this couple was investigated.

The experimental approach consisted in measuring current-time curves at a stationary mercury electrode at several potentials in the potential limiting region of the Eu(III)-Eu(II) voltammogram. A conventional analog potentiostat was used to control the cell potential. Current-time curves were obtained with the aid of a PDP-8/I computer. A program entitled FOC4LK, derived from FOCAL (incorporating clock, ADC, disk storage and retrieval, and core fetch-put routines), controlled the data acquisition and preliminary processing. The current-time data were obtained on a punched paper tape and analyzed via a nonlinear curve-fitting routine on the DEC-10 time-shared computer system. Formal potential data were acquired via direct potentiometry.

Preliminary results of the experiments indicate that, contrary to the self-exchange reaction, the heterogeneous reduction of Eu(III) is not enhanced by chloride ion. This result is totally unexpected, and the full implication in relation to the Marcus theory will require additional studies with other redox couples. Investigations of the V(III)-V(II), Fe(III)-Fe(II), and/or Ce(IV)-Ce(III) couples are planned. (L. N. Klatt, T. L. Croxton)

Coulometry and the determination of uranium. We continued work on the improvement of the method for the determination of uranium in highly radioactive solutions. The method of choice has been the coulometric reduction of U(VI) at a controlled potential in a sulfuric acid medium. Some samples must be determined in phosphoric acid. Although the accuracy of the method is better than 0.1% for cold samples containing more than 5 mg of uranium, this accuracy has not been demonstrated for "hot" samples.

Experiments were designed to establish those parameters in the method needing the most attention. Earlier work by Stephens et al.[20] demonstrated the validity of computer-assisted data acquisition and the prediction of the uranium content of a sample from measurements made before the titrimetric end point had been reached. The coulometric reduction of

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[17] R. A. Marcus, "On the Theory of Electron-Transfer Reaction. VI. Unified Treatment for Homogeneous and Electrode Reactions," *J. Chem. Phys.* 43, 679 (1965).

[18] J. B. Carraway, "Determination of the Rate Dependence of the Heterogeneous Reduction of Eu(III) to Eu(II) on Hydroxide Ion Concentration," M.S. Thesis, University of Georgia, Athens, 1974.

[19] D. J. Meier and C. S. Garner, "The Kinetics of the Europium(II)-Europium(III) Exchange Reaction," *J. Phys. Chem.* 56, 853 (1952).

[20] F. B. Stephens, Fredi Jakob, L. P. Rigdon, and J. E. Harrar, "Real-Time Computer Prediction of End Points in Controlled-Potential Coulometry," *Anal. Chem.* 42, 764 (1970).

U(VI) does not follow the simple exponential decay predicted from the mass transport model based on a simple, rapid, one-step reduction of the species of interest. The reduction process for U(VI) proceeds, as is well known, via the reduction to U(V) with subsequent disproportionation to produce U(IV) and U(VI). The rate of disproportionation is dependent upon the H^+ concentration and, to a lesser degree, on the sulfate concentration [possibly because of complexation of SO_4^{2-} with U(IV)]. It follows, then, that near the time of initiation of electrolysis the measured current results chiefly from reduction of "pristine" U(VI) [to U(V)] in the immediate vicinity of the electrode. Were it possible to obtain an accurate measurement of this current, there would be no need for continued electrolysis. It is during this initial phase of titration, however, that potential control is poorest: charging of the electrical double layer to the control potential adds a component to the measured current, and the total cell current is changing at a maximum rate. It is also during this time that cell resistance and the current-delivering capability of the potentiostat contribute a maximum to the uncertainty of the Faradaic current and thus distort the observed current from that predicted from the theoretical model. Therefore, integration of the current over a protracted time period (usually about 5 to 7 min) is required to achieve precision in the desired range. Further, it becomes obvious that simple curve-fitting routines applied in the very early stages of electrolysis cannot result in an accurate prediction of the end point except, perhaps, by a fortuitous set of compensating factors. Another complication arises in radioactive samples in that radiolytic damage to the electrolyte causes the appearance of peroxides. These are reduced at the same potential at which the uranium determination must be made. This reduction adds a current to that which results from uranium reduction and which is indistinguishable from it.

We have developed an electrochemical cell that appears to be superior to those presently in use in our laboratories. Potential control is within ±1.5 mV during initial electrolysis and within ±0.5 mV for most of the titration. We are able, with this cell, to perform the analysis in H_3PO_4 solutions without difficulty. With the conventional cell, the precipitation of U(IV) phosphate frequently caused the potentiostat to become unstable before the completion of electrolysis. We feel that the superior potential control afforded by the cell design results in this stable operation. We have also demonstrated a capability to acquire, store, and process coulometric data with the PDP 8/I computer. The added FOCAL functions reported last year[21] were used without modification and performed adequately. An exact program for continued work in this area is awaiting the outcome of analysis of data already taken. (T. R. Mueller, S. T. Crossman)

Trace-level voltammetry. Differential-pulse anodic stripping voltammetry (DPASV) combines the preconcentration advantage of anodic stripping with the discrimination against electrode double-layer charging current inherent in differential-pulse polarography to yield a very sensitive electrochemical method. During the past year we were concerned with the evaluation of DPASV for the determination of ppb levels of lead, using a hanging mercury drop electrode (HMDE) and a rotated thin mercury film electrode (RTMFE). Studies centered on ascertaining the experimental parameters critical to an accurate and precise analysis, seeking quantitation, and comparing the behavior and properties of the HMDE and the RTMFE.

Several experimental aspects become quite important when DPASV is used for analyses near its detection limit. These include the cleanliness of electrical contacts, quality of distilled water, the necessity for using clean Vycor frits between the analyte solution and the reference and counter electrodes, and the requirement for pretreatment of the HMDE capillary or the vitreous carbon support for the thin mercury film electrode. Careful and continuous attention must be given to each of these to minimize experimental difficulties.

The importance of using the standard addition technique instead of a standard curve for quantitation was demonstrated by a study of the matrix influence upon 0.03 *M* HNO_3 background solutions stored in polyethylene, polypropylene, and glass bottles. After storage of the background electrolyte for a predetermined time, lead was added and the sensitivity factor (μA/ppb Pb) determined. The background solution stored a few weeks in superficially cleaned polyethylene exhibited a sensitivity about two-thirds that of an identical background solution stored in a glass volumetric flask. Polypropylene showed intermediate sensitivity. This effect is presumably due to slow leaching of plasticizer and/or antioxidant material from the plastic containers. Storage in glass is not an acceptable alternative because of the possibility of

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[21] H. H. Ross et al., "Instrumentation and Advanced Methodology," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 4.

lead leaching from the glass. In any case, it is clear that environmental samples collected in plastic bottles and preserved by adding 2 to 3 ml of HNO_3 per liter should be analyzed by the standard addition technique to assure accurate results.

As expected, the detection limit for lead by DPASV using the RTMFE is about 0.01 ppb, once reproducible behavior is achieved; this is an order of magnitude lower than that at the HMDE. Reproducibility is always a problem with solid electrodes, and the mercury-plated vitreous carbon electrode is no exception. Best results are obtained by using a highly polished surface and successive in situ plating and stripping cycles of mercury in the presence of the analysis element. The number of plate-strip cycles required before reproducible voltammograms are obtained depends upon the concentration of the analysis element. Reproducibility is remarkably good on subsequent plate-strip scans after standard additions.

The utility of DPASV for analyzing real samples was demonstrated by analyzing rain and stream-water samples obtained from the Environmental Sciences Division. Using the HMDE and the standard addition technique, lead concentrations of 8 and 11 ppb ± 10% were reported respectively. Stripping peaks were observed for cadmium and copper in the rainwater and for copper in the stream-water sample, but these elements were not quantified. (L. A. Knecht)

Service instrumentation. With the reactivation of the Molten-Salt Reactor Project, the Metals and Ceramics Division undertook a project requiring the use of voltammeters to monitor selected electrochemical properties of the thermally heated salt test loops. These experiments use the test loop plumbing as the counter electrode in an electrochemical cell; consequently, the voltammeter must be designed in grounded counter electrode configuration. We provided the Metals and Ceramics Division with an electronic design based upon commercially available modular components. The instrument includes a triangular waveform generator with switch-selectable sweep rates ranging from 1 to 1000 mV/sec. Full-scale current ranges are 10 μA to 1000 mA. Normal or derivative cyclic voltammograms can be recorded. The derivative operation is accomplished through use of a two-pole-state variable active filter. Some provision for implementation of computer control of the voltammeter is included in the design. Construction of the instrument is being performed by the Instrumentation and Controls Division. On the basis of three units, the estimated unit cost is $4500, including complete engineering documentation. (T. R. Mueller, L. N. Klatt)

2. Nuclear and Physics Methods

W. S. Lyon, Head

The Nuclear and Physics Methods Group has continued to enlarge and refine the capabilities of its multielement techniques. This year the x-ray fluorescence (XRF) method both tube and radioisotope excited has been applied to a variety of samples to obtain quantitative data. Electron spectroscopy for chemical analysis (ESCA) has been used in a series of research studies elucidating surface corrosion in reactor components, as well as in a number of other applications. As part of this program, we are evaluating the potential of ESCA for quantitative surface analysis; preliminary data look promising. We have organized our efforts and techniques in a manner that can best be described as "an approach to the whole problem." In this approach, scanning spectroscopy, XRF, ESCA, x-ray diffraction, and associated separations techniques are brought to bear on an analytical problem in a coherent and programmed manner.

Our other multielement technique neutron activation analysis (NAA) continues to be used as an adjunct in a number of important studies. Coal, fly ash, tree rings, uranium exploratory samples, cherts from Indian sites, and special high-purity metals are some of the materials that were studied. Despite the end of our eight-year formal NASA commitment, we are still involved in radioactivity measurements in special flights such as Apollo-Soyuz. In support of reactor energy investigations, we continued to develop methods for very low amounts of transuranium elements in the environment; a cooperative study with the Neutron Physics Division is concerned with the decay heat released during fission an important parameter for safety design in reactors.

One man has been loaned to the Physics Division to assist in Controlled Thermonuclear Research. We ourselves have had a number of trainees: IAEA fellows, summer research participants, and visitors from elsewhere. Thus we continue to explore new fields while sharing our knowledge with others.

X-RAY AND ELECTRON PHYSICS

Quantitative analysis of alloys by x-ray fluorescence and x-ray photoelectron spectroscopy. To a first approximation, the intensity of an x-ray fluorescence peak in a given element is directly proportional to the concentration of that element in the specimen being analyzed. Unless one makes corrections, however, for the so-called "interelement effects," the results of the analysis may be in error by as much as 20 to 50%. The interelement effects are caused by the absorption of the x-ray fluorescence of elements of higher atomic number by elements of lower atomic number. The result will be that the fluorescence from the high-*Z* elements is decreased, while that of the lower-*Z* elements is increased. Some of the most pronounced interelement effects occur for alloys of Cr, Fe, and Ni (stainless steels, Hastelloys, Inconels). Chromium and iron both absorb the fluorescence of nickel, while chromium absorbs that of iron. Recently, Rasberry and Heinrich[1] proposed a method for interelement correction that is quite accurate for Cr-Fe-Ni systems. It takes into account nonlinear relationships between fluorescence intensity and concentration by empirical equations. Concentrations are calculated by an iterative method. The first step is to proportionate concentrations to

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[1] S. D. Rasberry and K. F. J. Heinrich, "Calibration for Interelement Effects in X-Ray Fluorescence Analysis," *Anal. Chem.* 46, 81 (1974).

their fluorescent intensities. The second step is to correct each of the concentrations by empirical relationships to all the others. The third step is the same as the second, using the new concentrations. Convergence of the corrections usually occurs after 4 to 5 iterations. The computation can be easily done on an 8K minicomputer, and we have used the method on our system. Below is a comparison for wet-chemical and x-ray fluorescence results, using the Rasberry-Heinrich correction:

	Carpenter 20 alloy			Inconel X		
	Cr	Fe	Ni	Cr	Fe	Ni
Wet chemical	20.7	42.08	28.72	14.69	7.84	72.89
XRF	19.53	42.07	28.61	15.36	7.82	73.28

The method appears to give excellent results for iron and nickel, but further work is needed for chromium. We hope to be able to extend this technique to other matrices. At present, we are examining a large number of alloys by XRF.

X-ray photoelectron spectroscopy is a very versatile method for surface analysis, but is very poor for bulk analysis. The ESCA technique samples only the top 10 to 50 atomic layers of solid materials. Surface layers will invariably be different in composition from their substrates. There have been many efforts to quantify ESCA results for surface analysis, however, because comparisons of surface and bulk compositions are important in the characterization of solid materials. There are also many applications such as electronics device technology and corrosion research in which surface analysis is much more important than bulk analysis. One of the main problems in quantifying surface analysis is the choice of a standard. One cannot purchase an "SRM surface" from NBS, because the composition will be altered in transport. It does appear, however, that we may be able to prepare surfaces of known composition in situ within the spectrometer. We are attempting to do this by the ion etching of Cr-Fe-Ni alloys. For Inconel (78% Ni, 14% Cr, 8% Fe) we found that the photoelectron spectrum of the as-received surface did not match the known bulk composition at all. The nickel and chromium peaks were hardly visible above background. The surface layer consisted mostly of carbon and oxygen with smaller amounts of nitrogen, silicon, and sulfur. After the surface was ion etched, the Cr, Fe, and Ni peaks were quite prominent. The N, Si, and S were completely removed, but some of the carbon and oxygen remained. The presence of the carbon and oxygen was due to adsorption of residual vapors from the spectrometer vacuum system. The ratio of Ni:Cr:Fe was almost exactly 78:14:8, the bulk percentages. Interpretations of the peak intensities were done by the method of Carter et al.[2] Our good agreement for the Inconel sample may have been fortuitous. We are presently examining some more samples of NBS stainless steel and Inconel. (L. D. Hulett, J. M. Dale, H. W. Dunn, P. S. Murty)

Characterization of solids by a coordinated analytical approach. In support of the various energy-related research and development programs at ORNL, we are often asked to characterize complicated mixtures of solids from many sources — corrosion scale, dusts, soils, coal, fly ash, for example. Our characterization involves much more than just elemental analysis. In general, we ask the following questions:

1. What elements are present?
2. What are the chemical states (compound and or ionic forms) of the elements?
3. How are the elements and compounds distributed?
4. What are the sizes and shapes of the particles that make up the specimen?
5. How do particle surfaces differ from their interiors?
6. What is the origin of the specimen (precipitation, corrosion, . . .)?

Figure 2.1 shows the approach we take to answering these questions.

By combining information from each of the steps indicated on the flow diagram, we are able to construct a general characterization picture. The information obtained from each step and how we assimilate it can be demonstrated by means of a specific example, a scale formed on an Inconel substrate. The specimen came from a corrosion study of nuclear reactor boilers. Our analysis proceeded as follows:

1. *X-ray-induced x-ray fluorescence (XR-XRF).* Capable of detecting all elements heavier than fluorine with sensitivities ranging from 1 to 10 ppm for heavier elements and 100 to 1000 ppm for lighter elements. Results apply to characterization question 1, above. For the corrosion scale we found the elements Fe, Ni, Cr, P, Si, and Br.
2. *Scanning electron microscopy x-ray fluorescence (SEM-XRF).* Capable of viewing solid surfaces

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[2] W. J. Carter, G. K. Schweitzer, and T. A. Carlson "Experimental Evaluation of a Simple Model for Quantitative Analysis in X-Ray Photoelectron Spectroscopy," *J. Electron Spectrosc. Relat. Phenom.* 5, 827 (1974).

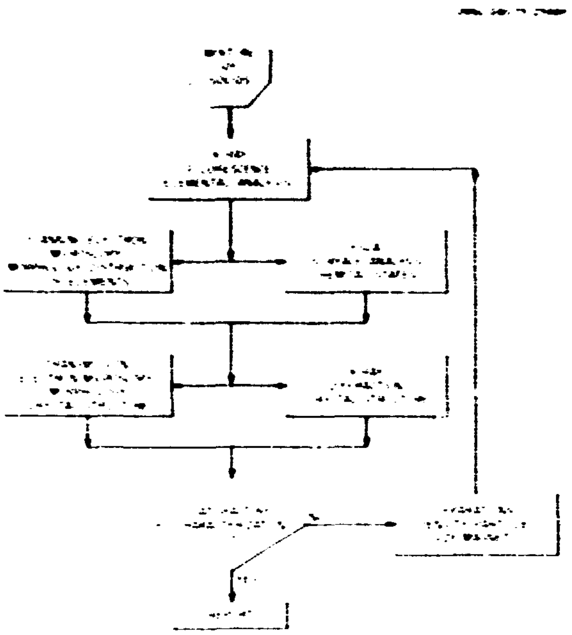

Fig. 2.1. General approach to the analysis of complicated mixtures of solids.

directly at magnifications of 10 to 10,000X. Individual particles as small as 1 μm can be analyzed by means of x-ray fluorescence induced by the electron beam. Results from this method address characterization questions 3 and 4. For the sample we found that Ni and Fe were segregated in high concentration at the outer surface of the scale. Inclusions with high concentrations of manganese were also found in the interior of the scale. Scale is approximately 150 μm thick.

3. *X-ray photoelectron spectroscopy (ESCA).* Capable of detecting all elements heavier than helium. Analyzes only the upper 10 to 50 atomic layers of solid surfaces. Capable of determining differences between surface and bulk composition. Chemical shifts in spectra indicate the chemical states of elements. Results from this method address questions 2, 3, and 5. For the corrosion specimen we found that the surfaces of the scale particles were covered with films of $NiCO_3$, Na_2CO_3, phosphates, bromates, and silicates. By applying the ion-etch-ESCA technique to the scale-alloy interface, we found that the corrosion process caused a chromium enrichment.

4. *X-ray diffraction (XRD).* Reveals what crystal structures are present. By combining crystal structure information with elemental analysis, we determine what compounds are present. Results from this method address characterization question 2. It was necessary to separate the scale into magnetic and nonmagnetic components. The magnetic fraction contained $Ni_xFe_{3-x}O_4$; the nonmagnetic fraction contained $FeCrO_4$ and $NiCrO_4$.

5. *Transmission electron microscopy–electron diffraction (TEM-ED).* This method was not used in this problem, but is often employed for examining submicron particles and determining crystal structure. TEM-ED results address questions 2, 3, and 4.

By combining the SEM-XRF data, which tells us that only Ni and Fe are present on the outer portions of the scale, with the XRD information, which says that $Ni_xFe_{3-x}O_4$ is present, we conclude that there is a separate phase of $Ni_xFe_{3-x}O_4$ segregated on the outer surface of the scale. The scale closer to the specimen contains $FeCrO_4$ and $NiCrO_4$. The ESCA data indicate that the scale particle surfaces are of a different composition from their interiors and that the corrosion process caused a chromium enrichment at the scale-alloy interface. SEM-XRF data also revealed manganese-rich inclusions. Our overall findings for this scale are illustrated schematically in Fig. 2.2.

Probably the most important characterization question of all, as far as the customer is concerned, is the origin of the specimen (question 6). Previously it had been concluded that most of the scale was precipitation from the boiler rather than corrosion, because the mass of the scale was too large to be accounted for by the mass loss of the Inconel. Our studies support this by revealing foreign cations such as manganese. Also, we can say that solid-state transformations are probably taking place in the scale, in that the outer portion of

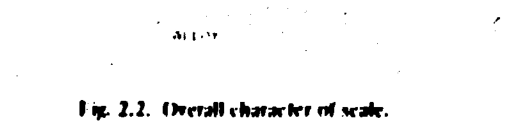

Fig. 2.2. Overall character of scale.

the scale is of different composition ($Ni_xFe_{3-x}O_4$) from the inner. **(L. D. Hulett, J. M. Dale, H. W. Dunn, P. S. Murty, J. L. Hibbard)**

MEASUREMENT OF RADIOACTIVITY

Decay heat for thermal-neutron-induced fission of ^{235}U and ^{239}Pu. This experiment was initiated early in 1974 as a joint Analytical Chemistry–Neutron Physics Division project to study the total decay heat from the thermal-neutron-induced fission of ^{235}U and ^{239}Pu over the range 2 to 2000 sec after fission. The total energy release rate will be obtained by measuring separately the beta and gamma decay energy.

The gamma-ray detector is a 12.7-cm-diam by 12.7-cm-thick NaI(Tl) crystal calibrated with known isotopic sources. The beta-ray detector is an organic scintillator calibrated in a like manner using beta-ray sources. Gamma-ray sources will be measured and used to correct any gamma-ray effects on the detector.

Both the beta and gamma-ray detectors have been constructed and calibrated, and trial runs have been completed.

Besides furnishing the irradiation facility, our Division has the primary responsibility of preparing the ^{235}U samples and determining the number of fissions. The ^{235}U used is the NBS-930 enriched uranium standard, and the number of fissions will be determined by measuring ^{99}Mo, a fission product with precisely known yield. J. K. Dickens and T. A. Love are the contributors from the Neutron Physics Division. **(J. F. Emery, K. J. Northcutt)**

Low-level gamma spectrometry. The low-level gamma-ray spectrometry facility[3] has been used for the determination of low-concentration radionuclides in a variety of environmental sample types. These sample types included monazite ores, soils, oil-shales, lyophilized deer meat, and filters from the ORNL local air monitors.

We analyzed the monazite ores for K, Th, and U by gamma-ray spectrometry after homogenizing the rock materials. This was a cooperative project with members of the Chemistry Division.[4]

The analysis of the deer meat was a feasibility study to determine the utility of the low-level equipment for ecological sample types. Due to the long storage time of the sample (>2 years), only ^{137}Cs and K via ^{40}K could be measured. We are prepared to analyze future road-killed animals of this type to determine ambient radionuclide concentrations as a measure of the transport of radionuclides in the vicinity of ORNL.

The soils, shales, and air filter samples are part of a methods-development project within our Division, and the results will be used by the Health Physics Division in a field monitoring program of microdosimetry as well as in their effluent monitoring activities. **(J. S. Eldridge)**

Radionuclide characteristics and measurements. We frequently receive inquiries about measurements and standards for radionuclides, and about their properties. Experimental work is required on some of these problems. In this period, inquiries involved measurement methods for ^{14}C, ^{147}Pm, and ^{67}Ga, properties of tracers for Eu, and production of ^{129}I. A ^{210}Po standard was obtained from NBS and used to check calibrations of a number of alpha counters, and measurements were made of a ^{60}Co standard. Information was obtained from ASTM Committee D-19 on quality control for gamma-spectrometric analysis. Our data on decay of ^{110m}Ag led to an estimate of 252.2 days for the half-life.[5] This was not published in our last paper on half-lives because it was suspected to be biased by the presence of long-lived ^{108m}Ag. At the request of the ORNL Nuclear Data Group, the data were reexamined and corrected for the estimated content of ^{108m}Ag, and the new value is 251 ± 1 days. Decay was observed by use of a gamma ionization chamber for five half-lives, using a chemically purified silver preparation. **(S. A. Reynolds)**

^{235}U determinations for safeguard inventories. The calibration and operational assistance program[6] for the NRC Region II Directorate of Regulatory Operations' mobile laboratory was concluded in the middle of September. We made several important changes in the laboratory that resulted in improved performance and operational convenience. For greater reliability in the operating program, as well as in data storage, a nine-track computer-compatible magnetic-tape system was added to replace a marginal cassette tape device. To complement the on-line utility of the magnetic-tape system, we developed off-line data processing that

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

[4] R. W. Stoughton et al., "Spontaneous Fission in Monazite Ores," *Chem Div Annu Prog Rep October 1975*, ORNL-5111, in preparation.

[5] J. F. Emery, S. A. Reynolds, and E. I. Wyatt, "Half-Life Measurements," *Anal Chem Div Annu Prog Rep Oct 31, 1969*, ORNL-4466, p. 75.

[6] W. S. Lyon et al., "^{235}U Determinations for Safeguard Inventories," *Anal Chem Div Annu Prog Rep Sept 30, 1974*, ORNL-5006, pp. 19–21.

utilizes the capabilities of the large computers at ORNL. This utility program converts spectral data stored on the magnetic tape to a variety of "hard copy" formats suitable for many purposes. In addition, the utility program was interfaced to an automated data reduction program that will provide a complete isotope identification package for future investigations, using a high-resolution Ge(Li) detector.

A digital stabilizer was added to the analog-to-digital converter so as to prevent excessive drifts in the position of photopeaks caused by temperature and/or line voltage variations. The stabilizer will improve the overall precision of ^{235}U measurement as well as reduce the need for frequent energy calibrations. An oscilloscope camera utilizing Polaroid film was added to complement the other readout devices in the system.

The laboratory was operated at several field sites during the past year by NRC personnel. On two of the field inspections, 50 to 80 inventory samples were collected at the licensee facility and returned to ORNL for detailed analyses. We used the ORNL ND 4420 system and a 7.6 X 7.6 cm NaI(Tl) crystal for those measurements and showed the complementary nature of ORNL-based measurements to the field measurements in the mobile laboratory.

A paper[7] describing the mobile laboratory and its operation was presented at the 16th Annual Meeting, Institute of Nuclear Materials Management, New Orleans, Louisiana. (J. S. Eldridge)

Primordial radioelements and cosmogenic radionuclides in rocks and soils from Descartes and Taurus-Littrow. Studies[8] on the distributions of the primordial radioelements K, Th, and U in samples from Apollo 16 and 17 have been extended to include material from additional sampling stations and material with a greater range of chemical properties. Measurements on yields of cosmogenic radionuclides, which are carried out simultaneously with determinations of K, Th, and U by our methods of nondestructive gamma-ray spectrometry, have provided much useful information on the character of the incident cosmic radiation and on details of lunar surface processes. Six samples of the Apollo 16 collection from Descartes and five samples of the Apollo 17 collection from Taurus-Littrow were studied.

The primordial radioelement content and the concentration of ^{22}Na, ^{26}Al, and ^{54}Mn in the seven rock and four soil samples were determined in this study. We were able to correlate primordial radioelement concentrations with two or three separate basalt flows at Taurus-Littrow and to demonstrate further chemical differentiation in the Th-U pair. Cosmogenic radionuclide concentrations were used to deduce the partial burial or recent exposure on the surface by the undersaturation of ^{26}Al.

This work concludes the NASA-sponsored lunar sample analysis program that was a cooperative project with G. D. O'Kelley of the Chemistry Division. An account of this work has been published.[9] (J. S. Eldridge)

Apollo-Soyuz test project: Passive crystal activation experiment. Radioactivity measurements were made on two experimental packages returned on the Apollo-Soyuz flight. One of the experimental packages was the same 7 X 7 cm sodium iodide detector that was flown on the Apollo 17 mission (Dyer et al.[10]). The other package contained six pieces of pure germanium ingot machined to fit a 7-cm-diam container with a height of 4 cm. The total weight of germanium was 724 g. Both packages were brought by courier in cadmium-shielded containers from Hawaii after an initial measurement aboard the recovery ship.

Direct measurements of induced radionuclides were made by optically sealing a photomultiplier tube to the activated crystal. Pulse-height spectra of the internal response were obtained beginning about 26 hr after splashdown. Such measurements are continuing in order to characterize the long-lived components.

Indirect measurements of the induced radionuclides were made using Ge(Li) detectors and a large anticoincidence shielded NaI(Tl) spectrometer in the low-level facility.

Preliminary results from the low-level spectrometer system ("4π system") yielded positive identification of ^{124}I, ^{126}I, and ^{24}Na in the sodium iodide flight detector. Tentative identification of ^{22}Na was also made, but verification must await refinement of the spectral analysis. Semiquantitative disintegration rate values are approximately one-third to one-half those

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[7] J. S. Eldridge, W. S. Lyon, and F. L. Clay, "Mobile Assay Laboratory for ^{235}U Safeguards Measurements," *Journal of the Institute of Nuclear Materials Management*, in press.

[8] W. S. Lyon et al., "Primordial Radioelement Concentrations in Rocks and Soils from Taurus-Littrow," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 18.

[9] J. S. Eldridge et al., "Primordial Radioelements and Cosmogenic Radionuclides in Rocks and Soils from Descartes and Taurus-Littrow," pp. 242–44 in *Lunar Science VI*, Lunar Science Institute, Houston, 1975.

[10] C. Dyer, J. I. Trombka, R. L. Schmadebeck, E. Eller, M. Bielefeld, G. D. O'Kelley, J. S. Eldridge, K. J. Northcutt, A. E. Metzger, R. C. Reedy, F. Schonfeld, S. Seltzer, J. R. Arnold, and L. E. Peterson, "Radioactivity Observed in the Sodium Iodide Gamma-Ray Spectrometer Returned on the Apollo 17 Mission," *Space Sci. Instrum.* 1(3) (1975), in press.

found in the Apollo 17 experiment by Dyer et al.[10] for ^{124}I, ^{126}I, and ^{24}Na.

Gamma-gamma coincidence data on the germanium experiment from the 4π system indicated the presence of at least one short-lived positron-emitting radionuclide. Decay curve analysis of the positron-positron coincidences yielded a half-life value of ~29 hr. The early measurements also show apparent gamma-gamma coincidences of 0.5 to 0.8 and 0.8 to 1.4 MeV. The radionuclide most closely fitting these characteristics is ^{72}As, a 26.0-hr positron emitter with an 0.834-MeV gamma ray in coincidence with its major positron branch. The positron-positron counting rate corrected to splashdown is about 2.7 counts/min with a corresponding system background of 0.1 count/min. At 41 days post-splashdown, the positron-positron counting rate is only 50% above background.

Detailed analysis of Ge(Li) spectra shows a tentative identification of ^{67}Ga, a 78-hr radionuclide that decays by electron capture. This is a cooperative effort with E. Schonfeld of the NASA Johnson Space Center. (J. S. Eldridge)

RADIOANALYSIS OF ENVIRONMENTAL MATERIALS

We are continuing the program[11] of research on, and special analyses of, low-level alpha emitters in environmental materials. In addition to Pu, Am, and Cm, the work now includes Th, U, Np, Po, and the members of the natural radioactive series. This program is supportive of investigations in several ORNL divisions, principally Environmental Sciences,[12] Chemistry, and Health Physics. Assignment of a second person (T. G. Scott) has resulted in a substantial increase in output of analytical results.

Aqueous behavior of actinides. Research has been carried forward on the interaction of actinides, particularly plutonium, with constituents of natural waters, soils, and plants. These included fulvic acid and polygalacturonic acid; both complex plutonium, and the latter carries it when precipitated by salt or acid. It was found that bicarbonate neither prevents nor reverses sorption of plutonium by surfaces, contrary to the complexing effect some have predicted. Details of these and other studies have been reported.[13-15] (S. A. Reynolds, T. G. Scott)

Actinide methods and results. The plutonium methods indicated last year[11,16] have been applied to substantial numbers of samples of water, soils, sediments, vegetation, and fish, and have generally been successful. Modifications have included $BiPO_4$ carrying for some sample types and additional wet ashing with H_2SO_4 and $HClO_4$ for others. Levels of plutonium have varied from about 0.05 to over 100 dis min^{-1} g^{-1} for soils and sediments, and from about 10^{-4} to 10^{-1} for plants and animals. Semiroutine analyses began in April in a temporary laboratory. Larger permanent facilities have been surveyed and are being equipped for use in the near future.

Americium and curium have been determined by the oxalate-hydroxide-fluoride method in effluents from the anion exchange separation of plutonium. Study of other separation techniques is in progress, particularly the use of TTA extraction as the final step. Levels have generally been one or two orders of magnitude below that of plutonium, but in White Oak Lake and burial ground seeps, ^{244}Cm has been the dominant alpha emitter (at about 1 pCi/liter in the lake). Exploratory analyses for ^{237}Np have been made by gamma-spectrometric measurement of its daughter, ^{233}Pa, but none has been detected. The more sensitive method, radiochemical separation and alpha counting, will be applied to a sufficient number of representative samples to determine whether neptunium is of environmental significance in this area. Thorium was measured in some soil samples and water by anion exchange separation and TTA extraction.

Reference materials of ^{210}Po, ^{239}Pu, ^{242}Pu, and ^{243}Am were obtained from the National Bureau of Standards. All were used to confirm calibrations of our instruments, and the latter two are also employed as "spikes" to determine recovery in many analyses. Further, these and other materials were furnished to personnel of Environmental Sciences, Health Physics,

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[11] W. S. Lyon et al., "Radioanalysis of Environmental Materials," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 21.

[12] R. C. Dahlman et al., "Plutonium in Aquatic and Terrestrial Environments," *Environ. Sci. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5016, p. 1.

[13] S. A. Reynolds, "Aqueous Behavior of Plutonium and Americium at Concentrations below 10^{-8} M," *Radiochemical and Radioanalytical Letters*, in press.

[14] F. A. Bondietti, S. A. Reynolds, and M. H. Shanks, "Environmental Plutonium Chemistry. I. Reactions of Plutonium with Environmental Organic Substances," submitted to *Soil Science Society of America, Proceedings*.

[15] F. A. Bondietti, S. A. Reynolds, and M. H. Shanks, "Interaction of Plutonium with Complexing Substances in Soils and Natural Waters," submitted to *IAEA/ERDA Symposium on Transuranium Nuclides in the Environment, Proceedings*.

[16] S. A. Reynolds and T. G. Scott, "Determination of Plutonium in Environmental Samples. I. Development of Methods. II. Procedures," *Radiochemical and Radioanalytical Letters*, in press.

and K-25, making results from their laboratories comparable to ours and traceable to NBS. A seawater sample from IAEA was analyzed for plutonium at about 0.1 pCi/liter, and the result agreed with that of IAEA within 19%, the estimated uncertainty. Other environmental "knowns" include sediment and seaweed from IAEA, sediment from NBS, and soil from ERDA. (S. A. Reynolds, T. G. Scott)

Other alpha emitters. In connection with research[17] in the Chemistry Division, spectra of a variety of low-activity mineral samples were taken with the 30-cm^2 detector (see below) in a search for alpha radiations of 1 to 4 and 9 to 14 MeV, and for disequilibrium in the natural series. Enriched ^{147}Sm was used to verify satisfactory performance at its alpha energy, 2.2 MeV. No alphas in the ranges of interest were detected, but cases of disequilibrium were found.[18] Because of indications that ^{210}Po in tobacco may be hazardous, samples prepared by members of the Bio-Organic Analysis Group were examined, and small amounts of ^{210}Po were identified and measured. A brief literature search for methods for ^{210}Pb and Po was made. (S. A. Reynolds, T. G. Scott)

Instruments. Four ZnS-Mylar counters were delivered early in 1975 and have proved very useful for total-alpha counting. Efficiencies are about 48%, and backgrounds average about 0.005 cpm. Most analyses require spectrometers for isotopic analyses of the separated radioelements and for measurement of recoveries by isotopic tracer. Two spectrometers are normally available for this work, so that the output is limited. However, a system with four detectors is being readied for service. For special purposes, a "state-of-the-art" surface-barrier detector 20 cm^2 in area was obtained. Its efficiency is about 36%. It has been used day and night since installation in June, except for two periods when the detector had to be replaced by the supplier, and when other instabilities occurred which were eventually traced to the preamplifier. (S. A. Reynolds, T. G. Scott)

ACTIVATION ANALYSIS

NURE national uranium resources evaluation. ERDA is funding a project for the measurement of uranium and other trace elements in waters and sediments throughout the U.S. The country has been divided into four sections; UCND is responsible for the central states, and ORGDP is the principal investigator.

A number of comparison H_2O samples were prepared at Y-12 and submitted to interested UCND laboratories for analysis. We analyzed these samples for uranium by delayed neutron counting and for multielements by NAA. Excellent agreement was obtained by most laboratories on trace elements, but uranium results varied tremendously. Mass spectrometric results (see Mass Spectrometry Section) indicated that the solutions all contained differing mass ratios of the uranium isotopes.

Work done in our laboratory proved that container contamination (probably in the storeroom) was the cause.[19] Uranium analyses of a second series of more carefully prepared samples were consistent.

MONSTR, a computer program for Ge(Li) detector gamma-ray spectral data acquisition and resolution for a PDP-15 Nuclear Data 50/50 system, has been modified for the IBM-360 for use by the service groups of the Division. At the same time DECAY GAM tables of radionuclides were enlarged from 520 to 700 isotopes. The quality of the original data was also improved by evaluation of nuclear parameters. MONSTR uses these tables for isotope identification. The IBM-360 version has been in use daily since June. (J. F. Emery, K. J. Northcutt, W. D. Reents)

Other projects and programs. Neutron activation analysis is being used to determine both major and trace elements in monthly composites of coal samples from the Bull Run and Kingston steam plants of TVA and the UCND Y-12 steam plant. These results will be used in a proposed energy study as well as in the Walker Branch Watershed study.

Another project is the characterization of cherts from seven locations in southern Ohio for Miami University, Oxford, Ohio. Multielement analyses were performed and the data examined to see if any trends were observable. The uranium in the first series of 40 samples was reasonably consistent; however, in the second series of 30 samples, there was much wider spread in the uranium concentration. Additional samples are being analyzed to determine if any pattern is discernable. (J. F. Emery, K. J. Northcutt)

Environmental baselines by analysis of tree rings. The activation analysis work on environmental baselines was completed.[20] Tree rings correspond to years of tree life; thus, tree-core sample impurities may be correlated

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[17] R. V. Gentry, "Radioactive Halos," *Annu Rev Nucl Sci* 23, 347 (1973).

[18] R. V. Gentry et al., "Radiohalos in Coalified Wood: New Data on U Disequilibrium," submitted to *Science*.

[19] W. D. Reents, J. F. Emery, and K. J. Northcutt, "Sampling, Preparation and Analytical Problems Associated with the Determination of Low Levels of Uranium in Water and Sediments" (unpublished).

[20] W. S. Lyon et al., *Anal Chem Div Annu Prog Rep Sept 30, 1974*, ORNL-5006, p. 14.

to past environmental conditions. We investigated chronological variations of environmental multielement baselines and contamination levels over a century by analyzing core samples from two similar shortleaf pines (*Pinus echinata*) located in the Walker Branch Watershed — a relatively unpopulated area — and in the city of Knoxville. Eighteen elements were analyzed in three cores of the Watershed tree, while 16 elements were determined in two cores of the Knoxville tree. We analyzed samples corresponding to four periods of time: 1872–76, 1932–38, 1958–63, and 1968–72. A total of 216 data items were obtained for the Watershed tree and 128 for the Knoxville tree.

No definitive conclusions can be drawn from this multitude of data until a detailed statistical study is made. However, we could make some preliminary observations. First, a general increasing trend is apparent for the "natural components" (Na, Al, Cl, K) against a decreasing tendency of the "contaminants" (Mn, Co, Zn, Rb, Ba). Evidence of this is strong for chlorine and potassium among the former, and for manganese and barium among the latter. Second, both concentration levels and chronological variation trends are remarkably similar for the Watershed and the Knoxville trees. These two observations show intriguing trends which already point out the power of the multielement tree-ring method. (E. Ricci)

Methodology for high-flux multielement NAA. We have completed our methodology work.[21] ORNL's High-Flux NAA Laboratory features a thermal flux of 5 × 10^{14} cm^{-2} sec^{-1} and a thermal-to-resonance flux ratio of 35 to 45. An instrumental absolute multielement method was developed for this laboratory, and errors were minimized through a series of careful methodology steps which can be easily adapted to other facilities.

The detector was calibrated for absolute counting with two independent sets of radioactivity standards for four detector-source distances: 3, 10, 27, and 39 cm. By using the resulting calibration curves we could reproduce the standards' absolute activities with 9% or better accuracies. To ensure analytical accuracy, five possible causes of systematic error were then investigated: (*a*) correction for counting of cylindrical sources for 26 gamma-ray energies and for the four distances, (*b*) flux variation during bombardment and within the irradiation capsule volume, (*c*) sample composition stability during high-flux bombardment, (*d*) correction for sample activation during rabbit transfer, and (*e*) multielement impurities in accessory materials (polyethylene and "Nucleopore" filters). We found (*b*), (*c*), and (*e*) to be acceptable for our method's sensitivity and accuracy. But (*a*) reaches 14 to 17% (depending on source-detector distance) for photon energies below 500 keV, and (*d*) becomes quite large for short bombardments, which are not uncommon in our high-flux facility, for example, 8.6% for 6 sec and 19.6% for 4 sec.

This methodology results in an accuracy of 10 to 15% for most elements, as determined by analysis of NBS orchard leaves and coal and of Bowen's kale standards. (E. Ricci)

Separation and determination of chlorine in aluminum metal by neutron activation analysis. A rapid method for the determination of chlorine in aluminum metal by neutron activation analysis was developed. The aluminum is irradiated, dissolved in hot NaOH, and ^{56}Mn activity removed by MnO_2 precipitation. The ^{38}Cl is precipitated as AgCl and counted on a Ge(Li) detector. Chlorine concentrations as low as 0.3 μg/g in the presence of several hundred times more manganese impurity have been measured with this procedure.

A paper describing this work has been written and will be submitted for publication. (L. C. Bate)

HFIR pneumatic tube system. The piston-type valves in the HFIR p-tube air system periodically malfunctioned and required removal and cleaning to operate the p-tube; these valves were changed to ball valves. Another valve, supposed to cause the rabbits to spin, was eliminated; it had never worked satisfactorily because the air pressure could not be balanced. Since the valves were changed, there has been no trouble with the p-tube operation.

The in-vessel section of the p-tube is required to be changed every five years. When the HFIR was shut down to change the beryllium reflector, the tube was in its fifth year, so it was decided to replace this section. The in-vessel section of the p-tube was redesigned to eliminate the air lines not used after the removal of a valve. The new in-vessel section is expected to be completed and the HFIR laboratory in operation by the end of the year. (L. C. Bate)

^{58}Ni(*n,p*)^{58}Co cross-section measurement at the HFIR p-tube. Five nickel foils were irradiated in the HFIR p-tube facility to determine the effective activation cross section for the reaction ^{58}Ni(*n,p*)^{58}Co based on the thermal neutron flux. The cross section of 3.17 mb was the average measured value. This cross section is used as one of the parameters to calculate the nickel concentration in samples by absolute neutron activation analysis. (L. C. Bate)

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[21] W. S. Lyon et al., *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 15.

Determination of elements in environmental samples by use of neutron activation analysis. Instrumental neutron activation analysis methods have been developed and used at the HFIR to determine the element content and or limit of detection for over 40 elements in environmental samples. This method was applied to a large array of environmental samples which include aerosols, water solids, water, sediments, and insect larva. The water solids and water samples were from both the Walker Branch Watershed and the Holston River. A series of water solids samples were taken each month at four sites in the Walker Branch Watershed to determine the output of elements in the water solids in the water flow from the area. The results from this study show that the element loss rate from the watershed varies seasonally as well as geographically. These results and the methods used to determine the elements in aerosols and water solids will be submitted for publication. (L. C. Bate)

CONTRIBUTION TO CONTROLLED THERMONUCLEAR RESEARCH

Reflection of neutral atoms from the ORMAK inner wall deeply affects plasma temperature and, therefore, stability. These phenomena are not yet completely understood. The Atomic Physics and Plasma Diagnostic Group (originally in the Thermonuclear Division and now in the Physics Division), headed by C. F. Barnett, is investigating these, among other means of plasma diagnostics. E. Ricci was loaned to this group on September 19, 1974.

Reflection experiments. We have reflected 1- to 5-keV H^+ and He^+ from copper and gold surfaces in various conditions of chamber pressure, previous chamber-target treatment, and at various incident and scattering angles. The targets were in a scattering chamber, and the reflected particles entered an energy analyzer (located inside the chamber) by which their energy distribution was determined. Resulting reflected-particle spectra helped us identify six parameters that require adjustment before conclusive reflection results can be obtained. They involve vacuum quality, beam intensity, energy and point of incidence at the target, cleanliness of the target, and data handling efficiency. (E. Ricci)

Quadrupole mass analysis of vacuum components. To achieve a vacuum of 10^{-9} torr for reliable reflection experiments it is important to know both the scattering-chamber vacuum components and their behavior under various conditions. We have investigated these two problems by means of a quadrupole mass analyzer; we subjected the scattering chamber's inside wall successively to the atmosphere, uv light, heating (or "baking") with heating strips, infrared light, and cooling by a liquid-nitrogen coil.

Our results show that the most abundant components at 10^{-6} to 10^{-8} torr are H_2, OH, H_2O, N_2 (or CO), and CO_2. In less proportion — about one order of magnitude smaller — we found O_2, O (or CH_4), and hydrocarbon fragments, such as the free radicals ethylene (mass 27), ethyl (29), propynyl (39), propene (41), and propane (43). Finally, C, N, Ar, acetylene (26), ethane (30), and methyl (15) appear in very small quantities.

Ultraviolet and infrared lighting cause sharp rises in most components' partial pressures, which result in quick chamber pressure jumps of more than one order of magnitude. Baking causes a much slower increase in partial pressures, while liquid-nitrogen cooling results in no change. (E. Ricci)

Surface analysis for thermonuclear research. The ISX (impurity study experiment) is a Tokamak proposed to be built at ORNL jointly with General Atomic Company. It would be specifically dedicated to research on plasma-wall interactions and plasma diagnostics. A preliminary proposal was submitted for specific work at the ISX entitled, "Experiments with Injected Neutral Atom Beams," by E. Ricci, D. H. Crandall, and C. F. Barnett. We would be involved mainly in a two-year, dual project — "ISX Inner-Wall 'In-Situ' Neutral Reflection Study and Surface Composition by Analysis of Neutral Impact Radiation." (E. Ricci)

POLLUTION ABATEMENT OF TOXIC MATERIALS

We continued our NSF(RANN) project on the solvent extraction removal and recovery of cyanide, zinc, and cadmium from industrial wastes of the metal-finishing industry. Selected quaternary amines were used to extract metal cyanides and free cyanide. The solvent was regenerated by stripping the metal and cyanide with dilute sodium hydroxide. Particular emphasis was focused on the treatment of actual effluents from an industrial plater. Our major objectives are (1) to "close the loop" by recovering and recycling costly chemicals (cyanide, metals) now wasted, (2) to eliminate current troublesome and expensive sludge problems, and (3) to recycle the decontaminated water for reuse in the plant, thereby minimizing sewer taxes and raw water costs — the major operating expenses of many plants. Of considerable importance is the fact that the treated water may be recycled, thus eliminating a large fraction of the total effluent volume. The Environmental Protection Agency is encouraging reductions in water discharge volumes in addition to lowering pollutant concentrations in the effluent streams.

On the basis of 60 laboratory-scale miniplant demonstration runs, the process appears most promising for the treatment of waste rinse solutions containing cyanide and zinc. Details of this work are presented in another ORNL report[22] and two open-literature publications.[23,24] A paper on the process demonstrations is in preparation, a patent application has been filed on part of the work. (F. L. Moore)

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[22] 22. F. L. Moore et al., *Ecology and Analysis of Trace Contaminants Annu. Prog. Rep. December 1975* ORNL-NSF-EATC-21, in preparation.

[23] 23. F. L. Moore, "Liquid-Liquid Extraction of Zinc with High-Molecular-Weight Amines from Alkaline Cyanide Solutions," *Sep. Sci.* 10, 489–97 (1975).

[24] 24. F. L. Moore, "Solvent Extraction of Cadmium from Alkaline Cyanide Solutions with Quaternary Amines," *Environ. Lett.* 10, 1 (1975).

3. Energy Programs: Molten-Salt Reactor Program

A. S. Meyer, Head

The long-term objective of the MSBR Analytical Chemistry Research and Development Group is to provide the chemical methodology and techniques required to achieve a safe and efficient Molten-Salt Breeder Reactor. The strongest emphasis is placed on the demonstration of the feasibility of in-line methods for constituents or properties of reactor streams essential for power operation. Essential determinations will include the redox condition of the fuel [U(IV)/U(III) ratio], oxide and bismuth contamination, and corrosion indicators of both fuel and coolant salts. Measurement of tritium distribution throughout the system is of utmost significance. A diversity of approaches will be investigated, including electroanalytical, spectrophotometric, and chemical methods.

At present, we are performing electrochemical in-line measurements in fuel systems. Our in-line responsibilities continue to increase. We are also conducting studies of the electrochemical behavior of bismuth and tellurium in fuel melts. At the Coolant-Salt Technology Facility (CSTF), first measurements have been made on the tritium distribution within the system.

Spectral and electrochemical research in actinide chemistry, which is in part associated with the MSRP, is being carried out at the Transuranium Research Laboratory. Spectral studies of actinides and their compounds are an outgrowth of experiments that were related to the MSRP, but the present investigation has expanded considerably to include studies of actinide compounds and possible schemes to determine these compounds in the environment. A new area of very sensitive element determination and identification by resonance ionization spectroscopy is also an outgrowth of MSRP interests that will later be applied to MSRP problems.

TRITIUM TRANSPORT EXPERIMENTS AT THE COOLANT-SALT TECHNOLOGY FACILITY

One of the important technological hurdles along the path to the realization of a molten-salt breeder reactor is control of tritium emissions. During this reporting period, several divisions participating in the Molten-Salt Breeder Reactor Project have cooperated in addressing this problem. The Analytical Chemistry Division has contributed about a 1½-*man-year effort* to the essential tritium measurements in mockup experiments at the CSTF.

Before the program was interrupted in 1973, plans had already been formed to establish experimentally whether or not a sodium fluoride–sodium fluoroborate eutectic mixture could successfully trap the tritium between the primary coolant (fuel salt) and the steam generating system. Tritium is produced in the primary salt by neutron absorption in lithium at a rate of about 2400 Ci/day in the 1000-MW(e) MSBR conceptual design,[1] but no more than a few pCi per liter of effluent water is allowed for light-water-cooled nuclear power reactors.[2] Clearly, the coolant loop(s) between the primary fuel-salt system and the steam generating system *must* be capable of trapping or chemically converting tritium for removal and disposal.

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[1] R. B. Briggs, J. R. Engel, and P. N. Haubenreich, "Environmental Effects and Safety," p. 391 in *The Development Status of Molten-Salt Breeder Reactors*, ORNL-4812 (August 1972).

[2] *Code of Federal Regulations*, Title 10, Part 50, Appendix I.

A test loop (CSTF) at the Y-12 Plant has been used for the circulation of a molten NaF-$NaBF_4$ eutectic mixture for corrosion and other studies. Original plans to measure the fate of hydrogen introduced into the salt stream called for the injection of deuterium into the salt. When the program was resumed in 1974, a series of discussions ensued, and a committee was formed to prepare a summary of possible alternate coolant concepts. The sodium fluoroborate system was seriously challenged mainly on grounds that possible heat exchanger leaks on either the steam generator side or the fuel salt side could produce reactions leading to costly or safety-significant situations. But some preliminary measurements[3] with the sodium fluoroborate system indicated a likelihood that elemental tritium might be significantly confined in the salt. Thus a decision was made to try some tritium injection experiments immediately to establish the efficacy of this system for tritium removal.

A method was developed for collecting samples of the cover gas for analysis. A low, but quite detectable, level of tritium was measured in the gas (helium and argon) contained in the empty loop during shutdown. This "background" level of 1 to 2 pCi/ml has not appeared to change over the past year, and the source is uncertain. However, some components were fabricated from MSRE materials which were known to contain significant quantities of absorbed tritium, but the loop has now operated at high temperatures for a time far in excess of that required for absorbed tritium to have diffused from the loop wall. Nevertheless, the small tritium background persists and was useful in the development of the analytical gas sampling apparatus. A conventional hot copper oxide bed converter oxidizes the tritium to tritiated water, which is collected in condensation and cryogenic traps, diluted, and counted by beta liquid scintillation in an emulsion cocktail. Early results were quite erratic and depended on the history of the connecting tubing from the loop to the analysis train. To exclude BF_3 from the copper oxide bed, a series of traps containing water were placed just before the bed. Quite remarkably, the tritium level measured in the scrubbed gas declined to near zero, and a measure of tritium in the water from the pretraps showed a nearly complete trapping of tritiated species in the water. This unexpected result was quite encouraging, since the conversion of elemental tritium to a water-soluble species was indicated. Some experiments were performed to establish that elemental tritium was *not* being trapped in the water via exchange reactions or enhanced solubility in a BF_3-water solution.

A steady effort was made to improve the sampling apparatus and gain increased reproducibility in the sampling of the background before commencing a tritium injection experiment. Copper and nickel sampling lines were both tried, and nickel gave the most reproducible analyses after a period of conditioning which probably involved some NiF_2 formation to form an inert film on the tubing walls. Although some important sampling problems still exist, a reasonable reproducibility and precision were obtained by permitting a small side stream (0.1 liter/min) of the normal off-gas flow (2 liters/min) to pass continuously through the nickel sampling line. This stream normally flowed to exhaust except when a sample was collected; then it was diverted through the analysis train, that is, the water-filled pretraps, heated copper oxide bed, condensation trap, cryogenic trap, and wet test gas volume meter. Since the principal gas component is helium, the gas meter reading is approximately equal to the total gas sampled. Samples of known volume were collected, and aliquots of the pretrap and after-trap solutions were counted. Thus, data were reduced to concentrations of water-soluble tritiated species and elemental tritium species.

Engineers in the Reactor Division designed the apparatus for injection of tritium into the circulating salt stream. Tritium was mixed with normal hydrogen (0.1% tritium) and diffused through a silver-palladium alloy scrubber to remove traces of other gases. The purified hydrogen mixture was stored in a holding cylinder and during an injection was allowed to diffuse through a nickel diaphragm in the insertion probe. A pressure differential measurement afforded a simple means of calculating the total hydrogen delivered.

Two injections have been made during this reporting period (Tables 3.1 and 3.2). In each case about 80 mCi of tritium was introduced into the salt stream over a period of about 11 hr. Only the cover gas and the salt were periodically sampled and analyzed. Because the response was unpredictable for the first injection, some arbitrary sampling times were selected. During the second injection the sampling times were more ideal, based on the previous experience. Water-soluble tritiated species continued to be present in a quantity much in excess of elemental species. One significant factor contributing to the scatter in the data from the first injection can be related to the discovery of a sample holdup region in the apparatus. After samples

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[3] W. R. Grimes et al., "Fuel and Coolant Chemistry," p. 157 in *The Development Status of Molten-Salt Breeder Reactors*, ORNL-4812 (August 1972).

Table 3.1. Tritium concentrations in cover gas samples from the CSTF

Date	Time	μCi tritium/m³ cover gas H$_2$O soluble	 Elemental
		First injection experiment	
7-17	1002[a]		
7-17	1046	2.3	3.4
7-17	1305	0.7	12
7-17	1700	1.4	170
7-17	1911	1.8	93
7-17	2050[b]		
7-17	2243	1.4	830
7-18	0100	3.2	430
7-18	0805	7.3	61
7-18	1000	44	71
7-19	1037	796	62
7-21	0905	1800	13
7-21	1325	50	13
7-22	0925	55	5.8
7-23	1303	85	29
7-24	1000	300	22
7-25	1315	340	26
7-28	1245	10	2.7
		Second injection experiment	
8-5	0730	96	0.5
8-5	0846[a]		
8-5	0930	110	2.2
8-5	1130	2,200	10
8-5	1330	5,300	20
8-5	1530	7,500	27
8-5	1830	13,000	34
8-5	1912[b]		
8-5	1930	13,000	34
8-5	2100	12,000	40
8-5	2315	9,300	39
8-6	0730	9,300	28
8-6	1100	7,000	16
8-6	1500	6,500	14
8-6	2000	4,700	10
8-7	0900	3,300	6.8
8-7	1415	2,400	4.9
8-8	0930	1,600	3.4
8-9	1450	1,600	5.2
8-10	1040	1,300	2.8
8-11	1230	900	2.5
8-12	1010	570	1.1
8-13	1010	230	0.8
8-15	1000	180	1.6
8-18	0935	80	0.5
8-28	1010	70	0.5
9-12	1020	50	0.4
9-15	1010	40	0.4

[a] Injection started.
[b] Injection stopped.

Table 3.2. Tritium concentrations in salt samples from the CSTF

Date	Time	nCi/g
	First injection experiment	
7-17	1002[a]	
7-17	1108	12
7-17	1300	23
7-17	1512	35
7-17	1718	51
7-17	1930	93
7-17	2050[b]	
7-17	2145	73
7-17	2321	112
7-18	1102	32
7-18	1912	30
7-19	0830	15
7-19	0952	7.5
7-21	1132	1.6
7-22	1400	1.6
7-23	1330	2.0
	Second injection experiment	
8-4	1313	0.8
8-5	0846[a]	
8-5	0954	9.0
8-5	1145	21
8-5	1350	36
8-5	1526	52
8-5	1848	71
8-5	1912[b]	
8-5	1932	68
8-5	2125	71
8-5	2335	50
8-6	0830	30
8-6	1507	19
8-6	2010	16
8-7	1014	9.5
8-7	1528	8.1
8-8	1018	3.6
8-9	0916	4.2
8-11	1248	2.9
8-12	1035	1.4
8-13	1048	2.2
8-15	1010	1.4
8-18	1010	0.7

[a] Injection started.
[b] Injection stopped.

had been collected for several days, a noticeable amount of liquid had collected in the short glass section between the stopcock, used to divert the gas stream, and the first trap in the analysis train. The liquid was washed from the glass, counted, and found to contain about 60 μCi of tritium. This discovery clearly complicates the interpretation of the data, since a substantial portion of the cover gas tritiated species never reached the analysis train. The source of the liquid was reaction of BF_3 with moisture in the air. Unfortunately, the short piece of connecting glass tubing was exposed to the air each time a sample was collected. No changes in the apparatus were made for the second injection, but the short length of glass tubing was rinsed each time with a hypodermic needle and syringe; these washings were added to the pretrap solution.

Results of the second injection show a much more continuous response for all three quantities measured. Insofar as data from the first experiments can be interpreted, the results from the second experiment are somewhat comparable; that is, the tritium levels in the salt peaked at roughly 2 hr after the injection was terminated, and the water-soluble tritiated species were 400- to 500-fold in excess of the elemental species.

These data establish that the salt or a component of the salt mixture reacts with hydrogen to produce a water-soluble gaseous species. This discovery is very encouraging, since a water scrubber on the off-gas of an MSBR coolant loop would be a simple and economical method to restrict tritium. Further tests are planned to determine a mass balance on injected hydrogen and to observe the effect of adding small amounts of water to the salt during an injection of tritium. (A. S. Meyer, B. R. Clark, R. F. Apple)

IN-LINE ANALYSIS OF MOLTEN FLUORIDE SALTS

Corrosion test loops described previously[4] continue to operate with circulating reference fuel salt, LiF-BeF_2-ThF_4 (72-16-12 mole %). Loop 31 was recently placed in operation, and several more are expected to begin operation within the next few months. The corrosion test loop experiments are under the general supervision of H. E. McCoy of the Metals and Ceramics Division and are designed to test the capability of Hastelloy N and other container materials with the fuel salt under various conditions. Correlations are made with respect to U(IV)/U(III) ratios, fuel salt composition, and salt temperatures.

Measurements made of the U(IV)/U(III) ratio in the forced-convection loop, FCL-2b, indicate a "steady-state" value of about 100. This is somewhat lower than the apparent steady-state value obtained with the experimental melt, LiF-BeF_2-ThF_4 (68-20-12 mole %), and indicates a less oxidizing melt. The melt which started at a ratio of around 1000 reached this level via a redox process which probably involves reduction of the U(IV) by the chromium in the container walls. No attempts have yet been made to reoxidize the melt by suitable additions of NiF_2 or some other oxidant. It is interesting that the decrease to a steady-state value occurred after about 75 days, with a rapid decrease in the first 30 days. The observed oscillations in the data probably result from air contamination, with subsequent oxidation of U(III) when the loop was not operating or during specimen examination. This was most prominent with the experimental melt when the U(IV)/U(III) ratio was substantially greater than the steady-state value reached at a later date.

Ratios of U(IV)/U(III) measured in the two thermal convection loops, NCL 21 and NCL 23, are approximately 7.6×10^3 for loop 21 and 5 for loop 23. No unusual trend is apparent in the history of the oxidation state of the fuel melt in NCL 21. This loop has operated for about 240 days with Hastelloy N corrosion specimens. It is observed that a rather dramatic rise in the ratio occurs whenever new specimens are added. This is attributed to the unintentional introduction of moisture and air which partially oxidizes the U(III). A recovery to lower ratios follows each increase in repetitive fashion.

The fuel melt in the Inconel loop, NCL 23, was rapidly reduced to a U(IV)/U(III) ratio around 40. Since then the ratio has continued to decline until reaching a relatively stable value near 5. A high level of chromium in the Inconel provides sufficient reductant to reduce the U(IV) more extensively than has been observed in Hastelloy N loops; therefore the greater U(III) concentration is not surprising. This melt is now one of the most reducing melts we have observed so far, and it may well be approaching the applicable limit of the voltammetric method.

Recently, electroanalytical measurements were initiated on loop 31, which is a type 316 stainless steel thermal convection loop that contains Li_2BeF_4. The purpose of this loop is to gain baseline corrosion data. Our program will be to record cathodic and anodic voltammograms on the melt during the period of operation to follow corrosion product behavior, changes in the equilibrium potential of the melt, and other parameters for which the current-voltage curves may give useful information.

The first cathodic voltammograms recorded at startup revealed two reduction waves with peak potentials at ~ 0.13 and 0.48 V vs Ir QRE. We believe the first

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4. H. E. McCoy et al., "Materials Development," *MSR Program Semiannu. Prog. Rep. Aug. 31, 1974*, ORNL-5011, p. 76.

and second waves correspond to the reduction of Fe(II) and Cr(II) respectively. After approximately one week of operation, however, the first wave was no longer detected, and the decomposition potential of the melt shifted anodically, which indicated that the melt had become more reducing. Since this initial period of reduction, the position of the Cr(II) wave has not changed significantly, indicating that the concentration of the diffusing species and the equilibrium potential are both remaining stable.

TeGen experiments are a series of ORR poolside experiments set up to irradiate prospective MSBR container materials. These experiments are designed to produce a fission product inventory similar to that in the MSRE when intergranular cracking was observed. Our role is to determine the U(IV)/U(III) ratio in situ in the salt charge prior to irradiation. Electrochemical measurements on the salt charge for TeGen-2 revealed a U(III) concentration of about 1.7%, which was considered acceptable. The voltammograms for the U(IV) → U(III) electrode reaction, although usable, were not generally as well defined as in the research melts and in the corrosion test loops. A small post-wave was observed on top of the U(IV) reduction wave which increased as the experiment progressed and became a nuisance during final measurements. It became difficult to determine the half-wave potential for the U(IV) wave from normal scans; however, by derivative techniques, we were able to resolve the derivative peak for the uranium reduction wave and thus assign half-wave potentials from which U(IV)/U(III) ratios were calculated.

The post-wave was not identified; in fact, it is not normally observed in uranium-containing melts. The wave exhibited the general characteristics of an adsorption wave which would result if melt conditions favored adsorption of U(IV) on the electrode. We have previously observed that uranium tends to be weakly absorbed at electrode surfaces. We will note if the post-wave occurs again during the electrochemical measurements for TeGen-3, and efforts will be made to better characterize it. (D. L. Manning, R. F. Apple, A. S. Meyer)

ELECTROANALYTICAL STUDIES IN MSBR FUEL SALTS

Electroanalytical studies of bismuth. Voltammetric studies of bismuth[5] in molten LiF-BeF_2-ZrF_4 (65.6-29.4-5.0 mole %) were continued to ascertain the lower limits of detection by linear scan voltammetry and anodic stripping techniques. This study is directed toward determining the feasibility of making in-line measurements of traces of bismuth in the return stream from processing systems.

As indicated previously,[6] bismuth is slowly lost from the melt, presumably by volatilization as BiF_3. Nickel is an anticipated interference, so it was decided to observe the effect of nickel on the bismuth voltammograms while enough bismuth (~5 mM) remained to yield well-defined curves. Nickel as NiF_2 was added to give a concentration of 15 mM Ni^{2+}. Voltammograms were recorded at gold, iridium, and glassy carbon electrodes. At the three electrodes, the reduction of bismuth occurs first at ~ 0.05 V followed by nickel at about 0.25 V. Thus the peak potentials are separated by about 200 mV, which, although not ideal, warrants investigation at lower concentration levels. In general, the best resolution, definition, and reproducibility are obtained at the gold electrode. However, on reverse scans, a single stripping peak is observed at gold which may correspond to a Bi-Ni alloy oxidation.

Voltammograms for the reduction of bismuth in the presence of nickel at an iridium electrode revealed that the nickel wave was poorly defined, although two clearly separated stripping peaks were obtained on reverse scans. The first peak could correspond to the oxidation of nickel or possibly Ni-Bi alloy, followed by the second peak, which corresponds to bismuth stripping from the electrode. When we start the scan at an initial potential of about +0.4 V vs Ir QRE, a small prewave is seen which is believed to be a bismuth adsorption wave resulting from adsorbed bismuth at the electrode surface.

The slow loss of bismuth from the melt at 600°C was followed voltammetrically; the concentration decreased from ~400 to about 7 ppm in 40 days. This is about the lowest concentration that can be measured by direct linear scan voltammetry. For measurements at lower concentrations, we relied on anodic stripping techniques. First, bismuth was plated under controlled conditions of time, potential, etc., onto glassy carbon at a potential sufficiently cathodic to reduce Bi(III) but not Ni(II). Then the bismuth was stripped from the electrode by scanning the potential anodically; the peak height of the anodic stripping curve is a function of the concentration of bismuth. Calibration of the anodic

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5. J. S. Hammond and D. L. Manning, "Studies on the Electroreduction of Bismuth(III) in Molten LiF-BeF_2-ZrF_4 by Voltammetry and Chronopotentiometry," *High Temp. Sci.* 3, 99 (1971).

6. A. S. Meyer et al., "Electroanalytical Studies in Molten LiF-BeF_2-ZrF_4 (65.6-29.4-5.0 mole %)," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 27.

stripping method was achieved by relating the peak height of the stripping curves to the concentration of bismuth calculated from voltammetry and assuming linearity at lower bismuth concentrations. The peak height of the stripping curves was observed to be approximately a linear function of plating time. Utilizing this technique with plating times of ~30 min, we followed the continued loss of bismuth from the melt to sub-ppm (<25 ppb) concentrations. At longer plating times, interference of nickel is more severe.

The prewave (bismuth adsorption) observed at the iridium electrode did not change appreciably until the bismuth concentration was below ~1 ppm; then the prewave decreased markedly but not linearly with bismuth concentration. In fact, a small prewave was still observed when the bismuth concentration was below detection by anodic stripping. It is believed that this wave may still prove of value — possibly as a qualitative indicator. We plan to carry out additional anodic stripping studies on bismuth concentrations in fuel melts, LiF-BeF_2-ThF_4 (72-16-12 mole %), that do not contain nickel. **(D. L. Manning, G. Mamantov)**

Electroanalytical studies of iron. Iron(II) is a corrosion product normally present in molten fluorides. We have previously carried out electrochemical studies of iron(II) in molten LiF-NaF-KF (46.5-11.5-42.0 mole %), LiF-BeF_2-ZrF_4 (69.6-25.4-5.0), and $NaBF_4$-NaF (92-8 mole %).[7,8] Since the fuel solvent for the MSBR is a thorium-containing salt, LiF-BeF_2-ThF_4 (72-16-12 mole %), it was of interest to conduct voltammetric and chronopotentiometric studies of iron(II) in this fuel solvent. To determine concentrations and/or diffusion coefficients by linear sweep voltammetry, it is necessary to know whether the product of the electrochemical reaction is soluble or insoluble. The measurements discussed below were done with this purpose in mind.

Voltammograms for the reduction of iron(II), $Fe^{2+} \rightarrow Fe^0$, at a gold electrode closely approximated the theoretical shape based on current functions tabulated by Nicholson and Shain[9] for a reversible wave where both the oxidized and reduced forms of the electroactive species are soluble. Thus, even though Fe^{2+} is reduced to the metal at gold, the electrode reaction very closely approximates the soluble product case, apparently through the formation of iron-gold surface alloys. Also, from chronopotentiograms, the ratio of the forward to reverse transition time (τ_f/τ_r) compares favorably with the theoretical value[10] of 3 for the soluble case, which again points to the formation of surface alloys.

For the reversible deposition of an insoluble substance at pyrolytic graphite, where $n = 2$, the voltammetric $E_p - E_{p/2}$ = 30.5 mV at 650°C is in good agreement[11] with the experimental value. The chronopotentiometric τ_f/τ_r is approximately unity,[10] which also is indication that Fe^{2+} is reduced to metallic iron without any apparent interaction with the pyrolytic graphite, and all the iron is stripped from the electrode upon current reversal. Iron appears, therefore, to be reversibly reduced to a soluble form at gold and an insoluble form at pyrolytic graphite.

The τ_f/τ_r ratio at an iridium electrode is approximately unity at 518°C and 3 at 600°C, which is evidence that Fe^{2+} reduction at iridium approximates the insoluble species case (as with pyrolytic graphite) at 518°C and the soluble product case (similar to gold) at 600°C. This change in reduction behavior with temperature was not as pronounced at gold or pyrolytic graphite.

Average diffusion coefficients for Fe^{2+} evaluated from the chronopotentiometric measurements by means of the Sand equation[12] are approximately 4.2×10^{-6}, 8×10^{-6}, and 1.5×10^{-5} cm^2/sec at 518, 600, and 700°C respectively. **(D. L. Manning, G. Mamantov)**

Electroanalytical studies of tellurium. Tellurium occurs in nuclear reactors as a fission product and recently has been considered as a prime cause for intergranular cracking in structural metals and alloys.[13] It is of interest to characterize this substance electrochemically and ascertain the feasibility of in situ measurements. We previously carried out preliminary polarization measurements at a small tellurium pool electrode in molten LiF-BeF_2-ZrF_4 (ref. 14) to establish the potentials at which tellurium is oxidized and reduced in the molten fluoride environment. These

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[7] F. R. Clayton, Jr., "Electrochemical Studies in Molten Fluorides and Fluoroborates," doctoral dissertation, University of Tennessee, December 1971, p. 82.

[8] A. S. Meyer et al., *MSR Program Semiannu. Prog. Rep. Aug. 31, 1974*, ORNL-4728, p. 44.

[9] R. S. Nicholson and I. Shain, "Theory of Stationary Electrode Polarography," *Anal. Chem.* 36, 707 (1964).

[10] W. H. Reinmuth, "Chronopotentiometric Transition Times and Their Interpretation," *Anal. Chem.* 32, 1514 (1960).

[11] G. Mamantov, D. L. Manning, and J. M. Dale, "Reversible Deposition of Metals on Solid Electrodes by Voltammetry with Linearly Varying Potential," *J. Electroanal. Chem.* 9, 253 (1965).

[12] Paul Delahay, *New Instrumental Methods in Electrochemistry*, pp 179 ff., Interscience, New York, 1954.

[13] H. E. McCoy, "Materials for Salt-Containing Vessels and Piping," p 207 in *The Development Status of Molten-Salt Breeder Reactors*, ORNL-4812 (August 1972).

[14] A. S. Meyer et al., *MSR Program Semiannu. Prog. Rep. Aug. 31, 1974*, ORNL-4728, p 42.

preliminary observations indicated that electrode reactions are complex.

For tellurium screening studies, J. R. Keiser (Metals and Ceramics Division) fabricated an experimental cell equipped with viewing ports and electrode ports to study the stability for lithium telluride, Li_2Te, in molten LiF-BeF_2-ThF_4. The Li_2Te was added as pellets, and voltammograms were recorded at gold and iridium electrodes.

As Li_2Te was added to the melt, the voltammograms became very complex and are not yet completely understood. For clarity, pertinent observations at the iridium and gold electrodes are listed separately.

1. When one 35-mg pellet of Li_2Te was added, a reduction wave observed at an iridium electrode at −0.9 V vs Ir QRE disappeared. This wave is not yet identified. The pellets did not melt or dissolve immediately. Relics of the pellets could be seen on the surface for several days. The windows of the viewports became coated with bluish-gray deposit after a few days which made viewing of the melt impossible. The bluish-gray deposit is believed to be tellurium metal. This is indicative that tellurium species added as Li_2Te are not stable in the melt.

2. Voltammograms recorded after additions of Li_2Te did not reveal any waves that could be attributed to soluble electroactive tellurium species. Chemical analysis indicated <5 ppm Te in the melt.

3. At an iridium electrode, a reduction wave was observed at 0.45 V vs Ir QRE that was reasonably well defined at a scan rate of 0.02 V/sec. This wave is due to Cr^{2+} reduction, and the wave height increased upon addition of CrF_2 but did not change upon addition of Li_2Te. At our normal scan rate of 0.1 V/sec, the wave was not well defined; this explains in part why it was not positively identified on background scans at this scan rate.

4. Voltammetric waves indicative of telluride films on a gold electrode were observed. These waves, however, disappeared after adding CrF_2 to the melt. The voltammograms recorded at gold following the Li_2Te additions became very complex and difficult to analyze; the electrode reactions are not yet resolved.

Additional voltammetric measurements are planned whereby the supposedly more soluble and stable $LiTe_3$ species will be added to the fuel melt. **(D. L. Manning, A. S. Meyer)**

SPECTROPHOTOMETRIC RESEARCH

Spectral techniques continue to be applied to the general area of actinide element research to provide information for the identification and characterization of various oxidation states and compounds of these ions. As these techniques are delineated, they are utilized in following chemical reactions of the transuranium elements, both to assess the purity of newly synthesized compounds and to characterize the usefulness of various synthetic routes. During this period these studies were applied almost exclusively to solid-state compounds and to samples weighing several micrograms or less. In the study of the thermal reduction of $CfBr_3$,[15] reported in the last annual, a refracting microscope-spectrophotometer of local design was modified, by the addition of a coil of platinum wire, to provide a heatable sample location. Further modifications have been made to the equipment, by the inclusion of critical light stops, Cassegranian reflecting microscope objective lenses, and quartz field lenses. With these changes, spectral studies, either absorption or luminescence, can be carried out over the wavelength range of 300 to 1200 nm on samples of less than 100 ng heated to temperatures as high as 700°C. Another member of the Transuranium Research Laboratory group, J. R. Peterson, has equipment to obtain heated or freshly annealed x-ray powder diffraction patterns[16] of the same sample. With these two identification techniques, we reexamined the H_2 reduction of $CfBr_3$.[17] We have identified $CfBr_3$, CfOBr, and $CfBr_2$ by both spectral and x-ray methods. Based on spectral results we have found that treatment of $CfBr_3$ with H_2 at a temperature below 650°C causes no discernable reduction of Cf(III). At slightly higher temperatures, approximately 675°C, the rate of reduction is increased and $CfBr_2$ is formed. However, at the increased temperature, the rate of formation of CfOBr is likewise increased. The extent of reduction is therefore a compromise of both temperature and time of heating. With too high a temperature or too long a time, CfOBr is the final product. With the above

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15. J. P. Young, K. L. Vander Sluis, G. K. Werner, J. R. Peterson, and M. Noe, "High-Temperature Spectroscopic and X-Ray Diffraction Studies of Californium Tribromide: Proof of Thermal Reduction to Californium Dibromide," *Journal of Inorganic and Nuclear Chemistry*, in press (1975).

16. J. N. Stevenson and J. R. Peterson, "Some New Microchemical Techniques Used on the Preparation and Study of Transplutonium Elements and Compounds," *Microchem. J.* **20**, 213 (1975).

17. J. P. Young, R. G. Haire, R. L. Fellows, M. Noe, and J. R. Peterson, "Spectroscopic and X-Ray Diffraction Studies of the Bromides of Californium-249 and Einsteinium-253," in *Proceedings of the 4th International Transplutonium Element Symposium*, W. Mueller and R. Lindner, eds., North Holland, Amsterdam, in press.

competing reactions, it has not been possible for us to prepare pure CfBr_2, although the dibromide has been a major component of some samples. It seems probable that CfOBr is formed by a reaction of reduced Cf species with SiO_2. Whether it is a direct reaction of CfBr_2 or a thermal disproportionation of CfBr_2 followed by a reaction of Cf metal with SiO_2 is not understood. Experimental work to elucidate the mechanism is under way, and other container materials or liners will be considered in an effort to make pure CfBr_2. It is interesting to note that this microspectral technique is able to show individual differences in individual crystalline masses that can only be observed as an "averaged" sample by x-ray methods.

In our studies of the synthesis of actinide compounds, we have prepared and identified $^{253}\mathrm{EsBr}_3$ for the first time by both spectral and x-ray diffraction patterns.[18] Prior to this study it was thought that perhaps the extreme radioactivity of $^{253}\mathrm{Es}$ (decay energy of 3660 kcal mole^{-1} min^{-1}) might prevent the preparation of any stable trivalent bromide. Einsteinium compounds represent examples of the heaviest element that can be obtained in directly observable amounts for the next several years. This and the radioactive nature of einsteinium make study of its chemistry, solution and solid state, of interest and importance. We have studied the reaction of EsBr_3 with H_2 and water vapor and have come to the tentative conclusion that we have prepared EsOBr and other compounds which do not appear to be divalent.[15] It is also possible that reduced einsteinium compounds are not compatible with SiO_2. Further work will be carried out after the influence of SiO_2 on Cf halide chemistry is understood. R. G. Haire, Chemistry Division, R. L. Fellows, a postdoctoral Fellow, and J. R. Peterson, University of Tennessee, are cooperating in the above studies.

Since there is interest in the determination of plutonium in the environment, the possible fluorescence of aqueous plutonium in its various oxidation states at room temperature has been investigated over the wavelength range of 300 to 800 nm. No emissions were observed for aqueous solutions of plutonium in any of its oxidation states of (III), (IV), (V), (VI), or (VII). Prior to this work there had been no reported systematic study of such possible fluorescence.

A reaction of thenoyltrifluoroacetone (TTA) with Pu(VI) was found to yield a fluorescent, organic product which might serve as a basis for a fluorometric determination of Pu(VI). In a slightly basic solution, pH 7 to 8, Pu(VI) will oxidize TTA within a matter of seconds to yield a product that exhibits an emission peak at 550 nm with a shoulder at 500 nm. At the same pH in the absence of plutonium, TTA is oxidized slowly, in a matter of days, to yield the product. Since the oxidation is rapid with Pu(VI), a fluorometric determination of Pu(VI) is possible using a standard calibration curve. It has also been demonstrated that Pu(VI) is reduced to Pu(IV) in the reaction with TTA. The method is therefore ideally suited to the fluorometric determination of Pu(VI), even in the presence of Pu(IV), and with the incorporation of photon counting techniques, the determination could be quite sensitive. Results of this work are in press.[19] (J. P. Young)

RESONANCE IONIZATION SPECTROSCOPY

During this report period we have carried out cooperative studies with G. S. Hurst's group, Health Physics Division, that should lead to the development of a new and unique analytical spectroscopic tool. The research effort of this project involves a study of the interaction of energy sources, protons generated by a Van de Graaff unit and/or laser photons, with various inert gases, elemental vapors, and impurities therein. The results of such interactions can be detected either by emission from the excited gases in the vacuum ultraviolet spectral region, or by transfer of the excited-state energy to impurity species, followed by lower-energy emissions from the impurities. A third possible method of detection has been named resonance ionization spectroscopy (RIS). In RIS, a vapor is allowed to interact with a high-energy source, proton beam or laser, to create a metastable or resonant excited-state species. During the lifetime of this state, it is allowed to interact with a laser beam of proper energy to further excite the atom to an energy state more than half-way to its ionization potential. A second photon of the same laser beam will then photoionize the atom in question, and the ion can be detected with excellent sensitivity by standard techniques. With a knowledge of the various excited-state energy levels of a particular vapor, it is possible to selectively, even specifically, detect very few atoms of the gas by means of this technique. The principle of RIS has been experimentally demon-

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[18] R. L. Fellows, J. R. Peterson, M. Noe, J. P. Young, and R. G. Haire, "X-Ray Diffraction and Spectroscopic Studies of Crystalline Einsteinium(III) Bromide, $^{253}\mathrm{EsBr}_3$," *Inorg. Nucl. Chem. Lett.* 11, 737 (1975).

[19] M. A. Lyster, R. L. Fellows, and J. P. Young, "Search for Plutonium Fluorescence," in *Proceedings of the 5th International Conference on Plutonium and Other Actinides*, H. Blank and R. Linder, eds., North Holland, Amsterdam, in press.

strated[20,21] by proton excitation of helium to the He(2^1S) state and subsequent photoionization of this excited helium by absorption of light of a wavelength of 501.5 nm. In this study it was shown that helium photoions are created by a two-photon absorption and also by a one-photon absorption followed by collision-induced associative ionization. We plan to study not only multiphoton single or multiple energy absorption by elemental vapors to produce photoions, but also multiphoton absorption followed by various collisional or energy transfer processes which also yield a detectable photoion. In general, the energy sources for these studies are tuned lasers, and at present the detector is a proportional counter. Within the limits of the range of tunable lasers, the specificity and extreme sensitivity of the RIS technique are ideal features to be exploited analytically. (J. P. Young)

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[20] G. S. Hurst, M. G. Payne, M. H. Nayfeh, J. P. Judish, and E. B. Wagner, "Saturated Two-Photon Resonance Ionization of He(2^1S)," *Phys. Rev. Lett.* 35, 82 (1975).

[21] 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).

4. Energy Programs: Gas-Cooled Reactor Programs

D. A. Costanzo, Head

The Gas-Cooled Reactor Group was established in July 1974 to provide analytical chemistry support to the Laboratory's GCR Programs, which include the High-Temperature Gas-Cooled Reactor and the Gas-Cooled Fast Reactor. Our primary objective is to provide analytical chemistry capabilities for the chemical characterization of HTGR fuel. To this end, we rely heavily upon our experience in other reactor technology programs and evaluate and adapt existing methods of analyses to this unique reactor fuel. Where applicable or adequate methods do not exist, new methods must be developed. A long-term objective of the analytical chemistry development program is to adapt the methods, established for the analyses of depleted uranium or ^{235}U-bearing fuel, to glove-box and hot-cell operations in order that they may be used to qualify commercial recycle fuel and meet specifications. During the past year, our development efforts have been directed to the determinations of the particle failure fraction (i.e., particles with defective coatings), heavy metal contained in silicon carbide coated fuel particles, and the nitrogen contained in fuel kernels.

A method to determine the particle failure fraction was developed and adapted to glove-box and hot-cell measurement of irradiated fuel. In this method, exposed fuel is removed by gaseous chlorine at elevated temperature, collected as the metal chlorides, and measured. The Kjeldahl and inert-gas fusion methods were evaluated, and a vacuum fusion isotope dilution method is under development for the determination of nitrogen in carbide fuel kernels. In addition, a rapid method was demonstrated for the dissolution of silicon carbide pyrocarbon-coated particles.

A secondary objective of our research and development program is to provide analytical assistance to various GCR technology development programs. These support activities include a time-of-flight mass spectrometer to monitor the effluent stream of an HTGR particle-coating furnace, continuous monitoring of tritium in a GCFR capsule irradiation experiment, surveillance of fission products in the Peach Bottom HTGR, and process control for loading of weak-acid resin with uranium.

METHODS EVALUATION AND DEVELOPMENT

Determination of particle failure fraction. The method for the determination of the number of broken particles by a high-temperature (1500°C) chlorine leach, as developed in 1974,[1] was applied on a routine basis during the past year with great success. All types of fuel elements, particles as well as rods, are now given a standard 2-hr treatment. In addition, the system has shown versatility in application to experiments which were conducted in cooperation with members of the fuel development program. One of these was the study of migration of uranium into the low-density pyrocarbon buffer coat that contains the mixed oxide-carbon fuel prepared from the weak-acid resin. We heated samples of buffer-coated, carbonized resin particles, 15 and 75% converted, in argon alone at 1650°C. Migration by contact with the graphite container was significant, but vapor phase transport occurred to only a slight extent. Of interest also was

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[1] D. A. Costanzo et al., "Determination of Broken-Particle Fraction," *Anal Chem. Div. Annu. Prog. Rep. Sept 30, 1974*, ORNL-5006, p. 32

whether the migration of uranium would continue beyond the buffer coat into the inner dense pyrocarbon LTI (low-temperature isotropic) coat of a triso-coated particle. Chlorination of particles showing no visual damage indicated that migration was continuous through inner LTI coatings less than 30 μ thick. The effect of temperature was also studied. At 1500°C, migration increased with time to apparent breakdown of the buffer coat. At 1250°C it was continuous and stable with time, and at 1000°C, small and decreasing with time. The same material treated in argon alone at 1500°C showed no significant migration.

A statistical evaluation was also carried out on an experimental run of 16 samples representing all types of fuel entities relative to size and method of fabrication. The purpose was to ascertain the effect of various parameters on the broken-particle fraction.

Another problem of interest concerned the triso-coated particle in which damage might exist only in the outer dense pyrocarbon layer. The SiC layer thus exposed would be removed as $SiCl_4$ which perhaps could be absorbed and determined. An effective absorber was found in LiF at 250°, which yields LiCl equivalent to the $SiCl_4$. Measurement of the chlorine in the LiF absorber would be equated to the number of particles with damaged outer pyrocarbon coatings. Because rigorous drying of the whole system is necessary before each run to prevent hydrolysis of the $SiCl_4$, routine use of this method is precluded.

It became necessary during the year to determine the broken-particle fraction in irradiated fuel rods. The level of activity of some samples required operation in a hot cell; for others, operation in a glove box was sufficient. Accordingly, we designed a new chlorine leach apparatus adaptable to both sites. Since induction heating could not be used, these systems were limited to resistance heating at 1000°C, where the slow reaction rate requires prolonged chlorination times. Since carbon is a necessary reactant in the production of the volatile heavy-metal chlorides, we considered the use of carbon monoxide to increase this rate of removal of exposed fuel. Normally, carbon had been provided by the fuel coating, but this solid-state contact is often tenuous and uncertain. The experiments we performed showed that using carbon monoxide in twice its stoichiometric ratio to chlorine increased the rate of removal so that previous overnight runs could be completed in 7 hr. (D. E. LaValle)

Evaluation of an ignition-leach method for determining defective SiC coatings. Ignition of triso fuel particles in air at 900°C effectively removes the outer carbon coating and should, theoretically, remove the inner carbon coatings of particles which have a cracked SiC coating and convert the heavy metal contained in the kernel to the oxide. If the particles are then leached with an HNO_3-HF solution, the fuel contained in particles with defective SiC coatings should dissolve. Determination of the thorium or uranium in the leach solution should then yield the number of particles with defective SiC coatings.

A large number of samples of triso fuel particles containing kernels of uranium were carried through this ignition-leach process. The uranium in the leach solutions was determined fluorometrically. Some of the samples were ignited and leached for a second and even a third time. On a number of occasions the uranium content of the second and third leaches would be greater than that of the first leach. One explanation for this is that cracks in the SiC coatings could conceivably be sealed during the ignition process by the oxidation of SiC to SiO_2. On leaching, the cracks might or might not be reopened. On additional ignitions the cracks could either be reopened or remain sealed, giving ambiguous results. Because of the number of varied conditions possible, it was concluded that the ignition-leach procedure was not an acceptable method of determining defective SiC coatings. (F. L. Layton)

Phase II HTGR interlaboratory comparison program. In the summer of 1972 a program was initiated by New Brunswick Laboratory (NBL) for the purpose of determining the state of the art of thorium and uranium measurements in carbon- and silicon carbide coated uranium-thorium carbide fuel particles. This program was designated as the HTGR Interlaboratory Comparison Program.[2]

At the completion of the program, there were a number of questions left unanswered. It was therefore agreed that a second phase of the program should be conducted. This second phase would try to provide more definitive answers to the question of the state of the art. In addition to reaffirming the accuracy and precision of the thorium and uranium measurements at each laboratory, it would examine variations in performance with time and with sample preparation.

As a participant in the program, ORNL received ten sample sets. Each set contained two samples of a mixture of nonhomogeneous UO_2 and ThO_2 powder, one sample of biso fuel particles, and one sample of triso fuel particles. One set of samples was prepared and analyzed each month, so that the entire program extended over a ten-month period from September 1974 through June 1975. The mixed oxide samples

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[2] NBL-272, Appendix (a), pp. 113–15 (1974).

were dissolved in an HNO_3-HF mixture, the biso and triso samples were ignited to remove the outer carbon coating and then crushed in a mixer-mill. The biso samples were subsequently dissolved in an HNO_3-HF mixture, while the triso samples were reignited to remove the carbon from the inner coatings. The triso samples were then leached with an HNO_3-HF mixture, and the residues were fused with Na_2CO_3. Uranium was determined in quadruplicate, using a slight modification of the NBL titrimetric method. Thorium was determined in duplicate by EDTA titration.[3]

A total of 232 determinations were made on the 40 samples. The data were forwarded to NBL for statistical analysis and comparison with data received from the other participating laboratories. A complete report on the results of the program will be published in a forthcoming NBL report. (F. L. Layton)

Effects of high-energy alpha activity and technetium on the NBL titrimetric method of determining uranium. In the future, the determination of uranium will be required in HTGR recycle fuel processing samples which contain fission product technetium and ^{232}U. Since the NBL titrimetric method[2] is used to determine uranium, it will be necessary to know what effect technetium and high-energy alpha radiation have on the NBL procedure. If the technetium interferes, it would be desirable to find some method of removing it prior to titration. For these reasons, a study was undertaken with L. Z. Bodnar of NBL to determine these effects.

A series of standard solutions of uranium containing ~100 mg of uranium and from 1 to 15 mg of technetium was titrated using the NBL method. The technetium was found to be a serious interference. Several attempts were made to remove the technetium by volatilization from a mixture of sulfuric and perchloric acids heated to fuming. Low results for the uranium determinations (0.5 to 1.0%) indicated that small traces of technetium remained. If after evaporation of the test solution to dryness, the walls of the titration vessel are heated with the flame of a Bunsen burner, the titration of uranium can be carried out with no difficulty. Evidently the last trace of technetium is removed only after the flaming process.

For the purpose of determining the effect of high-energy alpha radiation on the NBL titrimetric method for uranium, ^{244}Cm was substituted for ^{232}U. A typical 100-mg uranium test sample will contain 100 μg of ^{232}U, which is equivalent to approximately 2 mCi of activity. Therefore, several test solutions containing ~100 mg of uranium were titrated after the addition of 2 mCi of ^{244}Cm. In one case, 4 mCi of ^{244}Cm was added. No interference was observed. (F. L. Layton)

Determination of nitrogen in uranium-loaded weak-acid resin kernels. Because nitrogen retained in process weak-acid resin (WAR) fuel kernels is transmuted to ^{14}C, which must be accommodated in fuel reprocessing to prevent its release to the environment, a measure of the amount of nitrogen present is of great interest.

Two methods have been evaluated for the determination of nitrogen in WAR kernels: a modified Kjeldahl distillation procedure followed by colorimetry, and an inert-gas fusion method followed by gas chromatography. A vacuum fusion technique followed by isotopic dilution mass spectrometry will be evaluated at a later date.

The treatment of WAR kernels during processing precludes the presence of ammonia, nitrite, or nitrate, so that any nitrogen present is in the form of nitride or elemental nitrogen. The inert-gas fusion method will determine both of these forms of nitrogen, whereas the Kjeldahl method will not detect elemental nitrogen and detects the nitride nitrogen only after its conversion to the ammonium ion by digestion in concentrated sulfuric acid. The determination of nitrogen on a series of WAR kernel samples by the inert-gas fusion method gives values for nitrogen that are generally 30% higher than those obtained by the Kjeldahl method. This indicates that nitrogen is present both as elemental nitrogen and as nitride. Under these conditions, the Kjeldahl method is unsuitable for use for determining total nitrogen in the WAR kernels, but would be acceptable for determining nitride nitrogen. On the other hand, the inert-gas fusion method can be employed to determine total nitrogen. (F. L. Layton)

Dissolution of HTGR fuel particles, using Cl_2 and S_2Cl_2-SCl_2. One of the difficult and time-consuming problems in the analysis of HTGR fuel particles is the complete dissolution of the fissile and fertile elements, together with the fission products from biso- and triso-coated microspheres. For burnup analyses, it is advantageous to dissolve the particles in situ to eliminate contamination or material loss. We have demonstrated a method for the rapid dissolution of these particles. The carbon coatings are burned in oxygen at 800°C. For triso-coated particles, SiC is removed with a stream of Cl_2 at 1000°C. Thorium oxide and UC_2 or UO_2 are easily chlorinated at 800 to 1000°C with a stream of Cl_2 bubbled through S_2Cl_2-SCl_2. The chlorination reaction was complete in only a few minutes, as compared with hours for Cl_2 and carbon. The chlorination of UO_2 was much more rapid than that of

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[3] ORNL Master Analytical Manual, Method Nos. 1218771 and 900718771 (1960).

ThO_2. The sublimed metal chlorides were easily dissolved in dilute HCl. Other compounds were investigated as possible chlorination agents or chlorination promoters. These were CCl_4, hexachloropropene, CO, S, and NH_4Cl, but none was as effective as S_2Cl_2-SCl_2. **(D. A. Lee)**

Helium atmosphere glove box. A 6-ft helium atmosphere glove-box enclosure was put into operation. This glove box is being used for the preparation for analyses and storage of HTGR fuel materials requiring an inert atmosphere. The box is equipped with a Kewaunee Scientific Equipment gas purifier. This purifier is designed to recirculate the helium atmosphere at a flow rate of 30 cfm in the dry-box enclosure and to control the atmosphere, by removing moisture and oxygen, to a contamination level of less than 5 ppm.

The oxygen level of the box atmosphere is measured by Applied Electrochemistry, Inc., model S-3A oxygen analyzer. The moisture level is measured by a Parametrics, Inc., model 1000 hygrometer. **(J. L. Botts)**

HTGR information exchange meeting. An HTGR analytical chemistry information exchange among Allied Chemical Company (ACC), General Atomic Company (GAC), New Brunswick Laboratory, and Oak Ridge National Laboratory was held on September 26–27, 1974, at ACC, Idaho Falls. This was the first in a series of meetings to be held periodically at the participating laboratories. The next meeting was held on November 3–6, 1975. The purpose of the meetings is to establish liaison, to develop and facilitate the exchange of technical information, and to coordinate the analytical chemistry development efforts between ERDA agencies and contractors engaged in HTGR technology development. Presentations and discussions at these meetings include analytical chemistry methodology, technical requirements of related HTGR development projects, and analytical problem areas of mutual interest. These meetings should help to minimize the effective cost of HTGR analytical chemistry development programs of the participating laboratories. **(D. A. Costanzo)**

PROCESS DEVELOPMENT STUDIES

In-line monitoring of the HTGR fuel particle process effluent streams, using a time-of-flight mass spectrometer.* A CVC Products, Inc. (formerly Bendix), type MA-2, time-of-flight mass spectrometer (TOFMS) has been installed and is in operation in the Fuel Particle Coating Facility to monitor in-line effluents from HTGR fuel particle preparation reactions. These fluidized bed reactions include carbonization of uranium-loaded ion exchange resins, UO_2 conversion to UC_2, pyrocarbon buffer coating, low-temperature isotropic carbon coating, SiC coating, and high-temperature annealing. All of these reactions have been monitored except SiC coating. Mass spectral scans have been made throughout the runs. Significant mass peak heights have been measured and plots made of peak heights vs time or temperature for each particular mass.

During resin carbonization, spectral mass scans were made repeatedly throughout the heating and cooling period (6 hr). From each scan, 25 to 34 masses were selected for concentration change determinations. Profiles of plots of peak heights vs temperature indicated the temperature at which certain reaction phenomena occurred. These profiles are being used to postulate reaction mechanisms for resin pyrolysis and formation of the carbonized uranium microsphere kernel. Some of the phenomena include evolution of surface water and water produced by combustion, the two-stage decarboxylation of the acrylic acid copolymer, and the formation and subsequent degradation of many aliphatic and aromatic hydrocarbons.

The integrity of these microspheres is tantamount to a safe and successful reactor. Therefore, meticulous fabrication of these particles is essential. The property requirements of the particles which are so stringent include optimum particle density, coating thickness, strength, sphericity, ability to retain the fuel and fission products, and resistance to particle failure and to the "amoeba" effect. The aim of these coating studies is to improve the understanding of the mechanisms in pyrocarbon deposition (buffer and LTI) on fuel kernels to assure the quality of the product demanded. Preliminary experiments using the TOFMS have been made. The pyrolysis of ethyne and propene for the two carbon coating processes has been monitored using both the scanner and sequencer modes. The plotted data portray a short induction period during which new hydrocarbon compounds are formed at a peak concentration followed by a constant rate of hydrocarbon production at a lower concentration. At the same time there is a constant rate of hydrogen evolution and presumably carbon deposition at a higher concentration than during the initial induction period. These results are consistent with current hypotheses both for induction period and for pyrocarbon deposition mecha-

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*Cooperative investigation with Mass and Emission Spectrometry Group.

nisms in fluidized beds.[4-8] After more detailed studies of the effect of parameter variations upon the physical properties of the particles are made, we may be better able to elucidate the reactions.

From the few scans which we have made on the conversion process, the most significant observation has been the production of CO. One of the problems with the fuel particles has been the occasional creep of uranium into the buffer coat. This may be due to extraneous material or incomplete chemical reactions occurring during conversion. If this is true the TOFMS may be able to determine what reactions are causing the defect.

Nothing of significance has been noted during annealing thus far, but this process will be continued to be monitored.

These studies are still in the preliminary stages, but further development of the experimentation would produce interesting elucidation of reaction mechanisms for optimum fuel particle manufacture. (D. A. Lee, D. C. Canada, H. S. McKown, W. T. Rainey, Jr.)

Polynuclear aromatic hydrocarbons and related constituents in perchloroethylene materials.* Methods which have previously been applied to tobacco and coal-related materials have been used for resolution of polynuclear aromatic hydrocarbons (PAH) in perchloroethylene (perclene) materials obtained from the HTGR particle coating facility. Of particular interest were the PAH's which have been reported to be biologically active: tumor promoters, initiators, carcinogens, cocarcinogens, and mutagens.

Perclene is used to remove soot and organic compounds from the effluent gas stream of the particle coating furnace. These pyrolysis products are produced during the carbonization and conversion of uranium-loaded weak-acid resin and the subsequent coating of the particles with pyrocarbon and silicon carbide. The presence of biologically active materials in the perclene would require that due caution be taken in the handling, recovery, and disposal of the perclene materials.

A PAH-containing subfraction of a process perclene sample was prepared by a modification of the Kubota liquid-liquid extraction and column chromatography procedure. This subfraction was then subjected to GLC for resolution of PAH's in the range of 1 to 7 rings. The resulting profile contained 7 major and at least 50 minor constituents. A number of PAH's were tentatively identified by co-chromatography: *major PAH's* naphthalene, acenaphthalene, phenanthrene, fluoranthene, pyrene, chrysene (and or triphenylene), benzo[a]pyrene (BaP); *minor PAH's* 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthene, fluorene, anthracene, 4-methylpyrene, 1-methylpyrene, benz[a]anthracene, tri-phenylbenzene, perylene, picene, and anthanthrene.

Numerous small peaks were observed also in regions where methylchrysenes, methyl-benzanthracenes, and six-ring PAH's would be expected to elute. Mass spectroscopy would be required to confirm the above peak assignments, but their validity was suggested by the identification of several of these PAH's in process perclene samples by W. T. Rainey of the Mass Spectrometry Group.

Quantitative estimates of these constituents were achieved by incorporation of ^{14}C tracers and by external calibration of the GLC. The major PAH's of interest in this sample were BaP, a strong carcinogen, and fluoranthene and pyrene, both co-carcinogenic with BaP. The methylnaphthalenes, which are tumor promoters, were present at much lower levels. (W. H. Griest)

Density, pH, and conductivity measurements of acid-deficient uranyl nitrate solutions. Acid-deficient uranyl nitrate solution is used in the fuel kernel preparation development program to load weak-acid resins in the preparation of HTGR fuel materials. The loading efficiency of uranium on the resin depends on the uranium concentration and acid deficiency of the solutions. Therefore, the measurement of the acid deficiency and the uranium content of these solutions is important to the process control of the resin loading.

Conductivity, density, and pH measurements were made on a series of standard uranyl nitrate solutions to establish a correlation between these measurements and the uranium and acid content of the solutions.[9]

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*Cooperative investigation with Bio-Organic Analysis Group.

[4] R. O. Grisdale, A. C. Pfister, and W. van Roosbroeck, "Pyrolytic Film Resistors: Carbon and Borocarbon," *Bell Syst. Tech. J.* 30, 271 (1951).

[5] R. O. Grisdale, "The Formation of Black Carbon," *J. Appl. Phys.* 24, 1082 (1953).

[6] J. C. Bokros, "The Structure of Pyrolytic Carbon Deposited in a Fluidized Bed" and "Variation in the Crystallinity of Carbons Deposited in Fluidized Beds," *Carbon (Oxford)* 3, 17 and 201 (1965).

[7] K. I. Syskov and F. I. Jelikhovskaya, "On the Formation and Composition of Pyrolytic Carbon," *Carbon (Oxford)* 5, 201 (1967).

[8] R. J. Bard, H. R. Baxman, J. P. Bertino, and J. A. O'Rourke, "Pyrolytic Carbons Deposited in Fluidized Beds at 1200 to 1400°C from Various Hydrocarbons," *Carbon (Oxford)* 6, 603 (1968).

[9] D. A. Costanzo et al., "Energy Programs: Gas-Cooled Reactor Programs," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, pp. 36-37.

Experimentally derived mathematical expressions were established that yield the nitrate and uranium content of uranyl nitrate–nitric acid solutions, given the conductivity, pH, or density.

An assayed uranyl nitrate stock solution was prepared by dissolving UO_3 in nitric acid under reflux at 95°C. Six experimental solutions having NO_3/U mole ratios of 1.56, 1.70, 1.90, 2.00, 2.1, and 2.3 were prepared by diluting weighed aliquots of the stock solution with weighed portions of standard 2.00 M nitric acid. The experimental data were obtained using a total of 36 solutions, each containing different combinations of uranium and nitrate concentrations.

The densities of the experimental solutions were determined by pycnometric measurement. The conductivities were measured using a dip type of conductivity cell with a Radiometer conductivity meter, type CDM3. A Beckman Research pH meter was used to measure the pH of the solutions. These measurements of density, pH, and conductivity were made at 25, 50, and 75°C on each of the experimental solutions.

The experimental data were used to derive an expression to compare the uranium and nitrate concentration of uranyl nitrate solutions, given the density, conductivity, and temperature. Since most of the work is being done with acid-deficient uranyl nitrate solutions, the data were limited to the range of 1.56 to 2.0 nitrate to uranium mole ratios. These data were fitted to equations for density and conductivity, and the equations were solved for the uranium and nitrate concentrations.

The manual use of the resulting expressions would be cumbersome and time-consuming; therefore, a short program for use on the PDP-10 was written. This program is usable over a temperature range of 25 to 75°C, for solution densities up to 1.4 g/cm^3, and for solution specific conductivities up to 160 millisiemens.

The error between the calculated and known values for both uranium and nitrate is less than 2% for most of the 36 standard solutions. **(J. L. Botts)**

TRITIUM MONITORING SYSTEM FOR A REACTOR EXPERIMENT*

Work has continued on the tritium monitoring system for the GB-10 capsule irradiation experiment.[10] The GB-10 capsule contains a vented fuel rod and was designed to provide direct measurements of fission product release rates from an operating fast breeder reactor fuel rod.[11] The capsule has exceeded 700 days and 75 MWd/kg of irradiation in the ORR.

The design of a system for analyzing tritium quantitatively in the helium sweep gas from the GB-10 capsule has been described.[12] The components were laboratory tested and calibrated before installation in the ORR, and after installation, several experiments were made to verify the operating characteristics of the total system and the individual components. When tritium in helium (Matheson UHP) was passed through the HTO converter (magnesium granules at 500°C which convert HT to HTO), tritium was retained quantitatively. When hydrogen was used as a carrier, the HTO converter passed the tritium quantitatively. Also, the electrometer reached steady state more readily when hydrogen was present.

All experiments utilizing capsule gas were characterized by a rapid breakthrough of activity. On the first high-flow experiment, this activity was isolated in the ionization chamber for decay measurements, which indicated a half-life of 3.4 min. At the end of the experiment, a decay study of residual activity in the ionization chamber produced a half-life of 15.0 hr. The reactions

$$^{24}\mathrm{Ne} \xrightarrow[3.4\ \mathrm{min}]{\beta^-} {}^{24}\mathrm{Na}\ ,$$

$$^{24}\mathrm{Na} \xrightarrow[15.0\ \mathrm{hr}]{\beta^-} {}^{24}\mathrm{Mg}\ ,$$

explain these activities. Residual activity deposited on the molecular sieve was identified as ^{24}Na by gamma spectrometry. The ^{24}Ne and ^{24}Na significantly increase the electrometer baseline, but do not prevent useful tritium measurements.

Several experiments were completed on capsule gas in various flow modes. To date, all release rates have been considerably lower than the calculated production rates. As predicted, high-flow experiments show higher tritium release. Measurements have been made to determine the HT/HTO ratio. However, sufficient data have not been obtained to confirm this ratio. The tritium monitoring system for the GB-10 capsule is completely operational. Experiments can now be

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*Cooperative investigation with the Reactor Division.

[10] D. A. Costanzo et al., "A Continuous Tritium Monitor for a Reactor Experiment," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 37.

[11] J. A. Conlin et al., "GCFR Irradiation Experiments," *GCR Programs Annu. Prog. Rep. Dec. 31, 1972*, ORNL-4911, pp. 212–33.

[12] L. B. Yeatts, Jr., and D. A. Costanzo, "Evaluation of a Continuous Tritium Monitoring System for the GB-10 Capsule Experiment of the GCR Program," to be published.

planned to determine (1) tritium release, (2) molecular species of tritium (HT and/or HTO), and (3) the pathway of tritium leaving the capsule.

In future experiments it will be necessary to measure the moisture and hydrogen levels in the helium sweep gas both upstream and downstream. These measurements are important because the transport of tritium may be affected by these chemicals[13] and because both hydrogen and water can influence the fuel and fission product chemistry.[14] Tritium may be retained in the capsule or lines by mechanisms such as adsorption, or by tritide or tritoxide formation; tritium may be lost from the capsule by diffusion into the sweep gas or through the walls.[13-15] The extent to which these mechanisms apply is determined, at least in part, by the chemical form of the tritium and by the oxygen potential of the system, both of which are affected by the hydrogen and moisture present. Experiments have been proposed in which water vapor and normal hydrogen and/or tritium will be injected with the sweep gas.[13]

The ratio of hydrogen to water vapor will be measured continuously in the sweep gas by passing a sample through a Thermox oxygen analyzer. The moisture content will be measured with a Meeco electrolytic moisture analyzer in series after the Thermox. One pair of these units will be used for the upstream and one pair for the downstream gas. The four units, two of each, which were supplied by GAC are being tested in the laboratory and will be calibrated to ensure reliable performance before being installed in the GB-10 irradiation experiment. **(M. E. Pruitt, A. J. Weinberger)**

SURVEILLANCE OF FISSION PRODUCTS IN THE PEACH BOTTOM HTGR

We have continued our assistance to the ORNL HTGR fission product surveillance program.* In this program the behavior of fission products in the Peach Bottom HTGR (a 115-MW reactor owned and operated by the Philadelphia Electric Company) is being studied. Fission products are measured in fuel elements, coolant and purge gas helium, on coolant circuit surfaces, and in dust from the reactor cyclone dust separators. This work is being done to compare measured vs predicted behavior of fission products in an operating HTGR.

On October 31, 1974, the Peach Bottom Reactor was shut down for decommissioning. At shutdown, the second core of the reactor had operated 899 equivalent full-power days (EFPD).

During this reporting period, we completed the analysis of data obtained from coolant samplers operated in the spring of 1974 and finished two gamma scans of the loop 1 cold duct of the primary coolant circuit after the last two reactor shutdowns. We also completed and reported on the examination of fuel element E06-01, which was irradiated to 384 EFPD.[16]

We continued the examination of fuel element E11-07, irradiated to 701 EFPD, and have begun examination of two fuel elements, E14-01 and F03-01, that were irradiated to reactor end-of-life (EOL). These last two elements are part of a series of five EOL elements whose examinations are planned.

Examination of Peach Bottom primary circuit. The 1974 coolant samplers operated from March 13 to May 28, 1974. The design of the samplers was the same as those described by deNordwall et al.[17] and operated in 1973. Cesium-134 and -137 were the major activities found; minor activities were ^{90}Sr, ^{131}I, ^{136}Cs, and a few neutron capture products. Results obtained from the 1974 samplers have been compared with those of 1973 by Malinauskas et al.[18] We concluded that the ^{131}I concentration in the coolant entering the steam generator remained about the same (0.22 pCi/liter) as in 1973. The steam generator appeared to continue to act as a source of "organic" ^{131}I as found in 1973 and discussed previously.[17] The concentrations of ^{134}Cs and ^{137}Cs in coolant upstream of the steam generator were 12.3 and 7.6 pCi/liter respectively. The corresponding concentrations in 1973 were 0.23 and 0.59 pCi/liter, implying that their rate of release from the

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*Cooperative program with the Chemical Technology Division.

[13] R. J. Campana and B. D. Epstein, *Recommendations for Tritium Measurements during Irradiation of 12-Rod GCFR Fuel Bundles in the BR-2, He Loop, Mol, Belgium*, GA-FR 740926076 (September 1974).

[14] B. D. Epstein, *A Review of the Literature Pertinent to Fission-Product Migration and Interaction in Fuel Rods*, GAC Report GA-A13423, UC-77 (June 1975).

[15] R. A. Strehlow and G. C. Savage, "The Permeation of Hydrogen Isotopes through Structural Metals at Low Pressures and through Metals with Oxide Film Barriers," *Nucl. Technol.* 22, 127 (1974).

[16] F. F. Dyer, H. J. deNordwall, R. P. Wichner, W. J. Martin, and L. L. Fairchild, *Postirradiation Examination of Peach Bottom Fuel Element E06-01*, ORNL-TM-5189, in preparation.

[17] H. J. deNordwall et al., *GCR Programs Annu. Prog. Rep. Dec. 31, 1973*, in preparation.

[18] A. P. Malinauskas et al., "Fission Product Behavior During Operation of the Second Peach Bottom Core," IAEA-SM-200/SO, presented at the IAEA-OECD (NEA) International Symposium on Gas-Cooled Reactors in Munich, Germany, Oct. 13–17, 1975.

core increased by a factor of 10 to 50 during this period. The average concentrations of ^{134}Cs and ^{137}Cs in the coolant exiting from the steam generator (3.2 and 2.1 pCi/liter respectively) show that about 75% of both isotopes was deposited in the steam generator. During the fuel cycle in which the samplers were used, January 4 to May 28, 1974, the reactor operated about 3432 hr. The coolant flow rate in loop 1 was nominally 5.58×10^{6} standard liters per hour. From these data we estimate that about 11 Ci of ^{137}Cs and 17 Ci of ^{134}Cs deposited in the loop 1 steam generator.

The loop 1 primary coolant duct was gamma-scanned on five occasions during the life of Peach Bottom core 2. Two scans in 1974, May 28 and October 31, were made. (Only one location was measured in May 1974.) The results, expressed as microcuries per square centimeter, obtained at eight locations along the duct, were discussed elsewhere.[18] Briefly, it was found that the levels of cesium decreased through 1973 and then significantly increased in 1974. The increase amounted to a factor of about 8 for ^{134}Cs and 5 for ^{137}Cs.

A preliminary analysis of the gamma-scan and coolant-sampler data of 1974 indicated that the amounts of ^{134}Cs and ^{137}Cs found on the duct could be closely accounted for by the amounts of these isotopes measured in the coolant leaving the steam generator. **(F. F. Dyer)**

Examination of Peach Bottom fuel elements. A fuel element examination consists of an appraisal of the overall condition of the element and its components (documented by photographs), dimensional measurements, estimation of fuel particle failure fraction, burnup and chemical analysis of fuel, and determination of fission product inventories and distributions in all major components of the element. Gamma-emitting fission product inventories and axial distributions are measured by gamma-ray scanning.

Results from the examination of fuel element E06-01 indicated that rather small amounts of fission products were released from the fuel. Some 186 Ci of ^{137}Cs was measured in the fuel and 48 mCi, 0.02% of the total, in the graphite components of the elements. Inventories of fission products calculated by Tobias[19] were, for most fission products, in good agreement with measured values. An estimate based on diffusion models indicated that insignificant release of cesium from the element into the coolant occurred. Estimates of fuel burnup, FIMA (fission per initial heavy-metal atom), were computed from three independent data sources: (1) the measured cesium inventory, (2) the end-of-life inventories of zirconium, uranium, and thorium, and (3) the neutronics history of the element. Zirconium, uranium, and thorium were measured by J. L. Botts, using a spectrophotometric method.[20] The neutronics calculations were made by GAC using the computer code GAUGE. FIMA values based on the ^{137}Cs inventory were generally about 20% higher than those computed by GAC. The spectrophotometric FIMA values were also slightly higher than GAC values. Newer methods based on isotope-dilution mass spectrometry, which will soon be used to measure uranium and thorium, are expected to improve the determination of FIMA.[20]

Current work is devoted to the examination of the three elements E11-07, E14-01, and F03-01. gamma scans have been completed on the fuel, and work has begun on gamma-scanning of the E11-07 sleeve. Results obtained thus far for E11-07 indicate that perhaps about 50 Ci of ^{137}Cs was released from the fuel. The amounts of ^{137}Cs in the graphite components have not been measured. Gamma-scan results for E14-01 fuel show that the fission products in this element behaved about the same as those in E06-01, that is, little loss from the fuel. Preliminary results for F03-01 indicate that the fission product loss from the fuel was much higher than for E11-07.

Because of the high levels of ^{134}Cs and ^{137}Cs in the graphite of several of the fuel elements, it has become necessary to effect radial sectioning of graphite in a hot cell. Radial sectioning is done to measure the radial distribution of fission products in spine and sleeve pieces. A lathe has been acquired for this purpose, and it and other necessary equipment are being installed in the cell. **(L. C. Bate, F. F. Dyer)**

Burnup and fission product analyses of Peach Bottom fuel. Chemical analyses of fuel particles from Peach Bottom fuel elements include the determination of Zr, U, and Th for burnup calculation and the measurement of the elemental fission products Te, Ba, and the isotopes ^{129}I, ^{90}Sr, ^{3}H, and ^{14}C.

Zirconium, uranium, and thorium have been determined by the GAC method for burnup analysis.[21] The dissolution step of the method has been modified to eliminate the high zirconium blank associated with the

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[19] Melvin Tobias, *Estimates of Fission-Product Inventories in Fuel Element E06-01 of the Peach Bottom Core 2: Results, Comparison, and Sensitivity Study*, ORNL-TM-4705 (October 1974).

[20] D. A. Costanzo et al., "Energy Programs: Gas-Cooled Reactor Programs," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, pp. 35–36.

[21] F. F. Dyer, H. J. deNordwall, R. P. Wichner, W. J. Martin, and L. L. Fairchild, *Postirradiation Examination of Peach Bottom Fuel Element E06-01*, ORNL-TM-5189, in preparation.

crushing and dissolution of the particles in perchloric acid–nitric acid using a high-pressure high-temperature Teflon-lined container. This container is designed to withstand pressures up to 5000 psi and temperatures up to 275°C.

Intact BISO-coated particles were analyzed for ^3H, ^{90}Sr, and ^{14}C. The particles were oxidized at 900°C in a stream of moist oxygen for 2 hr. The ^3H was collected in a dry ice–acetone cold trap. This cold trap was followed by two scrubber towers containing hyamine hydroxide to retain the ^{14}C. After complete oxidation of the particles, the residue remaining in the platinum boat was reacted with concentrated HNO_3 at reflux temperatures to dissolve the ^{90}Sr, which was then determined by scintillation beta counting.

Samples have also been dissolved in the Teflon-lined steel container and the resulting solutions analyzed by isotope-dilution spark-source mass spectrometry for Ba and Te.

An attempt is also being made to determine the ^{129}I concentrations in these fuel-element samples. Attempts to remove ^{129}I from standard samples by pyrohydrolysis resulted in only about 35% recovery. A sodium carbonate fusion technique to convert the particles to a soluble form without loss of the ^{129}I is being evaluated. **(J. L. Botts, W. F. Rogers)**

GAMMA SPECTROSCOPY DEVELOPMENTS FOR HTGR PROJECTS

The automatic sample changer, described previously,[22] is now undergoing final checkout. The changer is interfaced to a Nuclear Data model 4410 computer-based pulse-height analyzer. Software to operate the changer was recently finished. Samples are counted at one of four stations located between 5 and 130 cm from a Ge(Li) detector. The operator specifies the number of samples in the changer, the time available for the run, the energy of a gamma ray of primary interest, the maximum counting statistical error associated with analysis of that gamma ray's photopeak, and a desired count rate for the entire spectrum.

The computer uses this information to optimally count each sample and to obtain minimum counting statistical errors in the total time allotted for the measurement. Because of the high versatility of the system, sets of samples (20 or less) whose members have wide ranges of activity levels can be analyzed in the shortest possible time. Checkout of the system is expected to be completed soon.

The Tennecomp TP-5000 computer-based pulse-height analyzer system previously described[22] has been used extensively for gamma spectroscopy of HTGR materials during most of the current year. Since the system was received, significant additions of hardware and software have been made. Hardware items include a multiplexer to permit simultaneous acquisition of up to three gamma spectra and a 3M "Datapacer" magnetic-tape unit. The Datapacer uses precision magnetic-tape cartridges and will record and retrieve very large amounts of data at speeds considerably higher than most other comparably priced magnetic-tape systems. The purpose of this tape unit is to permit the separation of computer programs, gamma spectra, and results derived from gamma-spectra processing on different magnetic tapes. Consequently, speed and reliability of the computer are increased.

Because the software supplied with the TP-5000 lacked several desirable features, we have written software to meet our needs. The programs include ANGEL, ISOFIT, EDIT, and EDITDATA. ANGEL acquires and processes gamma spectra and generates files containing such data as gamma energies, photopeak count rates, sample photon emission rates, and specific activities (microcuries per unit weight) for identified radionuclides. To acquire and process a gamma spectrum, ANGEL requires input for all bookkeeping information pertinent to the conditions of the analysis, for example, sample description, reference time and date, detector identification, counting geometry, etc. The resulting file containing the bookkeeping information, spectrum, and derived results are recorded on magnetic tape. Any desirable part of the file can be listed on the Teletype.

The programs ISOFIT, EDIT, and EDITDATA are used as support programs for ANGEL to prepare files of counting efficiencies and radionuclide decay data and to tabulate the analytical results generated by ANGEL. **(F. F. Dyer)**

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[22] D. A. Costanzo et al., "Energy Programs: Gas-Cooled Reactor Programs," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, pp. 39–40.

5. Mass and Emission Spectrometry

J. A. Carter, Head
R. L. Walker, Assistant

The Mass and Emission Spectrometry Group, having developed a high degree of expertise in inorganic isotopic analysis, now finds itself increasingly involved in programs where very sensitive, reliable analytical measurements are required. This expertise, coupled with a growing awareness among investigators that many analytical problems can best be solved by mass spectrometric techniques, has resulted in program expansion and acquisition of new equipment. The ion microprobe mass analyzer (IMMA), for example, makes possible unique elemental depth profiling and surface studies, principally for researchers in the Thermonuclear and Metals and Ceramics Divisions. To keep pace with the Laboratory's interest in organic studies such as those of the Coal Technology Program, a high-resolution, high-sensitivity MS-50 organic mass spectrometer has been added. The MS-50 will be one of three mass spectrometers interfaced with a DS-50 data processing system and with a quantitative gas inlet system. The mass spectrometer and data system is capable of real-time processing of high-resolution, low-resolution, and GCMS data.

The two-stage, 12-in.-radius solids instrument equipped with pulse counting for ion detection has increased the capability for inorganic isotopic analysis. The improved sensitivity for nanogram-size samples and high-abundance sensitivity are especially useful in actinide analyses for burnup, reactor fuel, and safeguards applications. Spark-source mass spectrometry (SSMS), coupled with stable-isotope dilution techniques, provides highly accurate elemental determinations. This method has been applied to investigations of such diverse materials as gasoline, solvents, coal and coal products, fuel oils, gasoline and fuel oil additives, and vegetation samples. Research is under way to increase the reproducibility and reliability of SSMS by using a scintillator-vidicon detector system for ion detection. By replacing the photoplate system now in use, we should be able to obtain real time results as well as trouble shoot and tune the equipment more easily.

During the past year, several isotope dilution procedures were developed for the thermal emission and spark-source instruments to provide more reliable and efficient operations. Development work continues under both the NSF(RANN) Ecology and Analysis of Trace Contaminants and the EPA Work for Others programs.

Applications to isotopic analysis of plutonium and uranium have continued along several lines. The resin bead technique for simultaneous determination of these two elements was applied to biological and environmental samples; the method is being extended to the determination of *zirconium* for burnup. The International Atomic Energy Agency has reached an agreement with ORNL whereby we will supply them with a two-stage instrument for Minor Isotopes Safeguards Techniques analyses. The mass spectrometer will be installed in the IAEA Safeguards Laboratory in Seibersdorf, Austria.

Organic mass spectrometry support was given to investigators in the Biology, Chemical Technology, and Metals and Ceramics Divisions. Assistance continues in proof of structure of synthetic nitrosamines and derivatives of naturally occurring amines.

Emphasis in our work for the Chemical Technology Division has shifted somewhat from the Body Fluids Analysis Program to the Coal Technology Program; techniques for both qualitative and quantitative analysis of hydrocarbon mixtures were developed. 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 40,000 analytical results were reported during this period. Major users are the Chemical Technology and Metals and Ceramics Divisions.

MASS SPECTROMETRY DEVELOPMENT

Ion microprobe mass analyzer. The ion microprobe mass analyzer has completed its first year of operation. During this period, considerable experience has been gained in the use of this new analytical technique. Problems have been investigated with the IMMA, and modifications have been made to improve the flexibility of the system.

The IMMA involves a surface technique and is therefore sensitive to adsorbed impurities on the surface being analyzed. To reduce adsorption of ambient species in the instrument, we have added an 80-liter/sec ion pump to help remove neutral beam gas before it reaches the sample chamber. Pressure in the sample chamber is now a factor of 2 to 4 lower during an analysis than previously; this has resulted in some improvement in mass resolution. To facilitate rapid mass scanning when small particles are being analyzed, a multiplier recording oscillograph was added. The 2-kHz response time of this recorder allows rapid qualitative mass data to be recorded. The flexibility of the X-Y recorder was improved by adding a logarithmic amplifier that allows signals, varying over four orders of magnitude, to be recorded on five-cycle log paper without manual range selection.

A Teletype printer/paper punch was added to automatically read data from the three instrument scalers when quantitative data are being taken. The data are typed out and simultaneously punched onto paper tape which can then be used as input to our computer for quantitative calculations. We have added a viewing port to the lower end of the sample chamber. When thin transparent or translucent specimens are being analyzed, they can now be viewed in transmitted as well as reflected light. Transmitted light makes viewing of embedded microscopic particles possible. Previously these particles were invisible or extremely difficult to see with reflected light.

We have completed the investigation of the silicon-related embrittlement of an Rh-Pt-W alloy.[1] The ion probe was used to show conclusively that external impurity silicon had diffused into the alloy along grain boundaries. The high concentration of silicon on the grain boundaries resulted in the failure of the alloy. A manuscript describing this study has been accepted for publication.[2]

Small sections of the first wall from the Princeton Tokamak were investigated to ascertain where the plasma beam limiters were being sputtered. The IMMA studies indicate that the limiters (made of tungsten or molybdenum) were being sputtered onto the first wall of the reactor. Depth profiling indicated alternate layers of tungsten and molybdenum, probably indicative of the chronology of which type of limiter was used. No large particles (1 to 10 μm) of either tungsten or molybdenum were observed on the first wall; the refractory nature of these materials probably accounts for this. Large (up to 100 μm) unexpected particles of stainless steel were observed to be sputtered into the layers of tungsten and molybdenum. This is believed to have arisen from an accident whereby a measuring probe used in the Tokamak was inserted into the plasma and thereby sputtered onto the first wall.

A continuing area of interest has been the study of radiohalos in a variety of minerals. These are micron-size inclusions of radioactive material embedded in a host mineral. These halos are of geologic and nuclear interest because they give some conflicting information about geological time scales and, in some instances, suggest the presence at one time of hitherto unknown radionuclides. The ion imaging capability of the IMMA has been used to study the distribution of various elements in and adjacent to these halos. As a rule, elements of the first group of the periodic chart (e.g., K, Rb, Cs) are depleted in halos of all sizes, and elements of the second group (Mg, Ca) are enriched, as are some third-group elements (such as yttrium). Cerite and yttrium rare earths as well as lead and uranium are

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[1] J. A. Carter et al., "Mass Spectrometry Development," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 42.

[2] W. H. Christie, David H. Smith, and H. Inouye, "An Ion Microprobe Study of the Tensile Failure of a Pt-Rh-W Alloy," *Journal of Radioanalytical Chemistry*, in press.

also found in the central inclusion. Uranium/lead ratios have been quantitatively estimated for the central inclusion. In some cases, isotopic measurements were made on these two elements. The extensive results of our investigations of radiohalos in coalified wood are reported in two publications.[3,4]

The ion microprobe is a powerful tool for metallurgical studies. We have looked at a variety of materials for the Metals and Ceramics Division. In one set of samples, the question was whether boron had diffused into the bulk of a Cr-Fe-Ni alloy from the surrounding $NaBF_4$ melt. Investigation of rectangular regions in a raster mode showed no cracks or grain boundaries along which preferential diffusion would be expected. Concentration profiles taken across the alloy surface revealed no discernible interstitial penetration of boron into the alloy matrix, although a considerable concentration was found on the surface.

In a second set of two samples, surface distribution of boron, particularly the presence or absence of localized boron concentrations, was of interest. In each case, substantial boron was found to be distributed evenly over a rectangular area 700 X 180 µm. Most of this rapidly sputtered away. In one case (Inconel 600), small particles ($d \geq 20$ µm) rich in boron persisted throughout the duration of the analysis (~1 hr), indicating significant boron localization. In the other alloy (Hastelloy N), no localization was observed greater than the resolution of the IMMA (~4 µm).

We have looked at some depth profiles of hydrogen in stainless steel samples. Hydrogen was cathodically deposited in the samples for varying periods of time. The samples were then cleaned and immediately stored in liquid nitrogen to immobilize the hydrogen, which tends to diffuse out of the samples with time. After transporting samples to the IMMA site, they were immediately loaded into the instrument. Preliminary studies were made in point mode to ascertain if IMMA techniques would have suitable hydrogen sensitivity. Hydrogen was indeed observed, and a maximum in the profile was observed at approximately 1 µm in depth. A control sample exhibited no maximum, but gave an approximately exponential decrease in hydrogen signal as a function of depth. Reexamination of these samples 24 hr later indicated that the hydrogen had diffused out of the implanted sample, which now exhibited a depth profile similar to that of the control. More experiments involving deuterium implantation are planned to evaluate the sensitivity of the technique for hydrogen in metals.

The IMMA does have its limitations. We were asked to investigate the distribution of tellurium in Hastelloy N, a problem of serious concern in the Molten-Salt Reactor Program. Tellurium is difficult to ionize using the conventional IMMA techniques and consequently has a relatively low sensitivity by this method. We were unable to help with the Hastelloy N tellurium embrittlement problem. Some literature work indicates that the sensitivity of the IMMA for tellurium can be enhanced significantly by doing the primary bombardment with Cs^+ ions; this will lower the work function of the surface being bombarded. Thus it should be possible to take advantage of the relatively large electron affinity of tellurium and produce better yields of negative ions. We plan to build a cesium source for the IMMA to verify these results. If this approach works, it should significantly improve our sensitivity for elements with high electron affinities. (W. H. Christie, D. H. Smith, H. S. McKown)

High-resolution MS-50 organic mass spectrometer. An Associated Electrical Industries MS-50 high-resolution and high-sensitivity mass spectrometer was installed and its performance evaluated. The instrument is located in Building 9735. This mass spectrometer is committed part time to a special research and development testing program for the Y-12 Plant, and for the remaining time the capabilities of this unique instrument will be used to study organic-related problems within the Nuclear Division. Studies associated with coal conversion technologies, plant production processes, and air quality are prime candidates for research with the MS-50.

The instrument, equipped with a solids probe, a liquids probe, a gas chromatograph separator interface, and reference compound inlet, has met or exceeded the basic performance specifications. The basic performance tests for the MS-50 are summarized in Table 5.1. The mass measuring accuracy was exceeded by an order of magnitude, and the sensitivity test for a fixed gas and for cholesterol was exceeded by 30%.

The measurement of accurate masses was done on a sample of hexachlorobutadiene, using heptacosafluorotributylamine as a reference compound. The accuracy of mass measurement is in the range of 0.1 millimass unit, so that an unequivocal determination of the empirical formula of a compound is feasible. The measurement of exact masses in Table 5.2 is repre-

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[3] R. V. Gentry, W. H. Christie, D. H. Smith, R. L. Walker, and S. S. Cristy, "Radiohalos in Coalified Wood: New Time Limits Imposed on Coalification Time and Geological Age," *Eos* 56, 473 (1975).

[4] R. V. Gentry, D. H. Smith, W. H. Christie, and S. S. Cristy, "Radiohalos in Coalified Wood: New Data on U Disequilibrium," submitted to *Science*.

Table 5.1. MS-50 performance

Test	Specification	Obtained
Static resolution (10% valley)	150,000	165,000
Scanning resolution (10% valley)	40,000	43,000
Cholesterol sensitivity	3×10^{-10} C/g	4.2×10^{-10} C/g
Nitrogen sensitivity	1×10^{-3} A/torr	1.3×10^{-3} A/torr
Mass measurement accuracy	5 ppm	0.5 ppm

Table 5.2. Accurate mass measurement in hexachlorobutadiene

Ion	Measured mass	Actual mass	Δmmu
$C_4{}^{35}Cl_5$	222.844284	222.844265	0.02
$C_4{}^{35}Cl_4{}^{37}Cl$	224.841331	224.841316	0.015
$C_4{}^{35}Cl_3{}^{37}Cl_2$	226.838418	226.838366	0.05
$C_4{}^{35}Cl_2{}^{37}Cl_3$	228.835334	228.835416	0.06
$C_4{}^{35}Cl_5{}^{37}Cl$	259.810549	259.810169	0.38
$C_4{}^{35}Cl_4{}^{37}Cl_2$	261.807474	261.807219	0.25

sentative of the type of mass identification possible from the MS-50.

Additionally, the MS-50 will be one of three mass spectrometers interfaced with a DS-50 data system and with a quantitative gas inlet system. The DS-50 data system is being factory tested and is scheduled for delivery this year. The data system will acquire, process, and output mass spectra. It is also capable of real-time processing of high-resolution, low-resolution, and GCMS data.

The mass spectrometer and associated data system provides a unique capability for high-resolution GCMS studies. The ability to collect GCMS data at a resolving power greater than 10,000 is a significant addition to our organic mass spectrometry capabilities. (**J. C. Franklin, W. T. Rainey, D. C. Canada, J. R. Walton**)

National uranium resources evaluation program activities. Members of the Group have participated in the early planning and development program for the selection of the analytical methodology to be used in the National Uranium Resources Evaluation Program. This hydrogeochemical survey requires analytical methods for uranium and trace elements at the low to sub-ppm level.

Methods have been established for uranium by thermal emission mass spectrometry, using isotope dilution, and for trace elements by spark-source mass spectrometry. The development work for spark-source mass spectrometry was done in cooperation with the special samples mass spectrometry laboratory in the Y-12 Product Certification Division. The ORNL thermal emission method using two-stage, 12-in.-radius instruments equipped with pulse counting for ion detection has provided sensitivity for uranium in the 10^{-10}-g/ml level without preconcentration and valuable isotope data for assessment of possible contamination from laboratory air and sample preparation. Spark-source mass spectrometry has been used for survey of the trace elements in water at the 10^{-10}- to 10^{-11}-g/ml level.

One of the first exploratory experiments for the program involved the analysis of some Clinch River water samples by different laboratories. These samples were analyzed in this laboratory for uranium and trace elements for evaluation and comparison with other methods. Also, some water samples from New Mexico were analyzed for uranium and thorium by the thermal emission method, using spikes of ^{233}U and ^{230}Th.

Recently, synthetic water samples (four controls with five replicates each) spiked with known amounts of uranium and trace or pathfinder elements were prepared in our clean laboratory, using stringent precautions to exclude laboratory contamination. These were distributed to several UCND laboratories to evaluate and compare the accuracy and precision of uranium analysis by fluorescence, thermal emission mass spectrometry, delayed neutron counting, and spark-source mass spectrometry. Trace-element analyses were to be done on these controls in the laboratories having multielement capability. Results obtained for uranium in our laboratory, using the short chemical preparation method and thermal emission mass spectrometry, checked within 1 to 2% of the theoretical amounts.

Additionally, we have provided analytical assistance to the program in the area of possible laboratory site selection. In this effort we analyzed air and smear samples from several laboratories for background uranium levels by thermal emission mass spectrometry and fission track counting, using the Lexan method. (**R. L. Walker, H. C. Smith, E. G. Miller**)

A novel ion detection system for SSMS. Other workers[5] have described ion detection systems involving the use of scintillators to convert the energy of mass-analyzed ions into light which is detected by a vidicon tube camera. These ion systems have been adapted to Mattauch-Herzog geometry focal-plane mass

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[5] J. H. Beynon, D. O. Jones, and R. G. Cooks, "Imaging Detector for Mass Spectrometry," *Anal. Chem.* 47, 1734 (1975).

spectrometers similar to the AEI MS-7 type spark-source mass spectrometers used in our laboratory.

We are testing a scintillator-vidicon detector of simpler and less expensive design which, hopefully, will have great application in our work with isotopic analysis and isotope dilution methods. The basic considerations in this design are that it require no elaborate and costly modifications to the AEI instrument, that it not interfere with the more commonly used photoplate detection method, and that it be analytically useful in terms of sensitivity, precision, resolution, and accuracy. The potential advantages of such a system are an increased reproducibility and reliability over the photoplate at a lower cost in the long run. It would also provide real-time results and facilitate instrumental troubleshooting and tuning procedures.

Preliminary work has shown that for ions impinging on a ZnS phosphor, there exists a dramatic mass discrimination against ions above $m/e = 20$ and a threshold in sensitivity which prevents detection of species lower than a few percent in concentration. A system which avoids such mass discrimination involves impinging the ions on an aluminum plate, producing secondary electrons accelerated by a high voltage onto a phosphor plate. The mass spectral resolution of such a system has been measured at 500 (compared with the basic resolution of the instrument of 1500). The sensitivity of the secondary electron system is a factor of 10 greater than for direct ion-phosphor bombardment.

Future work will involve the procurement and testing of a vidicon TV camera system and data-collection instrumentation. Also of interest will be the testing of various phosphors with a wide range of persistence. **(D. L. Donohue, J. A. Carter)**

Actinides and fission burnup monitor methodology. Work continues on the development of the simplified method[6] for simultaneously assaying plutonium and uranium in spent reactor fuels. Important applications are in safeguards analyses and burnup studies. The sensitivity and accuracy of isotope dilution make it possible to ship small samples without heavy shielding to participating safeguards laboratories; this reduces radiation hazards and high shipping costs. During the past year, we have used the method on round-robin samples from IAEA, and also determined that loaded beads will run and give reliable results over a span of at least six months. Valency adjustment of plutonium is not necessary in fuels, since they are dissolved and diluted in an oxidizing condition.

Applications of the method to environmental and biological research have been investigated. A comparison of isotope dilution mass spectrometry, using ^{242}Pu as tracer, and alpha spectrometry (Table 5.3) indicates that mass spectrometry is probably 100 times more sensitive for ^{239}Pu.

We estimate that the sensitivity of the method is 10^{-15} g of ^{239}Pu. A disadvantage of mass spectrometric analysis of low-level plutonium samples is that ^{238}Pu sensitivity is impaired because of interference from ^{238}U in the sample and filament.

Anion and other resin bead systems are being studied as a means of enhancing the signals from zirconium, one of the elements which may be used to monitor burnup in gas-cooled reactors. Promising results were obtained using thenoyltrifluoroacetone particles prepared by dropping melted TTA in water and contacting them with a 6 *M* HNO_3 solution containing 1.98 μg of normal zirconium plus 0.53 μg of ^{94}Zr. Reasonable signals were still obtained when the zirconium was reduced to 0.2 μg. Work continues on this project. **(R. L. Walker, E. G. Miller, H. C. Smith)**

Uranium in vegetation near Building 3019. We have been monitoring the total uranium and the amount of ^{233}U in vegetation near the 3019 process building at ORNL since 1972. Large amounts of ^{233}U are processed in this building, and because ORNL is the designated ERDA repository for ^{233}U, it was felt that possible environmental contamination should be assessed. Three points in different directions around the building are sampled every three months. The uranium is separated and isotopically analyzed after drying and ashing the samples. A spike of ^{233}U is added to one fraction for isotope dilution measurement of the total uranium, and a second fraction is analyzed for isotopic distribution of 233, 234, 235, 236, and 238. Results obtained to date do not indicate serious losses of ^{233}U

Table 5.3. Low-level plutonium analysis – mass vs alpha spectrometry

Sample No.	Total Pu (g)[a]	dis/min	
		MS	α Spec.
MS-1	1.5×10^{-11}	2.43	2.44
MS-2	1.6×10^{-12}	0.258	0.244
MS-3	5.3×10^{-13}	0.087	0.08

[a] Measured by isotope dilution MS after adsorption on resin bead.

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

to the environment. The ^{233}U content over this period averages approximately 2 to 3 × 10^{-4} ppb on a dry-weight basis, or about 5 × 10^{-3} dis min^{-1} g^{-1}. The total uranium over this same period averages about 50 ppb on the same basis. This surveillance will continue at least until the production runs are complete. (R. L. Walker, E. G. Miller, H. C. Smith)

Isotope dilution method for neodymium in Bi, LiCl, and Li_2BeF_4. Experiments using normal neodymium tracer, aimed at fission product removal from molten salts, are carried out in the Chemical Technology Division. In support of this effort, we developed isotope dilution methods for analyzing the amount of neodymium in bismuth metal or LiCl without chemical separation and in fused salts after a chemical extraction into TTA. Mass spectrometric techniques were established using synthetic solutions. For neodymium in bismuth or LiCl, a gram of sample is dissolved and spiked with enriched ^{142}Nd; after equilibration with spike, an aliquot (1 μl) is loaded onto a rhenium filament for measuring the 142/143 ratio. The change from the normal ratio to that measured permits a calculation of the amount of neodymium from a single determination. Excellent neodymium ion emissions were obtained after a short period of "burning off" excess bismuth or LiCl. Using optimum spikes of ^{142}Nd, 0.1-ppm levels are easily measured with ±10% precision; ppm levels are measured with 1 to 2% precision. (R. L. Walker, J. A. Carter, E. G. Miller, H. C. Smith)

Computer-operated densitometer. The computer programs used in processing data read from photographic plates produced by spark-source mass spectrometers have been improved. Photoplate information is read through the densitometer under control of a PDP-8E computer[7] and punched on paper tape for transfer to the IBM 1130 computer. The disk storage in the 1130 computer contains a file of elements, relative abundances of isotopes, and the sensitivity factors of the spark-source mass spectrometers. A subroutine was written to allow the 1130 to read real data as well as integer and literal information from the paper tape. The 1130 program was also changed to accept data from six or less exposures of one sample and to give an average result for each element analyzed. Individual results are flagged when the originating data fall outside the 5 to 95% transmission band. The elements being measured may be read by the densitometer in random order, but the output sheet lists the calculated results by decreasing *Z* value. (H. S. McKown, W. H. Christie, J. C. Franklin, D. H. Smith)

Pulse-counting tandem mass spectrometers. In an attempt to improve the accuracy of one of the tandem mass spectrometers, several modifications were made to the pulse amplifying and counting systems. First, the four vacuum-tube amplifiers were replaced by two transistorized A.R.L. model 104450 pulse amplifiers. The ORNL-constructed discriminator was replaced by an ORTEC model 436. In the multichannel analyzer, the high-speed scaler board was modified by using Schottky TTL integrated circuits. The instrument now has a dead time of 28 nsec as opposed to 90 with the old system. More reliable operation is expected by the elimination of the vacuum-tube circuitry. (H. S. McKown, R. L. Walker)

Low-level lithium measurements by isotope dilution. A method for the analysis of low-level (ppb) quantities of lithium in graphite has been developed. The lithium content of the graphite used in gas-cooled reactors should be as low as possible, since the resulting tritium and helium from the ^{6}Li(*n*,*α*)T reaction would cause serious problems from the buildup of gas and tritium activity. This study was begun to evaluate the contribution of lithium as an impurity to the possible buildup of tritium activity for HTGR-type graphites. Previous attempts to evaluate the impact of lithium, employing measurements by both atomic absorption and emission techniques, were inconclusive.

The method of analysis involves ashing of the graphite in a low-temperature asher followed by isotope dilution mass spectrometry, using a spike of ^{6}Li enriched to 99.99%. Five grams of graphite requires about 12 hr to ash, depending on the physical character of the graphite. After ashing, the residue is dissolved in the spike solution, transferred to a small centrifuge cone, and evaporated to dryness. The final residue is dissolved and is loaded on prebaked, precertified lithium-free filaments and analyzed in a 6-in.-radius, 60° solids mass spectrometer equipped with an electron multiplier for ion detection for increased sensitivity. Ten nanograms of lithium gives sufficient signals for analysis.

Graphite standards have been analyzed by isotope dilution mass spectrometry and cross-checked by flame emission, using the standard addition method. Satisfactory agreement (±10%) with the stated values was obtained; certified values for the standards are not expected to be better than ±5%.

Using highly enriched ^{6}Li (99.99%) as a spike, the limit of detectability has been found to be in the sub-ppb level for 5-g samples. However, even with this

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[7] J. A. Carter et al., "Mass Spectrometry Development," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 46.

sensitivity, we have chosen a reporting limit of <5 ppb, because the chances for variable levels of contamination and possible losses in the low-temperature asher exist. These parameters were checked with ppm-level standards, but cannot be studied fully in the low ppb concentration, because standards in this range are unavailable.

After analyzing six samples of HTGR graphite for General Atomic in which the sample results were <5 ppb Li, the impact of lithium as a contributor to the possible tritium activity is now considered negligible. **(J. R. Walton, C. A. Prichard)**

Trace elements in coal and coal products by SSMS. The coal and coal product and waste stream samples from the COED process were surveyed for trace elements by spark-source mass spectrometry, using an added internal standard. The data were collected on Ilford Q2 photographic plates; the various elements were determined by comparison of the density of the lines of erbium, the internal standard element. The density of the lines was measured with a microphotometer equipped with a data system for data collection and emulsion calibration. Because of the complexity of the samples, the broad range of concentrations and elements involved, the unknown behavior of the elements in this matrix, and the use of only one internal standard, the data obtained were semiquantitative.

The samples were quite varied in nature; the suite included powdered coal, oils, aqueous waste, and semisolid tars. The powders were spiked with an internal standard in an organic solvent, dried, and ignited; the solutions and oils were first spiked and analyzed directly; these solutions were then dried and ignited for residue analysis.

Concentrations or detection limits were estimated for 47 elements in the various materials. Detection limits were in the 0.1 wt ppm range, and concentrations for the elements detected ranged from 1 ppm up to several percent.

The data obtained indicate that spark-source mass spectrometry can be used in the analysis of coal and coal products. The nature of the samples requires further study of the methods of preparation. To obtain precise and accurate data for coal product samples, methods must be developed which remove the organic components and ensure equilibration between the sample and added internal standards or isotope spikes. **(J. C. Franklin, D. L. Donohue, L. Landau, R. C. Bryant)**

ORGANIC MASS SPECTROMETRY

Major support has been given to investigators in the Biology, Chemical Technology, and Metals and Ceramics Divisions. Assistance continues in proof of structure of synthetic nitrosamines and derivatives of naturally occurring amines being studied by Lijinsky and Singer.[8] Assistance to the Chemical Technology Division has shifted in emphasis from the Body Fluids Analysis Program to the Coal Technology Program, leading to the development of techniques for both qualitative and quantitative analysis of hydrocarbon mixtures. Cooperation has continued with Industrial Hygiene personnel at all plant areas in studies of possible air pollution and exposure of workers to hazardous chemicals in compliance with OSHA regulations.

Intradivisional development activities have continued, especially in the Tobacco Smoke Research Program and the Gas-Cooled Reactor Programs. The Perkin-Elmer model 3920 gas chromatograph is being interfaced to the single-stage spectrometer to give improved GC capability, both capillary and packed column; this will be particularly valuable in qualitative analysis of smoke gas phase and condensate components. A silicone membrane separator is being installed for interfacing the capillary column, and a glass jet separator for the packed column. Necessary valving and splitters will permit either column to be used with flame ionization detector and/or the mass spectrometer. We have replaced one of the ion pumps on the analyzer section of the spectrometer with a 2-in. diffusion pump to increase the differential pumping of helium. This improvement allows us to operate a GCMS for long periods without excessively high analyzer pressure or ion pump heating.

We are aiding in the use of the time-of-flight mass spectrometer (TOFMS) in the Gas-Cooled Reactor Programs for analysis of effluent products from the Particle Coating Facility of the Metals and Ceramics Division. The TOFMS has been installed at the Facility and is operating routinely in carbonization and coating runs. This work is discussed in detail in the section on Gas-Cooled Reactor Programs. In addition, we are working with Metals and Ceramics Division personnel in qualitative identification of products from the perclene recovery process used in conjunction with the Particle Coating Facility. This information is of value, both in assessing personnel exposure and in studying the reac-

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[8] G. M. Singer, W. Lijinsky, and W. E. Rainey, Jr. "Mass Spectrometry of *p*-Toluenesulfonamides: Useful Amine Identification Derivatives," *Org. Mass Spectrom.* 10, 473–82 (1975).

tions involved in the processes. More detailed information is given on this work later in this section.

We have a contract with Cyphernetics Corporation for use of the Mass Spectral Search System developed by NIH and EPA personnel and formerly handled by the General Electric Company. The data base has been expanded to include 40,000 spectra, and all modes of search are operable, including a Biemann search option, the McLafferty STIRS routine, and a plotting option which enables the user to obtain a plot of any spectrum in the library. The system is accessed through a Teletype and acoustic coupler to commercial phone lines. We will attempt to access through the Tektronix visual display unit of the DS-50 when it is installed. The data base of this system is being continually enlarged by contributions from mass spectrometry laboratories worldwide (including ORNL) and is expected to be the ultimate source of organic mass spectral data. (W. T. Rainey, D. C. Canada, C. A. Pritchard)

Gas analysis programming. A general-purpose computer program has been written for the IBM 1130 computer system to facilitate calculation of relative compositions of organic mixtures from the composite mixture mass spectra. A series of linear simultaneous equations, involving relative component intensities, is solved to yield instrumental responses for the individual components. Previously determined sensitivity factors are then used to obtain relative compositional data. Conversely, the program may be used to obtain sensitivity factors for individual components from spectra of mixtures of known composition. This matrix calculation technique weights accuracy of component composition in favor of major components, and components <1% (moles/mole %) are difficult to quantify by this technique. Therefore, a second program was developed to be used for mixture quantification that uses a residual calculation. In this technique, normalized standard mass spectra are subtracted from the sample spectrum until the residual approaches zero. Sensitivity factors are then used to calculate compositional data. This technique does not favor major components and is being used routinely for coal pyrolysis gas analyses. Further information on these analyses is given in the Spectrometry Services Section of this report. (D. C. Canada, R. E. Eby, W. T. Rainey)

Heated glass inlet system for high-boiling organic mixtures. A portable heated glass inlet system has been built for introduction of organic mixtures into the mass spectrometer, and we expect to use it with all organic spectrometers. This inlet system is necessary for quantitative analysis of organic high-boiling mixtures. Four glass vacuum valves have been ground, polished, and installed for use in isolation of the sample from the diffusion pump, the expansion volume, and the mass spectrometers. These valves are operated by manual magnetic lifts. Presently, an optically flat glass flange seals the sample container to the inlet system. A 6-mil stainless steel capillary viscous leak will sample the contents of the inlet system. A sample size of 1 to 10 mg is required and yields an inlet pressure of 1 to 5 torr at ~350°C.

Sensitivity factors have been determined for a variety of aromatic compound types (i.e., naphthalene, phenanthrene, fluorene, pyrene, fluoranthene, chrysene, etc.) at 70 eV ionization potential. These sensitivity values are essential for component quantification. The calculation of quantitative data for a complex mixture can be carried out with the programs described for gas analysis. However, qualitative compound identifications can be inferred from mass measurements alone.

Coal liquid samples were analyzed by this technique (no sensitivity factors had been determined for components in these mixtures). Mass spectrometry results indicated molecular weights of components and the degree of saturation of components. The latter information was confirmed by complementary low-voltage ionization (~10 eV), using the heated inlet system. (C. A. Pritchard, W. T. Rainey, D. C. Canada)

Identification of products from particle coating scrubber. We have carried out rather extensive GCMS analyses of samples supplied by M. S. Judd of the Metals and Ceramics Division. These samples are distillates and residues resulting from studies on methods to recover perclene used in the effluent gas scrubber of the Particle Coating Facility. This perclene has been exposed to the soot formed in the coating operations as well as all gaseous products from carbonization and coating processes. As a result, the compounds formed during the processes are concentrated in the perclene, and this solution forms a good source of product data for the effluent gas streams. Unfortunately, only one has been restricted to scrubbing in a single process, so most of the data refer to combined processes. Chromatograms of these samples vary widely in complexity from the very complex pot residues to the rather simple low-boiling distillate fractions. As many as 35 compounds have been identified in single chromatograms. Table 5.4 lists the compounds found in perclene which had been used in scrubbing effluent from a carbonization run. No attempt has been made to identify the isomeric configurations of these products, so there is some ambiguity possible in many cases. These products are not unexpected, since the carbonization process involves pyrolysis of an acrylate divinyl benzene

Table 5.4. Compounds in single chromatograms

Benzene	C_3-substituted styrenes	C_4-substituted styrenes
Toluene	Naphthalene	C_2-substituted biphenyls[a]
Xylenes	Divinyl toluenes	C_4-substituted naphthalenes
Styrene	Methyl naphthalenes	C_3-substituted biphenyls[a]
C_3-substituted benzene	Divinyl xylenes	C_4-substituted biphenyls[a]
Methyl styrenes	Biphenyl[a]	Phenanthrene[b]
C_4-substituted benzene	Acenaphthylene	Fluoranthene
Dimethyl styrenes	C_2-substituted naphthalenes	Pyrene
C_5-substituted benzenes	Methyl biphenyls[a]	Benzopyrene[c]

[a] Or acenaphthenes.
[b] Or anthracene.
[c] Or isomers.

copolymer, and the coating runs involve pyrolysis of propene. The chromatograms obtained with a packed column suggest that many of the peaks are unresolved multiplets. Therefore, the use of capillary or support-coated, open tubular columns in the newly installed chromatograph should improve these analyses.

The Organic Mass Spectrometry Laboratory has analyzed approximately 500 samples during the past year. As in the past, the single-stage instrument was used for most of the samples. A major portion of the samples has required the combined GCMS capability available only with the single-stage instrument. Complex mixtures of hydrocarbons have been handled in this fashion, with identification of as many as 35 components in a single sample. (**W. T. Rainey, D. C. Canada, C. A. Pritchard**)

WORK FOR OTHERS

One new sizable contract has been added to our Work for Others Projects: the construction of an ORNL-type pulse counting two-stage mass spectrometer for the International Atomic Energy Agency. This mass spectrometer when completed will be used in the international safeguards assessment program. We are continuing development of mass spectrometric methodology for NSF(RANN) within the Ecology and Analysis of Trace Contaminants Program, and also developmental work and fuel analyses for EPA.

Construction of two-stage mass spectrometer for IAEA. The International Atomic Energy Agency, Seibersdorf Laboratory, Vienna, Austria, requires a mass spectrometer with abundance sensitivity and sample size and capacity specifications that no commercial vendor was able to meet. Because of the unique capabilities of our mass spectrometry group, we were asked to build for them a two-stage pulse counting mass spectrometer similar to those in operation here for some years. A description of the ORNL-type mass spectrometer is given elsewhere.[9] The principal differences between the new instrument and the ones in use will be up-dated electronic components, including a faster counting system and an on-line Digital Equipment Corporation PDP-11 computer.

The magnets and the track upon which they rest have been shipped and are now in Vienna. Various vacuum components have been assembled and tested for leaks, including source and slit cans, flight tubes, and sundry peripheral devices, such as a rotary-motion feedthrough. The necessary electronic equipment has been ordered, and much of it has arrived. Three ion sources have been assembled and aligned. A substantial fraction of an instruction manual is in rough-draft form, and a documentation package is being prepared. Several parts for the job are under way in the local shops, involving fabrication of mechanical and electrical components. Completion date of the project is projected for mid-1976. Installation and testing of the instrument will be carried out in Vienna by ORNL Mass Spectrometry Department personnel soon after this date. (**H. S. McKown, W. H. Christie, D. H. Smith, L. K. Bertram, J. A. Carter**)

Development and application of multielement isotope dilution spark-source mass spectrometry and ion microprobe mass spectrometric techniques – NSF-EATC. The two main objectives of this study are: (1) to convert the semiquantitative multielemental capabilities of spark-source mass spectrometry into a quantitative technique by establishing multielement isotope dilution methodology, and (2) to investigate isotope dilution as a means for quantifying ion microprobe mass analysis. For convenience of data output when measuring several elements, we are planning to use the PDP-8 system to

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[9] A. E. Cameron et al., *Analytical Mass Spectrometry at Oak Ridge National Laboratory*, ORNL-4645 (January 1971).

collect data and the IBM-1130 to calculate and output isotope dilution data.

The most fundamental requirement of isotope dilution is that chemical equilibrium of the spike and sample isotopes be obtained. If the materials to be analyzed are nonorganic, such as water or alloys, this equilibrium is almost invariably obtained in the process of dissolution and extraction of the sample. The analysis of organic materials such as gasoline, solvents, coal, fuel oils, and tissue samples present difficult problems of equilibration. The metallic impurities in organic materials are present as unknown organometallic compounds. The isolation and identification of these organometallic compounds is not practical at the submicrogram level. This problem is compounded by the fact that the enriched stable isotopes are available as *pure elements or oxides and are best prepared as acid solutions.*

For organic base materials, for example, gasoline, various methods of equilibration were investigated. Initial work included oxidation with bromine, wet acid oxidation under reflux, and various means of equilibration during extraction.

For gasoline we now add the sample to concentrated HCl that contains the multielement spike and reflux the two-phase system for 4 to 6 hr. Afterward, the aqueous phase, which is about one-tenth of the organic phase, is removed and dried on graphite electrodes for SSMS analysis. To confirm this procedure, synthetic samples were made from alkyl metal sulfonates obtained from Continental Oil Company and from NBS organometallic standard reference materials. The recovery rate for most metallic elements in the synthetic samples is greater than 80% by the reflux method. The precision at the 0.5 to 1 × 10^{-6} g/ml level is about 10%. The gasoline samples are analyzed for 26 elements at concentration levels between 1 × 10^{-9} and 1 × 10^{-6} g/ml. Mononuclidic elements such as bismuth are determined using isotopes of other elements as internal standards.

Analysis of fuel oil and gasoline and oil additives is accomplished by wet ashing the sample in $HClO_4$-HNO_3 followed by addition of the spike mixture. The spiked solution is dried on graphite electrodes and sparked as for the gasolines.

Isotope dilution techniques have been employed for the analysis of distilled water, tap water, and stream waters. A spike solution for use with water samples consisting of 11 enriched isotopes (^{204}*Pb*, ^{199}*Hg*, ^{183}W, ^{106}Cd, ^{97}Mo, ^{77}Se, ^{67}Zn, ^{65}Ca, ^{61}Ni, ^{57}Fe, ^{53}Cr) and isotopically normal erbium has been prepared. Mononuclidic elements such as As and Co are compared with the enriched isotope nearest in mass; that is, ^{75}As is compared with ^{77}Se. Detection limits are limited only by the volume that has been preconcentrated. The sample volumes in most of this work have been sufficient to provide detection limits for most elements in the range of 5 × 10^{-11} g/ml. Waters with high mineral content leave a complex residue on the electrodes and may raise the detection limit by a factor of 10. The isotope dilution studies have also aided in the determination of relative sensitivity factors useful in routine survey analysis.

Spark-source mass spectrometry, using isotope dilution techniques, has been shown to be an accurate method of analysis for trace-level impurities in a wide variety of sample types. The method has also been successfully employed in the analysis of dust, $^{233}UO_2$, *animal tissues, cigarette tars, and various alloys. Multi*-element isotope dilution analysis adds new dimensions of precision and accuracy to the high sensitivity and broad elemental range of SSMS.

The stated objective for IMMA as applied to isotope dilution methods will require that sensitivity data for many of the elements be obtained. This report summarizes the status of the analytical capability of IMMA, using relative sensitivity factors as well as isotope dilution methods.

Work has been done this past year investigating the quantification of data from IMMA. Sensitivity factors for the elements vary over a range of at least six orders of magnitude and are complex functions of ionization potential, chemical state, primary bombarding ion, pressure in the instrument, etc. IMMA is extremely sensitive for alkali elements and relatively insensitive for the Group VI elements.

Two approaches have been used to attack the quantification problem; both necessitate the use of a computer to process the data. The first method, developed by Andersen,[10] involves the assumption of local thermal equilibrium (LTE) and the use of the Saha-Eggert equation. The program tests an array of temperatures and electron density values for the minimum in the error function of one or two internal standards. Even though the underlying assumptions are questionable, the model has had some success. The CARISMA[10] program has been set up on the IBM 360 at ORGDP; in addition, an altered version of a simplified LTE model has been stored on our IBM 1130

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

computer.[11] In this program, corrections for the formation of negative ions and doubly charged positive ions are neglected.

The NBS 660 series of steel standards were analyzed, and the data obtained from CARISMA and the modified program were compared with regard to elemental composition. The differences between the two programs were not great, considering the overall accuracy of the LTE approach. In general, either program calculated metals to an accuracy of within a factor of 2 (molybdenum was an exception) for concentrations less than 1%, and completely failed on nonmetallic and amphoteric elements such as arsenic.

The sensitivity factor approach to quantification is similar to the technique used successfully in spark-source mass spectrometry for some years.[12,13,14] The major complicating factor in applying this technique to the IMMA is that the data are sensitive functions of the sample matrix. Therefore, the composition of the standard must be very similar to the sample, and probe standards are not yet common. However, a simple determination of sensitivity factors from the NBS-660 suite of iron standards indicates that the approach is worth further investigation.

Some work has been done on NBS glass standards, and the results show that reasonable data are obtainable. One of the problems involved in the analysis of nonconducting samples is the buildup of surface charge during bombardment with positive ions. Unless prevented, the resulting instabilities in the ion optics of the system preclude reliable collection of data. A negative primary ion beam is usually successful in controlling instability, but results in a significant loss of sensitivity for electropositive elements. Charge buildup can be prevented by application of a thin film of carbon, but this technique is not completely successful. To improve our sample-handling flexibility, we installed an electron gun in the sample chamber of the IMMA. The addition of the electron gun required modifications to the primary lens pieces. The electron beam successfully neutralized excess positive charge and allowed us to study samples that would have caused problems, for example, the leaf described below. An improved version of the electron gun is in the design stage and will be installed later.

A leaf from the vicinity of a lead smelter was analyzed and the surface distribution of K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Cd, and Pb determined. Ion micrographs showed the presence of lead in all particles; the other elements were not present in all particles. Spark-source mass spectrometric analysis by isotope dilution gave the following concentrations: Cd, 0.57; Cu, 3.5; Zn, 9.8; Pb, 75 µg/cm^2.

The question of the chemical state of lead on such samples is important, because the chemical state will determine the ease with which the lead enters the ecosystem. Although the IMMA gives no direct information on chemical form, it is possible to make inferences from the presence or absence of certain masses in the spectrum. Since lead was shown to be present on the leaf, a differentiation between PbS or $PbSO_4$ was desired. A primary ion beam of Ar^+ was used to allow investigation of oxygen and sulfur distribution, and negative ions were monitored to enhance the sensitivity for electronegative molecular species. A series of ion micrographs, all showing the same spatial distribution, was made at the following masses: 96(SO_4^-); 208(Pb^-); 224(PbO^-); 240(PbO_2^-, PbS^-); 256(PbO_3^-, $PbSO^-$); 272(PbO_4^-, $PbSO_2^-$); 288($PbSO_3^-$); 304($PbSO_4^-$). The presence of the higher masses (288 and 304) is strong evidence for the presence of $PbSO_4$. Since both lead sulfide and a series of lead oxide ions would be expected to form from $PbSO_4$, nothing can be said concerning the presence or absence of PbS and PbO on the leaf.

A number of studies were done to investigate the applicability of the multielement spike to IMMA analyses. A suitable substrate for solutions was found to be pyrolytic graphite, which did not absorb the sample, as copper and pressed graphite did. Unfortunately, due to the differing solubilities of the various elements, it was not possible to obtain a uniform distribution of them on the surface. The solutions were loaded as 1-µl drops on the pyrolytic graphite surface. As the drop evaporated and contracted, the least soluble species precipitated out of the solution first and the most soluble last. Thus, while it was easy to obtain a signal for each element, the composite of any one area was no longer representative of the solution as a whole.

The quantity of a given element in the solution could still be obtained by measuring the ratio of one of its natural isotopes to the spike isotope. We are able to measure about 0.2 ng of zirconium on pyrolytic

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[11] David Simons, private communication, University of Illinois, 1975.

[12] R. E. Honig, *Advances in Mass Spectrometry*, p. 101, vol. III, W. L. Mead, ed., Institute of Petroleum, London, 1966.

[13] W. L. Harrington, R. K. Skogerboe, and G. H. Morrison, "Quantitative Spark Source Mass Spectrometry Using Cryosorption Pumping," *Anal. Chem.* 37(12), 1480 (1965).

[14] J. A. Carter, A. E. Cameron, and J. A. Dean, "Spark Source Mass Spectrographic Techniques for the Analysis of Lanthanide and Actinide Elements in Microgram and Sub-Microgram Transuranium Samples," *Anal. Lett.* 4, 351–55 (1971).

graphite with a precision of about 10% relative standard deviation. (J. A. Carter, D. L. Donohue, D. H. Smith, W. H. Christie, J. C. Franklin, R. W. Stelzner, E. H. Waters)

Fuels analysis by IDSSMS for EPA. Due to the increasing interest in trace-metal constituents of energy-related samples, we have begun a study of the sub-ppm level of inorganic species in gasoline by isotope dilution spark-source mass spectrometry (IDSSMS). This work capitalizes on experience with multielement isotope dilution techniques.

The National Fuels Surveillance Network, through its ten regional offices, collects gasoline and fuel additive samples as an Environmental Protection Agency monitoring function. Trace-metal, physical, and chemical analyses are performed on these collected samples to detect constituents which may be present as harmful pollutants. Our multielement detection method, IDSSMS, is being used for monitoring the trace constituents; EPA employs ASTM methods in the physical and chemical monitoring effort.

The Fuels Network Program enables EPA to detect constituents in fuels that could poison catalytic exhaust control systems; to detect toxic heavy-metal constituents in fuels that may be introduced during transport or storage; to develop and to assess emission control factors for additives and/or trace metals; to design other studies needed to identify emission problems; and to enforce federally regulated trace-metal limits such as those established for lead and phosphorus in gasoline.

Trace-metal analyses were made by IDSSMS on some 250 gasolines and about 70 fuel additives. For this trace-element monitoring effort, a multielement spike solution was prepared, containing 14 separated stable isotopes, along with a normal isotopic internal standard used to determine those elements not amenable to the isotope dilution technique.

The combination of multielement isotope dilution with the broad elemental range and good sensitivity of spark-source mass spectrometry provided EPA with a new capability in trace analyses. Techniques and tests for achieving equilibrium of the multielement spikes are described in the Mass Spectrometry Development Section. (D. L. Donohue, R. C. Bryant, J. C. Franklin, J. A. Carter)

SPECTROMETRY SERVICES

Mass spectrometry service laboratory. This laboratory performs mass spectrometric measurements on a wide variety of elements and gases. During the past year, more than 17,000 results were reported, an increase of about 3.3% over the previous year. A large part of the increase was due to samples generated in the Coal Gasification Program. Isotopic results were reported on a total of 47 different elements. About one-third of the work was performed for the Chemical Technology Division, another third for the Isotopes Division, and the remaining third diversified between ten other ORNL divisions and six "work for others" programs.

Actinides. Samples of actinides, thorium through californium, are analyzed routinely. In addition, occasional requests for isotopic analyses of other elements are performed in this laboratory. J. K. Poggenburg of the Operations Division requested that we analyze a ^{204}Pb sample before and after irradiation. He used the results to calculate the cross section of the ^{204}Pb. Other unusual samples include lead from India containing 87.6% ^{208}Pb, for S. Raman, Physics Division; a sample of ^{249}Cf of 99.87% purity; and a 55.9% ^{243}Cm sample from J. Knauer of the Chemical Technology Division.

Isotope dilution analyses on Sm, Th, U, and Pu were performed, and several uranium and plutonium dosimeters and U-Al and Pu-Al alloys were analyzed isotopically and quantitatively for H. L. Adair of the Solid State Division.

Work continued on the isotope dilution mass spectrometry technique, using a double spike containing ^{230}Th and ^{233}U for use in evaluating burnup in the HTGR program. Less than 0.5 ml of a solution from the dissolution of two Peach Bottom fuel particles was received; each aliquot usually contained less than 2 and 10 μg of uranium and thorium respectively. From each sample solution, 100 μl was spiked with our double-spike solution. Isotopic uranium results were also obtained on the original solution. The total uranium and thorium content in the fuel particles could then be determined.

We participated in the PAFEX-2 experiment for the IAEA Safeguards Program, and in the SALE Program. The objectives of these experiments are to evaluate on a test-run basis the operational problems in carrying out the safeguards analytical work on input solutions for fuel reprocessing plants in a network of laboratories and to determine plutonium and uranium content and isotopic composition of dissolved low-enriched uranium fuel. Samples were analyzed for other ERDA laboratories, including plutonium samples for LASL and uranium samples for the Ames Laboratory.

Stable Isotopes. Isotopic analyses were performed on 31 different elements in the past year, primarily for the Calutron Separations Program (now in the Chemical Technology Division). During the past year the emphasis has been on Te, Sn, Se, Ni, and Yb.

Gases. Until March 1975, work on gases was almost entirely inorganic. About half of the work was usually certification of argon and helium cylinder gases, with some isotopic analyses of H, O, Kr, and Xe being performed. In March the first request for analyses on samples from the Coal Technology Program was received. Since that time, approximately 250 smaples from three different investigators have been analyzed.

Because of fragmentation, organic mass spectrometry, even of the relatively simple light hydrocarbons, is much more complicated than for inorganic gases. Fairly good results on H_2, CH_4, H_2O, N_2 + CO, O_2 and H_2S, and on Ar and CO_2 are possible if they are large compared with the C_1 fragments. We also reported C_2, C_3, C_4, etc., fragments observed by summing the three largest peaks from each group. Even with this rough calculation, definite worthwhile trends were observed. To improve the analyses, a computer program was written to calculate the results, using a residual technique. With this program, saturated and unsaturated hydrocarbons can be separated and identified. At present, standard spectra and sensitivity factors from the API tables are used. As many standard gases as are available are being obtained for establishing sensitivity factors for gas analysis. Additionally, an improved pressure gage was installed on the manifold which should further improve reliability. **(R. E. Eby, M. M. Honaker, L. Guinn, R. L. Sherman, C. I. Whaley)**

Elemental spectrometry. Emission spectrochemical and spark-source mass spectrometry analyses were provided to 16 ORNL divisions and related projects. A total of 72,756 analyses were reported during the past year, a 27% increase since the last report period. Metals and Ceramics, Chemical Technology, and Isotopes Divisions were the largest users of our elemental spectrometry services.

The Paschen emission spectrometer has been used for the analysis of various nickel alloys, aluminum and steels of several types, and for determination of added Nb, Ti, and Si in nickel-base alloys. To improve the quality of data from the Paschen, we have established an in-house quality control program for nickel-base alloys, stainless steels, and aluminum alloys. Samples of an NBS steel, four different Hastelloy N heats, and a 6061 aluminum are being retained and run with each new batch of samples. Sufficient data have been accumulated to show that the precision of an analysis is less than 5% relative standard deviation.

Spark-source mass spectrometric analyses have been provided for the Ir–0.3% W alloys and for the Ir–0.3% W alloy doped with several trace elements at the 20- to 100-ppm level. This analytical program has included analysis of the powders that are used in preparation of the alloys as well as the product alloy.

Requests for service analysis of radioactive materials have been heavy this year. Analyses have been performed on ^{244}Cm, ^{241}Am, ^{239}Pu, and ^{36}Cl. Samples of ^{253}Es have been analyzed by solution methods.

The fuel analysis for the LWBR program has continued. A continuous control program based on repeated analyses of a New Brunswick Laboratory uranium standard has been established. We have requalified on anonymous control samples for 11 impurity elements. Requalification for Th, Pu, and Hg in UO_2 is under way. The precisions for Fe, P, and Al in the ^{233}U program are 6, 35, and 15% at the 100- to 200-ppm level. **(J. C. Franklin, S. A. MacIntyre, W. R. Musick, L. Landau, G. I. Gaunt, R. C. Bryant, E. H. Waters)**

6. Bio-Organic Analysis

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

We continue to be involved in programmatic research and services, with approximately 85% of current funding provided by the National Cancer Institute Smoking and Health Program (NCI SHP) and the Council for Tobacco Research-USA, Inc. (CTR-USA, Inc.). The remainder of our studies deals with the chemical characterization of fossil-fuel-derived materials. Research and services in both tobacco and energy-related sciences emphasize defining the environmental and/or health hazard associated with advanced technologies.

The Bio-Organic Analysis Group is organized into two major sections, with each consisting of two projects. "Chemical Characterization" is subdivided into "tobacco smoke" and "energy technologies." "Bioassay and Bioanalyses" is subdivided into "inhalation bioassay instrumentation" and "bioassay development and monitoring." Although considerable overlap exists, the first section is primarily concerned with characterizing the insult and the second with defining the impact on experimental models of exposures to the insult. Mouse skin painting and inhalation exposure are the bioassay models of principal concern.

The topics discussed in this report were selected as being among our primary accomplishments in this period and best representing studies of the group as a whole. Significant progress has also been made in areas not discussed in detail below. Our study[1] of the multialiquot and multicomponent chromatographic analysis of the total particulate matter (TPM) of cigarette smokes is complete. The multialiquot approach has been found best and is in routine use following an extensive practical evaluation. We find that Fourier transform infrared spectroscopy (FTS/IR) is applicable to the determination of gas phase constituents in the presence of smoke particulates. Analyses of contained aerosols now under way will determine whether the artificial production of gas phase using Cambridge filters is a legitimate approach to the analytical chemistry of inhalation bioassays. No other technique, to our knowledge, is capable of the nondestructive analyses of whole smokes for individual gas phase constituents. Our study of chemical measurements of contained smokes as a superior method for determining dose accepted by experimental animals is now complete. By using the procedure we can accurately predict the quantities of individual constituents normally determined in the animals by laborious analyses of body fluids and tissue samples. A convenient method for the noninvasive determination of doses of individual constituents of smokes is now in hand. Instrumentation development in the past year has included the design and construction of a continuous smoke generator optimized to expose tracheal grafts.

Scientific progress, changing funding agency priorities, and an increasing interest in bio-organic analytical services in-house are leading to new areas of responsibility. While

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[1] M. R. Guerin et al., "Multialiquot Determination of Protocol Components," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 59.

we anticipate that most routine services will be required by the NCI in the coming year, an increasing number of samples will be submitted by in-house sources. A one-man-month study of temperature gradients along burning cigarettes as a function of paper porosity was carried out for the NCI during this report period. Such special studies are being requested more frequently. A pilot study of ^{210}Po in whole smoke has led to discussions with both the NCI and CTR-USA, Inc., which may produce new programmatic research for the Division. A new contract was initiated on September 1, 1975, to establish this Group as the Quality Monitoring Facility for all NCI SHP inhalation bioassay contractors. This is expected to be a long-term activity, including an opportunity to increase our involvement in bioanalytical research. Finally, experiences of the past year in chemical studies of coal-derived samples and new interactions with researchers in the Environmental Sciences Division and the Biology Division have prepared us for a significant contribution to fossil fuels technologies in the coming year.

CHEMICAL CHARACTERIZATION

Advanced organic analytical services. The control analyses[2] section of the tobacco smoke characterization project is being considered the "core" of a general service activity. The expertise available in this section is well suited to respond efficiently to requests for special studies and special analyses. Gas filter pads, extracts of industrial site filters, and a Perclene sample associated with nuclear fuel technologies are typical of the growing number of samples submitted by in-house groups. A number of special studies (not included in the contract commitment of the control analysis section) are being requested by the NCI SHP. Special requests have included analyses of Phillipine and Japanese commercial cigarettes, the characterization of marijuana smokes, and the characterization of experimental cigarettes scheduled for inhalation bioassay. Pilot studies of ^{210}Po deliveries of selected cigarettes and determinations of the uranium content of fertilizers have been completed with the cooperation of the Mass and Emission Spectrometry Group. The standard characterization of primary experimental cigarettes for the NCI SHP continues to represent 80 to 90% of the sample load. Approximately 3000 such analyses, many in quadruplicate, are carried out in a typical 12-month period.

Table 6.1 summarizes constituents and analyses which presently constitute our service capability. Although most are optimized for analyses of smokes and smoke condensates, we find the procedures to be applicable to other samples with little or no modification. The "profile" methods are generally used to acquire rapid measures of chemical complexity and as an early step toward structural identification. Identified constituents of the profiles can be quantitated when necessary.

A few constituents are determined by spectroscopy, titration, or gravimetry. The most widely used technique is gas-liquid or gas-solid chromatography. Combining gas-solid chromatography with chemical preseparation and isotope dilution provides our most advanced methods. High-performance liquid chromatography is finding increased use in research studies, but is not yet widely used in routine services.

Bioanalytical services have been limited to a small number of closely collaborative studies with in-house and out-of-house groups. Services include inhalation bioassay dosimetry and clinical chemistry related to the impact of exposure. We anticipate an increasing level of bioanalytical services in the next year. (W. H. Griest, H. Kubota, R. B. Quincy)

Polynuclear aromatic hydrocarbons. Polynuclear aromatic hydrocarbons (PAH's) and the PAH-enriched fractions of complex organic mixtures are classic carcinogens. Methods are being developed and applied to smoke- and energy-related samples to allow an increased characterization of health hazards associated with these materials. Our existing method to determine selected constituents is being improved by increasing the efficiency of the procedure and the reliability of results. Simultaneous multicomponent analytical procedures and procedures optimized to determine newly selected constituents are under development.

Improvements to the lengthy sample preparation procedure necessary to determine benz[*a*]anthracene (BaA) and benzo[*a*]pyrene (BaP) have focused upon the final chromatographic isolation step. The BaA subfraction from the alumina column step is now routinely submitted to final purification on an acetylated cellulose column, using a solvent of ethanol-toluene-water (17-4-1). Quantitation of BaA is achieved by isothermal gas-liquid chromatography (GLC) on a

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[2] M. R. Guerin et al., "Control Chemical Analyses," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5016, p. 56.

Table 6.1. Constituents and analyses constituting advanced organic analytical services capability[a]

Total particulate matter (pm)
Water (pm, cond)
Nicotine alkaloids (pm)
Tar (pm)
Isoprene (pm)
Acetaldehyde (gp)
Acrolein (gp)
Formaldehyde (gp)
Hydrogen cyanide (gp)
Oxides of nitrogen (gp)
Nitric oxide (gp)
Carbon monoxide (gp)
Carbon dioxide (gp)
Hydrogen sulfide (gp, ff)
Carbonyl sulfide (gp, ff)
Sulfur dioxide (gp, ff)
Carbon disulfide (gp, ff)
Dimethylsulfide (gp, ff)
Methyl disulfide (gp, ff)
Miscellaneous organic sulfurs (gp, ff)
Acetone (pm, cond, gp)
Neophytadiene (pm, cond)
Phenol (pm, cond, ff)
o-Cresol (pm, cond, ff)
m-Cresol (pm, cond, ff)
p-Cresol (pm, cond, ff)
m- + p-Cresol (pm, cond, ff)
Phenolics (pm, cond, ff)
Catechol (pm, cond)
Weak acids (pm, cond, ff)
Very weak acids (pm, cond, ff)
Palmitic acid (pm, cond)
Oleic, linoleic, linolenic acids (pm, cond)
Stearic acid (pm, cond)
Indole (pm, cond, ff)
Skatole (pm, cond, ff)
Phenanthrene (cond, ff)
Benz[a]anthracene (cond, ff)
Benzo[a]pyrene (cond, ff)
Methylchrysenes (cond, ff)
Miscellaneous PAH (cond, ff)
Glycerol (pm, cond)
Cannabinoids (pm, cond)
Composition profile (gp, pm, cond, ff)
Sulfur constituent profile (gp, pm, cond, ff)
PAH profile (pm, cond, ff)
Terpene enriched profile (pm, cond)

[a] pm, particulate matter; gp, gas phase; cond, condensate; ff, applied to fossil fuel samples. Related constituents, for example, benzene, alcohols, butylated hydroxytoluene, and methane are often readily determined.

6-ft × 1/8-in.-OD column packed with OV-25. This GLC packing allows a very good resolution of BaA from chrysene. Collecting acetylated cellulose column effluents into separate fractions is not as critical as when we used a nonselective GLC phase. The BaP subfraction from the alumina step is also purified on an acetylated cellulose column with the same solvents in the ratio 17:7:1, and fluorometry is used for final quantitation. Fractions from the column separation are more reproducible and of better purity than from the previously used paper separation. A major additional advantage is that the columns can be used up to 100 times without replacement.

A number of coal liquefaction products in addition to the routine cigarette smoke condensates have been examined for BaP and BaA by this procedure. In general, we have found BaA and BaP concentrations of 20 and 40 ppm, respectively, in some liquefaction products. The concentrations of these PAH's in condensed smokes are usually less than 2 ppm. In addition, approximately 10 ppb of BaP was found in one coal liquefaction product aqueous process sample which could be discharged into the environment.

The high levels of BaA and BaP in the coal-derived samples suggested that a more complete characterization of the PAH content was necessary. A multi-PAH assay has been developed and applied to several liquefaction products. This method departs from our traditional procedure in that the entire PAH-enriched fraction rather than separate subfractions is collected in the alumina column effluent. After concentration, this fraction is directly analyzed by GLC on a 22-ft × 1/8-in. glass column of 3% Dexsil 400 on 80/100 HP Chromosorb G. A column temperature program from 110 to 320°C at 1°/min allows the resolution of PAH's in the range 1 to 7 rings. A comparison of the PAH fractions from a smoke condensate and a coal-derived oil is shown in Fig. 6.1, with peak identifications in Table 6.2. A visual comparison of the profiles reveals that the oil contains about ten times the PAH content of condensate across the entire range of PAH's visualized. In addition, the oil contains a greater concentration of higher ring systems than does smoke condensate, which itself is centered mainly about the two-ring PAH's and their alkyl derivatives.

Quantitative estimates were achieved by incorporation of a ^{14}C-BaP tracer in the samples. The assumptions were made that the recovery of the entire PAH fraction is equal to that of the BaP tracer, that each peak tentatively identified by cochromatography is

Table 6.2. PAH profile peak identifications and quantities of selected constituents in a coal-derived liquid

Peak No	PAH
1	*cis*- and *trans*-Decahydronaphthalene
2	1,4-Dihydronaphthalene
3	Naphthalene (347)[a]
4	2-Methylnaphthalene (1325)
5	1-Methylnaphthalene (383)
6	Azulene
7	Biphenyl (8a)
8	2,6-Dimethylnaphthalene (328)
9	1,3-Dimethylnaphthalene (181)
10	Butylated hydroxytoluene
11	Acenaphthalene (20)
12	Acenaphthene (61)
13	Fluorene (205)
14	9,10-Dihydroanthracene
15	9-Methylfluorene
16	9,10-Dihydrophenanthrene
17	Octanthrene
18	1-Methylfluorene (152)
19	Phenanthrene + 1,3,6-trimethylnaphthalene (Phen, 413)
20	Anthracene
21	1-Phenylnaphthalene
22	2-Methylanthracene
23	1-Methylphenanthrene (167)
24	2-Phenylnaphthalene
25	9-Methylanthracene (42)
26	Fluoranthene
27	Pyrene
28	1,2-Benzofluorene
29	2,3-Benzofluorene
30	4-Methylpyrene
31	1-Methylpyrene
32	5,12-Dihydrotetracene
33	1,2-Benzanthracene (BaA, 18)
34	Chrysene + triphenylene (Chry, 98)
35	2,3-Benzanthracene
36	7,12-Dimethylbenz[*a*]anthracene
37	Triphenylbenzene
38	1,2- + 3,4-Benzopyrene (BaP, 41)
39	Perylene
40	Impurity + 3-methylcholanthrene
41	1,2,5,6- + 1,2,3,4-Dibenzanthracene
42	*o*-Phenylenepyrene
43	Picene
44	1,12-Benzoperylene
45	Anthanthrene
46	3,4,9,10-Dibenzopyrene + coronene

[a] Concentration in ppm found in one coal-derived liquid product.

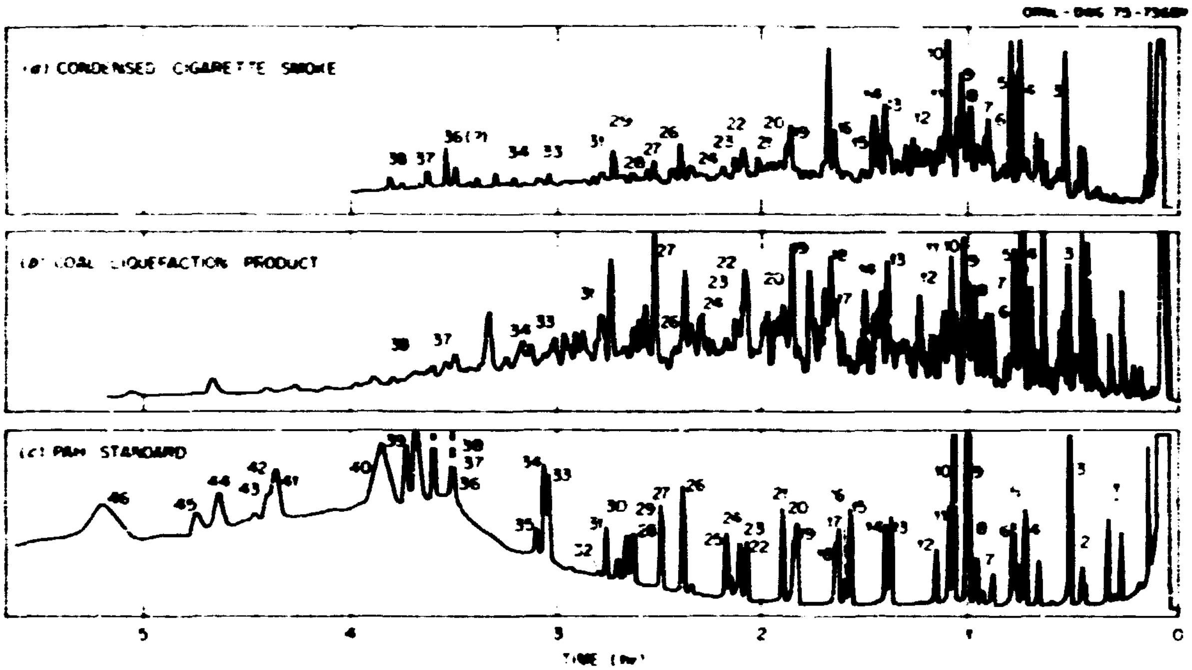

Fig. 6.1. Gas chromatographic profiles of PAH standards and PAH-enriched isolates from smoke and a coal-derived liquid.

reasonably pure, and that the detector responses of isomeric PAH are approximately equal. We will refer to "estimates" rather than "determinations" until these assumptions are proven.

A separate procedure is necessary for determining the methylchrysenes, because methylbenzanthracenes interfere in the gas chromatogram. The benzanthracenes selectively react with maleic anhydride[3] and can be separated from the chrysenes by passing the reaction mixture through Florisil. The unreacted methylchrysenes are selectively eluted, concentrated, and determined by isothermal GLC, using a column packed with OV-22.

Typical results are included in Table 6.2. The most striking features of these data aside from the 41 ppm of BaP, a strong carcinogen are the relatively high levels of the methyl naphthalenes, particularly 2-methylnaphthalene (more than 1000 ppm). This finding may be quite significant in view of the known tumor-promoting activity of the methylnaphthalenes, again, particularly of 2-methylnaphthalene. Although we were unable to measure the cocarcinogens pyrene and fluoranthene in this particular oil sample because of chromatographic interferences, we found 73 ppm of pyrene and 19 ppm of fluoranthene in a process stream leading to this particular oil. 3-Methylchrysene, a weak carcinogen, is present to the extent of 106 ppm, but we were unable to detect any 5-methylchrysene, a very potent carcinogen. An assessment of these data showing the presence of carcinogens, tumor promotors, and cocarcinogens would lead us to predict that these materials would possess considerable carcinogenic potential, as has been observed for at least one coal product in the past.[4] (W. H. Griest, H. Kubota)

Tobacco smoke terpenes. Several studies have suggested that terpenes may be related to the carcinogenicity of tobacco smokes. This work is to determine the relationship of tobacco smoke terpenes to biological activity.

Methods have been developed to isolate a terpene-enriched fraction of tobacco smoke. A series of solvent extraction and precipitation steps are used to give a terpene-enriched fraction suitable for gas chromatographic profiling. The blind assay technique[5] was applied to the chromatographic data from GLC profiles

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[3] S. S. Hecht et al., "Chrysene and Methylchrysenes. Presence in Tobacco Smoke and Carcinogenicity," *J Natl Cancer Inst* **53**, 1121 (1974).

[4] L. J. Sexton et al., "The Hazards to Health in the Hydrogenation of Coal. Pt. I-IV," *Arch Environ Health* **1**, 121 (1960).

[5] M. R. Guerin et al., "Multicomponent Profiling and the Blind Assay," *Anal Chem Div Annu Prog Rep Sept 30, 1974*, ORNL-5006, p 58.

of the terpene fractions of TPM from eight NCI series I experimental cigarettes. Gas chromatograms were obtained on each of the fractions, using a glass column packed with a Dexsil-400 coated solid support and temperature programming. Approximately 50 peaks were obtained in each profile.

Correlation of the entire terpene fraction peak area and 16 individual peaks with data from three different skin-painting bioassay parameters indicated that the terpene fraction as a whole and at least 12 of its constituents correlate well with biological activity. Six of these constituents were tentatively identified as *d*-limonene, damascenone, norphytene, neophytadiene, phytol, and squalene (neophytadiene and squalene were confirmed by mass spectrometry). Correlations also were made between the TPM concentrations of these constituents and the total terpene fraction in search of the best "terpene indicator." Again, high correlations were observed. Of the individual terpene constituents, *d*-limonene would act as the best indicator of the tobacco smoke biological activity related to this terpene fraction. *d*-Limonene in the gas phase also was found to correlate highly with biological activity. A direct correlation of *d*-limonene measured in the gas phase by an independent method with the concentrations of *d*-limonene in the terpene-enriched fraction from the TPM of eight cigarettes produced a simple correlation coefficient of 0.99. *d*-Limonene in the gas phase therefore would be a very good indicator for total smoke terpenes, and the gas-phase *d*-limonene analysis might be able to replace the TPM terpene profile for an assessment of terpene biological activity. (C. H. Ho)

Sulfur-containing compounds. Sulfur-containing constituents of fossil fuels are known to be important to engineering considerations. The role of sulfur constituents in environmental and health effects of smoking and/or advanced fossil fuels technologies is less well known. This work has included the development of new analytical methods, quantitative determinations of sulfur compounds in smokes and coal-related gas samples, and identifications of higher-molecular-weight sulfur-containing constituents in smoke condensate and coal conversion products.

Sulfur constituents have been determined in the gas phase of smokes and in coal-derived gaseous samples by direct gas chromatography with sulfur-selective photometric detection. An 18-ft glass column of "free fatty acid phase" (FFAP) was temperature programmed from 25° (held isothermally for 6 min) to 180°C at 4°/min. Considering five different cigarettes made of synthetic smoking materials we found concentrations (per puff) ranging from 2.8 to 3.5 μg COS, 0.7 to 7.8 μg H_2S, and <0.02 to 0.097 μg thiophene. It seems that the high concentrations of sulfur compounds in some of these synthetic products are sufficient to raise the question of possible health importance. Considering the concentrations of sulfur-containing constituents in pyrolysis and stack gas samples from a coal liquefaction process,[6,7] we found H_2S, COS, $(CH_3S)_2$, and thiophene to be present. The stack gas contained approximately 10 ng/ml of H_2S and COS, while the pyrolysis gas contained 68 ng/ml of COS. The pyrolysis gas also contained 16 ng/ml of thiophene and 1 ng/ml of methyldisulfide. These samples were shipped in gas sampling bags, and inorganic sulfur constituents can react with organics in the samples. We therefore estimate that results for H_2S are artificially low and that organics such as thiophene are present in lower concentration in the materials actually discharged into the environment in this process.

Cigarette smoke condensate, an aqueous sample from one coal conversion process, and two coal liquefaction products have also been examined. A sulfur-enriched fraction of smoke condensate can be prepared by extracting the neutral portion with nitromethane. Nitromethane concentrates subjected to sulfur-selective profiling have been found to contain as many as 50 sulfur-bearing constituents. Dibenzothiophene and benzothiazole have been tentatively identified in condensed smoke by cochromatography. The number of high-molecular-weight sulfur-bearing organics observed in various coal-derived samples has ranged from 8 to 120.[6,7] A product separator liquor (aqueous sample) from one process contained 15 distinguishable sulfur-containing organics.

Positive identification of these compounds is difficult, since direct GLC-MS is only useful after nonsulfur constituents are chemically removed. Mercury salt solutions are found to offer a means to selectively trap sulfur constituents for GLC-MS and form the basis for further isolation procedures. Efforts are now being directed at the isolation of individual constituents from macro samples to obtain sufficient material for positive structural identification. (C. H. Ho, A. D. Horton)

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6. W. D. Shults, ed., "Preliminary Results, Chemical and Biological Examination of Coal-Derived Materials," in preparation.

7. M. R. Guerin, W. H. Griest, C. H. Ho, and W. D. Shults, "Chemical Characterization of Coal Conversion Pilot Plant Materials," Third ERDA Environmental Protection Conference, September 25, 1975.

Fractionation of synthetic crude oils from coal for biological testing. A separation procedure[8,9] used to fractionate cigarette smoke condensate into reproducible class fractions for biological testing has been applied to coal-derived liquids. This classic procedure involves acid-base partition, precipitation, and column chromatographic subfractionation of the neutral constituents. Much information is available about the biological activity and chemical composition of the fractions. Chemical-biological relationships are also well known for the fractions.

One sample of smoke condensate has been fractionated to establish our ability to reproduce the original work. The results of this test agreed reasonably well with those published for the acid and base fractions and for total neutrals, despite a large difference in sample size and the use of different starting materials.

This separation procedure was also applied to products from two coal liquefaction processes. Four samples of COED process Syncrude and one sample of uncentrifuged Synthoil process product oil have been fractionated. Distribution into the major fractions of these two products as well as cigarette smoke condensate are shown in Table 6.3. Reproducibility for the COED samples was generally of the same order as found for the condensate fractionation.[8] These three products represent very different types of materials which can be processed by this method. The COED Syncrude is a relatively light oil, mainly hexane soluble, which is much easier to handle than smoke condensate, while the uncentrifuged Synthoil product oil contains a substantial amount of solids in the form of finely divided char and catalyst and is much more difficult to handle than condensed smoke. Some variations in the original chemical extraction procedures were necessary, but no major changes were made except to extract the COED oil by a continuous procedure rather than batchwise.

Further separation of the major fractions has not yet been attempted beyond collecting each of the gross eluates from the Florisil chromatography in three equal portions. Gas chromatographic profiling has been applied to each of the neutral subfractions of the COED oil. With this procedure, very few peaks were detected in the benzene-ether and methanol phases. A number of constituents in the hexane and hexane-benzene fractions have been tentatively identified by cochromatography. The polyaromatic hydrocarbons apparently are eluted in the latter two-thirds of the hexane fraction and the first third of the hexane-benzene fraction. Gas chromatographic profiles were also obtained from the three corresponding Synthoil fractions. Comparison of the two sets of profiles shows some substantial qualitative and quantitative differences.

Table 6.3. Distribution of class fractions from coal-derived liquids and cigarette smoke condensate

Fraction	Quantity found (%)		
	COED	Synthoil	CSC
1. NaOH insol.	0.9	14.1	7.9
2. Weak acids, insol.	0.2	2.0	2.9
3. Weak acids, Et_2O sol.	1.9	6.5	9.7
4. Strong acids, insol.	0.2	0.1	3.5
5. Strong acids, Et_2O sol.	1.1	1.9	3.6
6. Strong acids, H_2O sol.	1.6	1.7	36.2
7. Bases, insol., *a*	0.2	3.6	0.8
8. Bases, insol., *b*	0.2	0.3	1.2
9. Bases, Et_2O sol.	2.2	1.6	10.6
10. Bases, H_2O sol.	7.3	0.6	3.6
Neutrals			
11. Hexane	74.2	27.6	7.6
12. Hexane-benzene	4.9	7.4	2.4
13. Benzene-ether	4.7	21.7	13.0
14. Methanol	2.4	11.1	10.2
Total recovery	101.7	100.2	111.3

Samples of the major fractions of the COED Syncrude have been examined for mutagenic activity at the Biology Division.[10] Relatively strong mutagenic activity has been found in the hexane, hexane-benzene, and benzene-ether fractions of the neutral portion, as well as in the ether-soluble base fraction. These tests are being extended to subfractions of the neutral samples, and where activity is detected, these fractions will be further subdivided. Gas chromatographic profiling of an underivatized portion of the ether-soluble base fraction reveals the presence of over 100 constituents. Several of these have been tentatively identified by cochromatography. This fraction will be further subdivided by column chromatography for more detailed mutagenic testing and chemical characterization.

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[8] A. P. Swain, J. E. Cooper, and R. L. Stedman, "Large Scale Fractionation of Cigarette Smoke Condensate for Chemical and Biologic Investigations," *Cancer Res.* **29**, 579–83 (1969).

[9] J. H. Bell, S. Ireland, and A. W. Spears, "Identification of Aromatic Ketones in Cigarette Smoke Condensate," *Anal. Chem.* **41**, 310–13 (1969).

[10] J. L. Epler, Biology Division, unpublished data.

There is some concern that the acid and base treatment in this separations procedure could lead to changes in the composition of the test materials. Consequently, other separations schemes are being investigated which reputedly do not create artifacts and which may be faster and more suitable for mechanization and scale-up. These methods involve ion exchange and adsorption chromatography[11] and gel permeation chromatography.[12] Studies on the distribution of specific constituents of coal-related materials by standard liquid-liquid extraction procedures are also in progress. (I. B. Rubin)

Final characterization of marijuana smokes. The last of the NCI-supplied marijuana cigarettes were consumed to produce samples for a further analysis of the smoke. This work is summarized here as an example of our present capabilities in characterizing a given complex sample. Analyses carried out in this study are: (1) BaA and BaP, (2) indole and skatole, (3) carbazole, (4) gas-phase sulfur compounds, (5) gas-phase nitrogen compounds, (6) gas-phase organics, (7) PAH profile, (8) TPM profile, (9) terpene profile, (10) metals, and (11) physical characteristics of the cigarettes. All analyses have been completed except for (6), (9), and (10). Metals are being determined by the Mass and Emission Spectrometry Group, while the other analyses are carried out in this Group.

A batch of 21 85-mm nonfilter marijuana cigarettes visually selected for completeness of packing exhibited a mean weight of 1.175 ± 0.157 g and a resistance-to-draw of 159 ± 83 mm H_2O. The large variation in resistance-to-draw is the result of nonhomogeneous packing – large pieces of stems and seeds are present in every cigarette. Loss of filler on handling required us to select cigarettes only upon the basis of completeness of packing. These were randomly grouped for TPM generation at 15 cigarettes/pad. In spite of these variations, these groups probably represented a more uniform product than one would find "on the street."

The lower PAH's such as napthalene and its alkyl derivatives (possible tumor promoters) were found to be present at lower levels than those in cigarette smoke condensate, but this trend does not hold for the other ring systems. We found elevated levels of BaA (19 ppm) and BaP (6 ppm). The latter is a strong carcinogen, and both are present in condensed smoke at about 1 ppm. The fluorenes, particularly the methylfluorenes, appear in amounts somewhat greater than in condensed smoke, and fluoranthene is also in somewhat greater amounts. Both indole (1198 ppm) and skatole (1061 ppm) are in considerably higher amounts than in condensed smoke (about 600 and 350 ppm respectively), and the amount of carbazole (estimated at about 55 ppm) is also elevated. The concentrations of indole and skatole in marijuana are more nearly equal as compared with condensed smoke, but the carbazole/indole ratio of about 1/20 for marijuana is approximately that observed for tobacco smoke.

Examination of the gas phase of marijuana smoke with element-selective gas-solid chromatography revealed essentially no differences from the Kentucky reference cigarette (1R1) for the gas-phase sulfur profile. The following constituents were identified and measured: COS (3.3 μg/puff), H_2S (8.0 μg/puff), and thiophene (0.2 μg/puff). However, the nitrogen-compound gas-phase profiles of the marijuana cigarette and 1R1 were quite different, with the 1R1 exhibiting higher levels. Acetonitrile was measured in marijuana smoke at 0.99 μg/puff and *n*-butylyamine at 0.38 μg/puff. The corresponding levels in 1R1 smoke are 3.76 and 1.1 μg/puff respectively. The TPM profiles, which represent a broad scan of the TPM constituents, also revealed some significant similarities and differences between the marijuana and 1R1 cigarettes. Phenol, the cresols, catechol, hydroquinone, and neophytadiene are present in the marijuana-TPM at about the same levels as in 1R1-TPM. However, the marijuana apparently contains a considerably larger amount of glycerol and the free fatty acids. This point may require mass spectroscopic confirmation. In place of nicotine in 1R1-TPM, the marijuana-TPM contains large amounts of cannabinol, Δ^9-tetrahydrocannabinol, and cannabidiol. These are the last three major peaks of the marijuana profile. In addition, several other major differences in unidentified TPM profile peaks can be easily seen.

The significance of these differences and their relation to the biological activity of marijuana smoke is not yet clear. The disparity of results among the various reported tests of the biological activity of marijuana smoke prevents us from drawing any conclusions in this area, but the data do show that significant compositional differences do exist between marijuana and tobacco smoke, and these could result in different biological activities.

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[11] D. M. Jewell, J. H. Weber, J. B. Bunger, H. Plancher, and D. R. Latham, "Ion-Exchange, Coordination, and Adsorption Chromatographic Separation of Heavy-End Petroleum Distillates," *Anal. Chem.* 44, 1391–95 (1972).

[12] H.-J. Klimisch, "Anreicherungs-und Trennverfahren zur Analyse polycyclischer aromatischer Kohlenwasserstoffe," *Z. Anal. Chem.* 264, 275–78 (1973).

The results described above are being added to previously acquired results on selected gas-phase constituents for publication. (W. H. Griest, C. H. Ho, H. Kubota)

BIOASSAY AND BIOANALYSES

Analytical methods to characterize inhalation exposure systems. Our responsibility to characterize tobacco smoke inhalation exposure systems and the exposures provided by these systems depends heavily on the development of analytical methods. Methods to analyze standing and flowing smoke aerosols were generally unavailable when this contract was initiated. Complicating factors include (1) the need to analyze the smokes in the presence of animals under normal operating conditions, (2) the need to continuously monitor the exposures, and (3) methods applicable to analyzing a standing aerosol often inapplicable to analyses of flowing streams. A final complication is that little guidance is available to aid in selecting appropriate constituents or parameters to measure. This selection is heavily dependent on the results desired (e.g., effect of animals on the aerosol, concentration monitoring, distribution of constituents in the chamber, etc.).

Previously described[13] methods have undergone final development and/or final evaluation through routine use. The following constituents of particulate matter can now be determined on grab samples from exposure atmospheres: nicotine, water, neophytadiene, phenol, fatty acids, and catechol. Taken together, the relative concentrations of these constituents can provide a measure of TPM composition. Nicotine and neophytadiene are promising as measures of smoke concentration. Gas phase concentrations of carbon monoxide, carbon dioxide, hydrogen, oxygen, and nitric oxide can also now be determined routinely. Except for hydrogen, these constituents are particularly important as measures of animal effects on the aerosol and animal respiration. Hydrogen promises to be a useful indicator of gas phase concentration and can be monitored continuously by thermal conductivity. TPM and organic gas phase constituents can now be profiled routinely as measures of smoke composition.

A new sampling device has been developed for studies of flowing aerosols. Smoke is withdrawn through a micro-Cambridge filter at a constant rate (3.8 ml/min) by a syringe pump. The particulates accumulated on the filter and the gas phase materials retained in the syringe are analyzed later to provide a time-averaged concentration. The device has performed excellently for analyses of nicotine, carbon monoxide, and carbon dioxide, but we feel it is inapplicable to analyses of reactive gas phase constituents such as nitric oxide and hydrogen sulfide.

Methodologies to determine particle size (discussed in detail below) and to monitor particulate and gas phase concentration have also received attention. An optical light scattering device has been constructed which appears to respond quantitatively to particulates. The device allows continuous monitoring, but it is not yet clear whether the response can be converted to absolute values for concentration. We also find that methane and hentriacontane (n-C$_{31}$) are particularly promising indicators of gas phase and particulate matter concentrations respectively. A method has been developed for the collection and gas chromatographic analyses of smoke streams for methane. Initial studies show that methane is easily determined, we anticipate little retention of methane by animals, and a separate study using FTS/IR shows that cigarette to cigarette and puff to puff variation in methane delivery is relatively small. Hentriacontane can now be determined on microsamples of TPM by heating the filter pad to 320°C while sweeping the off-gases into a gas chromatograph. Hentriacontane is completely dissolved in the particulates and, like methane, is unreactive, making it an excellent indicator of particulate matter concentration. (J. R. Stokely)

Chemical composition of tobacco smoke in inhalation exposure systems. The chemical composition of smoke offered to animals in exposure systems is of considerable importance in inhalation studies. The relationship of animal studies to the human experience requires that animals receive smoke that duplicates human smoke as closely as possible. We are investigating the chemical composition of smoke in the exposure systems and the effect of exposure variables on the composition.

One study addressed the question of compositional changes in organic gas phase constituents for smoke offered by the Walton horizontal exposure system. A high-resolution gas chromatographic profiling method[14] was used to analyze smoke in the exposure chamber of the system. This method visualizes approximately 125 organic components of the gas phase of

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13. M. R. Guerin et al., "Smoke Exposure System Characterization," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 67.

14. M. R. Guerin and P. Nettesheim, *ORNL Tobacco Smoke Research Program Summary Report*, ORNL-5008 (March 1975).

smoke and allows reliable quantitation of peak areas for approximately 75. Changes in composition due to aging of the smoke in the exposure chamber were studied by sampling the chamber early in the exposure period (5 sec after puff) and late in the period (25 sec). A normal exposure with this system requires up to about 30 sec in which smoke stands in the exposure chamber. Visual comparison of the chromatograms suggested that major changes in composition do not occur. Detailed analysis of chromatographic peak-area data for 77 of the peaks in the chromatogram confirm the absence of major compositional changes. Only five peak areas were affected by aging, and for these peaks, changes were small and probably insignificant. From this study, we have concluded that compositional changes in the organic gas-phase constituents due to smoke aging are minimal.

Studies with mice undergoing exposure on the Walton horizontal system revealed that the animals cause a general decrease in the concentration of all organic gas-phase constituents in the exposure chamber and produce significant compositional changes in the smoke. With 20 mice undergoing exposure, all peaks in the high-resolution chromatogram decrease in area during a normal 30-sec exposure. Detailed analysis of the peak areas of 77 peaks in the chromatogram showed that the average area of all peaks decreases by a factor of 1.8 during a 20-sec exposure. Components with high boiling points (peaks with large retention times in the chromatograms) were affected more than low-boiling components. These effects are believed to result from the uptake and selective retention of components by the animals.

Evidence that other smoke components in the Walton horizontal exposure chamber are affected by animal interaction has also been obtained. Nitric oxide is a physiologically important smoke component present at a level of 0.2% in the gas phase. Our initial concern was that nitric oxide could react with oxygen to form nitrogen dioxide during exposures, producing a smoke depleted in nitric oxide. Analysis of the chamber contents by a new gas chromatographic method[15] showed that the nitric oxide concentration was not significantly reduced in time periods of up to 30 sec. Further studies with animals, however, showed a steady and rapid decrease in the nitric oxide concentration during the exposure. In a 30-sec exposure of 20 mice, the concentration decreases from an initial value of 72 ppm to 30 ppm at the end of the exposure. Animal uptake and retention of the nitric oxide is thought to be the primary cause for the reduction in the concentration in the exposure chamber.

These and other studies on animal depletion of smoke components suggest a serious limitation of small-volume, static exposure systems such as the Walton horizontal. Since the volume of the exposure chamber of these systems is small relative to the cumulative respiratory volume of the animals undergoing exposure, the animals breathe and possibly rebreathe a major portion of the chamber contents. The animals are, therefore, exposed to a smoke of continuously changing composition.

Gas chromatographic profiling techniques have also been used to evaluate prototype exposure systems and components. For example, the gas-phase profiling technique was used to evaluate tubing materials used to transfer smoke in a system which provides a stream of fresh smoke for exposure. It was found that the tubing (Tygon) used initially in the system absorbs appreciable amounts of high-boiling constituents of the gas phase as the smoke passed through the tubing. Selective absorption of high-boiling components yielded a smoke altered in chemical composition. A systematic study was made of other tubings to find a material with minimal absorption characteristics. Teflon, polyethylene, and metal tubing were found to produce negligible absorption of gas phase components. Future models of this exposure system will incorporate one of these materials for smoke transfer lines. (C. E. Higgins, J. R. Stokely)

Particle size characteristics of tobacco smoke. Cigarette tobacco smoke is an aerosol of spherical liquid particles suspended in a gas phase. Most of the known biologically active constituents are contained in these particles. On inhalation they deposit in various regions of the respiratory system in a size-dependent manner. Thus one of the important variables of tobacco smoke dosimetry is the distribution of sizes of the particles. A standard puff of smoke contains about 10^{11} particles almost all of which are less than 1 μm in diameter. Both the number of particles and their size distribution change rapidly, primarily by coagulation, but other processes such as evaporation, size-selective impaction on walls, gas turbulence, and stirring may also contribute.

None of the standard instrumental techniques (e.g., light scattering, gas centrifugation, cascade impaction, electrostatic analysis) for measuring size are without objection when applied to the tobacco smoke problem. Most require extensive dilution prior to measurement;

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[15] A. D. Horton, J. R. Stokely, and M. R. Guerin, "Gas Chromatographic Determination of Nitric Oxide (NO) in Cigarette Smoke," *Anal. Lett.* 7, 177 (1974).

some are insensitive and unreliable, particularly at the lower end of the size distribution. Direct microscopic observation of the particles has also proved unsuccessful. The liquid droplets spread when collected and evaporate in the high-vacuum environment of an electron microscope.

The compound methyl 2-cyanoacrylate (MCA, Eastman 910 adhesive) polymerizes rapidly on the surface of catalytically active substances. It was first used in the gas phase to replicate ice crystals for microscopic investigation as they fell through its vapors.[16] Recently, Carter and Hasegawa[17] reported the fixation and stabilization of tobacco smoke particles for electron microscopic observation by contacting them with MCA vapors. We have undertaken a parallel investigation of this technique with the aim of developing a method whereby the particles may be easily collected and their number and size distribution reproducibly and quantitatively determined with an electron microscope.

With this aim in mind we have chosen to collect the particles by filtration. Of a number of commercially available filters, we have found Nucleopore filters to be most satisfactory. They have well-defined, sufficiently small pores, and their surface appears smooth at high magnification, allowing easy observation of the MCA-fixed particles in a scanning electron microscope (SEM). Routine experiments are now done with filters of 0.1- or 0.05-μm pore diameter.

In a typical experiment, MCA vapors are filtered into a heated vessel. The smoke sample is then drawn in and mixed with the MCA vapors. After a few seconds the fixed particles are filtered onto the Nucleopore membranes. These are cut and mounted on SEM stubs. Prior to observation they are coated with a thin layer of conductive material. Both carbon and gold have been used; the gold gives somewhat better emission. Typical results are shown in the electron photomicrograph of Fig. 6.2. The magnification of this figure, about 10,000 times, is typical of that used to adequately display the smallest particles for measurement. The particle diameters have been measured from the SEM photographs or enlargements, using an Elograph Graphic Digitizer coupled, via punched tape, to a minicomputer. Typically, 500 to 1000 particles are measured. The minicomputer is programmed to calculate and classify the diameters and output the statistics necessary to define the size distribution.

We have found that the particle diameters do not continue to grow on prolonged contact with MCA vapors, nor do they change when the reaction temperature is increased from 50° to 70°. At these temperatures the particles are completedly fixed in the few seconds necessary to mix and filter the mixture. At room temperature an unduly long contact of about 1 min is necessary to fix the particles. These results indicate that once a layer of polymerized MCA is formed on the smoke particles, further deposition of polymer does not occur.

In analogy to the work on ice crystals[16] it was originally assumed that the smoke particles were encapsulated in a thin film of MCA polymer and that, like water, the tar of the cigarette smoke would largely diffuse through this film and evaporate in the high vacuum of the electron microscope, leaving a thin bubble of MCA polymer. A measurement of the thickness of this shell would establish the bias of the method: the relation between observed and true smoke particle diameter. We have eroded MCA fixed smoke particles with a beam of argon ions and have examined them in the SEM. The thin shell conjectured was not confirmed. The smaller particles, those less than about 0.5 μm, appeared solid. Larger particles were sometimes hollow, but with a thick diffuse shell (about 0.3 μm). Apparently the MCA diffuses into the liquid smoke matrix as it polymerizes.

We have since resorted to a less-direct test of the bias of the method. The particle size distribution of very dilute smoke was measured and compared with well-regarded gas centrifugation (conifuge) results.[18] Accepting the conifuge results as a standard, then, if the addition of MCA to a smoke particle significantly increases its diameter, the size distribution curve from our MCA-SEM method should be shifted to larger sizes. In fact, both methods gave similar size distributions, peaking at 0.2 μm, with 90% of the particles in the range 0.1 to 0.7 μm. We have found no evidence, from this test, of a significant diameter bias. It thus appears that the MCA-SEM method is at least as reliable as other methods for measuring the size distribution of volatile liquid aerosols such as tobacco smoke and, in addition, is fully capable of quickly sampling the concentrated smokes of interest to the Smoking and

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[16] R. I. Smith-Johannsen, "Resin Vapor Replication Technique for Snow Crystals and Biological Specimens," *Nature* 205, 1204 (1965).

[17] W. L. Carter and I. Hasegaw, "Fixation of Tobacco Smoke Aerosols for Size Distribution Studies," Abstracts of 28th Tobacco Chemists Research Conference, Raleigh, N.C., October 28, 1974.

[18] C. H. Kieth and J. C. Derrick, "Measurement of the Particle Size Distribution and Concentration of Cigarette Smoke by the 'Conifuge'," *J. Colloid Sci.* 15, 340 (1960).

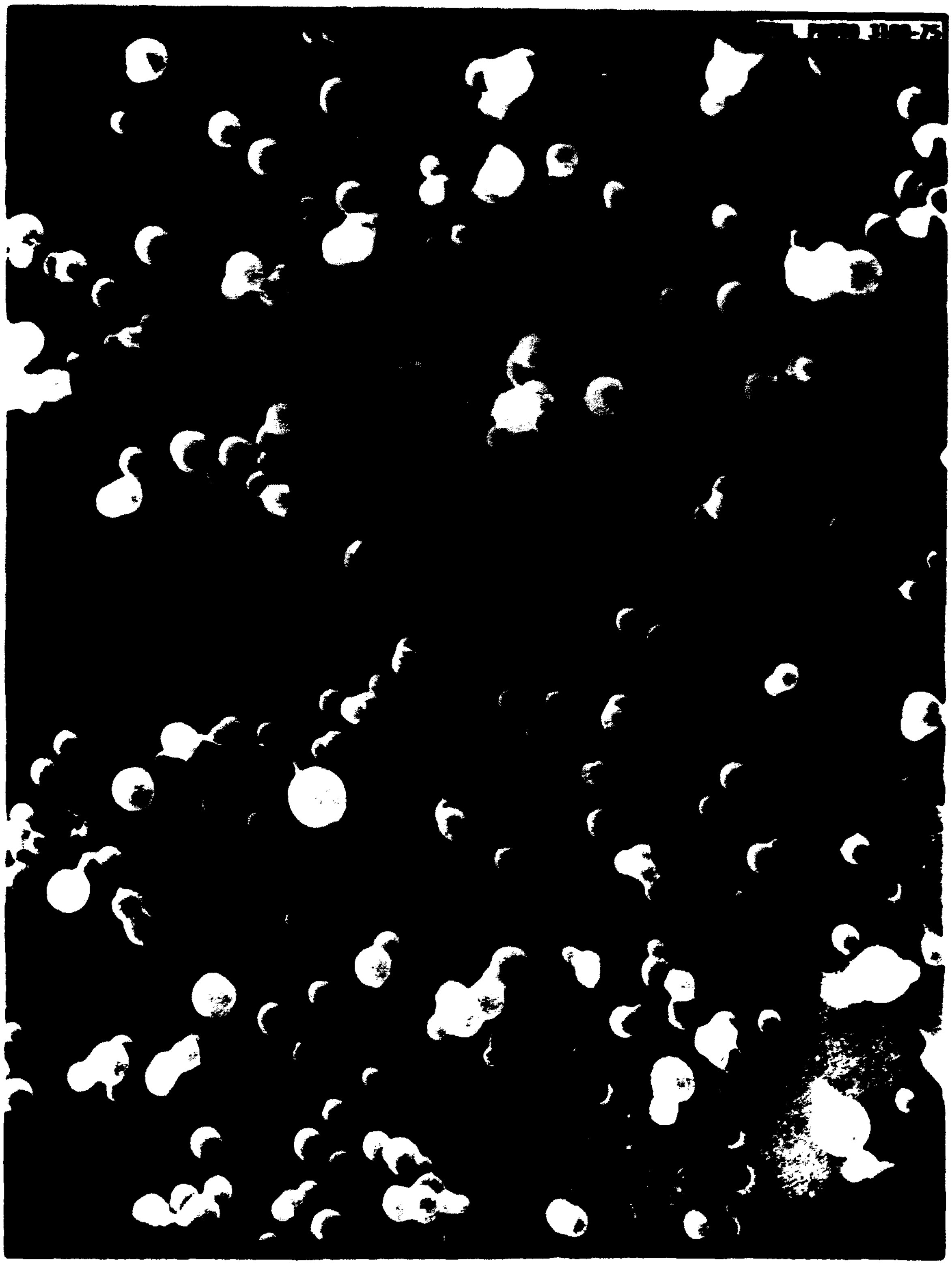

Fig. 6.2. MCA-fixed cigarette tobacco smoke particles on Nuclepore filter.

Health Program. The sampling technique has been refined so that repetitive samples can be taken at closely spaced time intervals. The changes in particle size distribution can be monitored as a single puff of smoke ages in an inhalation chamber; the uncertainties arising from cigarette to cigarette irreproducibility are largely eliminated.

We have begun to monitor smoke particle size distributions and their change throughout an animal exposure cycle in some of the smoking machines of interest to this project. The aim is to monitor these distributions in existing machines as they are normally operated and to use particle size analysis as a tool for improving their operation. The changes in size distribution with time in the exposure chamber of a Walton horizontal smoking machine are shown in Fig. 6.3. The midpuff of a 1R1 cigarette was injected into the chamber, and 5-ml smoke samples were taken at 1, 15, and 30 sec after the puff. Particle densities, normalized to the same maximum, are plotted vs the logarithm of their diameter. All curves are quite symmetric and within experimental error fit a logarithmic normal distribution. (None of the distributions measured show the skewness to high diameters that has been previously reported[17] for tobacco smoke.) The geometric mean diameters are 0.30, 0.47, and 0.68 μm, respectively, at the three times. The distributions of Fig. 6.3 are for a stirred exposure chamber without animals. Preliminary data suggest that there is a large perturbation with mice present and that the particle size increases significantly more rapidly with stirring than without. (R. W. Holmberg)

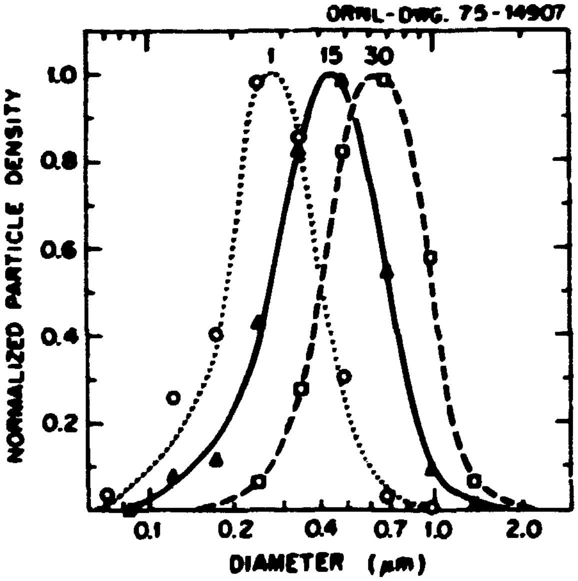

Fig. 6.3. Particle size distribution of aging cigarette smoke in Walton exposure chamber. ○, 1 sec; Δ, 15 sec; □, 30 sec.

Dosimetry. A study was designed to determine the effect of smoke concentration and of smoke exposure time on the amount of smoke particulate deposition following inhalation exposure in the Maddox exposure system, using hamsters. The selected animals were conditioned for one week. They were then exposed to the smoke from code 9 cigarettes containing ^{14}C-dotriacontane to trace the fate of the particulate portion of the aerosol. Immediately after exposure, the animals were sacrificed, and the internal distribution of tracer was determined. Such distributions were determined for three smoke concentrations at three different time intervals. These experiments were done in duplicate with ten animals per experiment. Thus, distribution data were obtained for 180 individual animals.

We found that the amount of particulate matter retained by the animal after exposure increased linearly with smoke concentration and increased exponentially with exposure time. Distribution throughout the body changed somewhat with exposure time but generally ranged around 65% in the lungs, 7% in the larynx, 12% in the upper airways, and 12% in the stomach. Negligible amounts were present in various other organs.

Information from this study is necessary for the design of chronic inhalation exposure experiments. Such experiments are designed to bioassay aerosols in which the object is to get maximal deposition in the target organs of the respiratory tract of experimental animals during a lifetime exposure. The relationship between aerosol concentration, exposure time, and deposition can be used to establish chronic exposure conditions that will yield maximal dosing while having a minimal toxic effect on the animal. Comparable but much more extensive studies are under way in collaboration with Microbiological Associates to establish maximum dose conditions for mice exposed using the Walton horizontal system.

The use of smoke tracers has the advantage that localized distribution can be determined. Major disadvantages are that most constituents cannot be traced in this manner and that the animals must be sacrificed. An important finding is that by measuring the decrease in quantities of smoke constituents in the chamber during the exposure stand period, we can make an accurate prediction of animal dosimetry. We find that the depletion of ^{14}C in chambers containing ^{14}C-dotriacontane and ^{14}C-BaP-labeled smokes is quantitatively recovered in the exposed animals. Carboxyhemoglobin levels in the blood of smoke-exposed animals can be accurately predicted from measurements of carbon monoxide depletion in the chamber. Although this method, "dosimetry by depletion," does not permit determination of the site of deposition, it does allow dosimetry measures to be obtained for any individual constituent in the chamber. Because it is nondestructive it also allows one to follow the cumulative dose to given animals. (J. E. Caton)

Impact measurements. Measurements of "impact" deal with the evaluation of changes caused by an insult. Our interests are generally confined to chemical changes occurring either to invading chemicals or to molecules native to the living organism. One such change thought to be indicative of the impact of some insults is the level of aryl hydrocarbon hydroxylase (AHH) induced by the insult. Our approach to the investigation of AHH activity has been to study it on the molecular level. Thus, preparations of induced rat liver microsomes have been studied by electrophoresis and anion exchange chromatography. The anion exchange chromatography technique uses DEAE cellulose as a stationary phase and stepwise elution with phosphate buffers of increasing ionic strength and decreasing pH. The method separates the crude preparation into seven fractions. Electrophoretic analysis indicates that each fraction contains several nonserum proteins. At least one fraction appears to contain enhanced AHH activity compared with the original preparation. These efforts to carefully isolate AHH activity are aimed at development of a more sensitive and more specific AHH assay. Such an improved assay might involve quantitation on electrophoretic separation media or the development of a specific immunochemical reagent.

Other work on monitoring the impact of experimental smoke exposures involves the periodic screening of urine samples, using high-pressure liquid chromatography, and applying a battery of clinical analyses, using the GeMSAEC. A unique sample bank of blood specimens from animals scheduled to undergo long-term smoke exposure at several laboratories throughout the country will soon be established. These samples will provide the first opportunity to examine biochemical changes, in a given animal, resulting from chronic exposures. Animals exhibiting pathological changes can be compared with those which do not. (J. E. Caton)

Chemical evaluation of beeswax pellet implantation. A tracheal graft procedure has been developed at the Biology Division as a means of testing various types of carcinogens on respiratory tract epithelium without endangering the whole animal.[19] This concept includes the mixing of the carcinogen with an inert carrier and inserting the resulting pellet into the tracheal graft. The result should be a long-term, low-level insult to the tissue, a situation generally analogous to the effect of smoking on humans. The tracheal graft studies have been extended using pure test compounds such as 7,12-dimethylbenz[*a*]anthracene (DMBA) in beeswax pellet implants.[20] Any damage to the tissue should be related to the amount of the single compound released to the animal system. On the other hand, if a complex mixture such as cigarette smoke condensate (CSC) were to be used, it would seem logical that some constituents would diffuse from the pellet faster than others, analyses for any given compounds would be very difficult, and assessment of tissue damage as related to the parent material would be complicated. Veal and Doyle[21] have developed an in vitro model to study release rates. This model has been modified and adapted to the study of trace quantities of various constituents in a CSC-beeswax matrix.

Reproducible pellets were obtained by heating equal parts by weight of CSC and beeswax, agitating the mixture vigorously, and immediately freezing it in liquid nitrogen. The rod-shaped pellets were formed by extruding the mixture from a syringe. The CSC content of each pellet was equivalent approximately to that from one cigarette. Because almost all of the components would be present in quantities too small to measure, each mixture was made up with a ^{14}C tracer compound. These tracers represented different classes of constituents. Control pellets from each batch were analyzed for CSC content by fluorimetry and for ^{14}C content, average relative standard deviations per batch were 3% and 2% respectively. The test pellets were inserted in small lengths of glass tubing, and isotonic saline was

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[19] J. Kendrick, P. Nettesheim, and A. S. Hammons, "Tumor Induction in Tracheal Grafts: A New Experimental Model for Respiratory Carcinogenesis Studies," *J. Natl. Cancer Inst.* 52, 1317–25 (1974).

[20] R. Griesemer, J. Kendrick, and P. Nettesheim, "Studies with Tracheal Transplants," International Symposium on Experimental Lung Cancer, Seattle, June 23–26, 1974.

[21] J. T. Veal and G. E. Doyle, Battelle Northwest Institute, "Evaluation of Beeswax-Tricaprylin Vehicle for Pulmonary Carcinogenesis Studies," submitted to *Toxicology and Applied Pharmacology*.

pumped through at about 250 ml/day. The ^{14}C content of the effluent was measured at regular time intervals, and at the end of the specified test periods, the residual ^{14}C in the test pellets was measured.

We found substantial differences in the rates at which the various constituents were released from the pellets. The smaller and more soluble compounds were released quite rapidly. Some components, nicotine and phenol, for example, are completely depleted by the end of the third day, while others at that same time appear to reach a low level with very slow further release. The less soluble compounds were released only slowly, if at all. There are obvious differences in release rates, depending on molecular structure or size within a family of compounds. The three-ring phenanthrene is more than 90% released after 28 days, while the 4- and 5-ring compounds remain essentially in the pellet. In the fatty acid and alcohol groups, release rate appears to increase with decreasing size and with increasing unsaturation. Release rate is also influenced by flow rate to a greater or lesser extent, depending on the nature of the molecule. If the flow is double, the increase in the release of phenol in a 12-hr period is at about the limit of experimental error (~10%), but the release of phenanthrene after nine days increases by a relative 25%.

Carbon-14 tracer compounds were used, not only for ease of analysis, but also to prevent artificial concentration effects. Griesemer et al.[22] have studied release rates of DMBA from beeswax pellets in a number of in vivo tests.[22] A large number of pellets containing varying quantities of this compound have been analyzed after they had been removed from test animals at specified time intervals. The release of DMBA appears to be concentration dependent in the range of about 0.5 to 2.5 mg/pellet, but at lower concentrations, the data are inconclusive. Since many of the compounds studied in the in vitro tests are in concentrations that might range from 3 to 6 orders of magnitude less than those low milligram values per pellet, the role of concentration in the comparison of these release rates is open to question.

The in vitro release rate model is a useful one for assessing the directions that in vivo studies could take. The results of the above tests demonstrate that beeswax will not permit equal rates of release for a large variety of compound types such as exists in cigarette smoke condensate or liquid fuels, and consequently is not a suitable carrier for such mixtures. On the other hand, since whole-smoke condensate or other complex mixtures may be fairly toxic, and the nontoxic, biologically active compounds may be present in low concentrations, the parent materials may not be appropriate subjects for investigation. Fractionation of the mixtures into portions which contain similar compound types in higher concentrations may result in more suitable test materials for which a proper inert carrier can be found.
(I. B. Rubin, J. E. Caton)

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[22] R. A. Griesemer, P. Nettesheim, D. H. Martin, and J. E. Caton, Jr., "Quantitative Exposure of Respiratory Airway Epithelium to 7,12-Dimethylbenz[a]anthracene," submitted to *Cancer Research*.

Part B. Service Analyses

The support activities of the service laboratories follow closely the changing Laboratory programs. As new projects are conceived and implemented in other divisions, new analytical services are required. In response to the needs of the growing Coal Technology Program, for example, a coal laboratory was established to provide analytical assistance to these investigators. Techniques and equipment used in this laboratory mark a break with most of our past experiences, which have been primarily in inorganic chemistry. Such projects as the HTGR, the MSR, and the TRU programs do, however, still supply the bulk of samples received, and elemental and radiochemical analyses continue to be in demand.

As seen in Table B.1, "Summary of Analytical Work," elemental mass and emission spectrometry accounts for a large fraction of these determinations and is indicative of the highly sophisticated, automated methodology that is replacing traditional separations and individual analytical laboratory methods. Thus, for the Environmental Laboratory we have acquired two Technicon AutoAnalyzers and a new Perkin-Elmer model 503 atomic absorption spectrophotometer. The gamma-ray spectrum resolution program MONSTR was adapted for use in the radiochemical laboratory; here hand plotting and "eyeball" nuclide identification was replaced by computer computation and assignment.

Such changes from hand and eye operation to AutoAnalyzer, mass spectrometer, computer-controlled nuclide identification, or other machine-type analyses obviously require close statistical controls to assure that results reported are valid. Consequently, an expanded and more detailed quality control program was begun. Working closely with the Quality Assurance Committee, we have set up quality control procedures for every laboratory in the Division. One immediate result has been a 25% increase in the number of control determinations.

The service laboratories are a vital and necessary part of many of the Laboratory's largest projects. In addition, they perform critical determinations for a number of individual investigators. To meet the challenge of providing quantity without sacrificing quality requires vigilance and adaptability. These goals will continue to be pursued in the coming year.

Table B.1. Summary of analytical work

Organization	Number of results reported by					Total
	Elemental Spectrometry[a]	Mass Spectrometry Service Laboratory[b]	General Analyses Laboratory[c]	Radioactive Materials Analytical Laboratories[d]	Environmental and Radiochemical Analyses Laboratory[e]	
ORNL divisions						
Analytical Chemistry	3,817	1,153	1,395	8	151	6,524
Chemistry	765	593	1,974	17	586	3,935
Chemical Technology	20,598	6,678	9,190	30,721	5,516	72,703
Director's				3	4	7
Energy	11	340				351
Environmental Sciences	2,022	86	5,670	3,380	46,848	58,006
Health	1,421				5	1,426
Health Physics	180	40	73	711	1,072	2,076
Inspection Engineering	29					29
Instrumentation and Controls	48				5	53
Isotopes	13,995	6,185	15	1,160	1,400	22,755
Metals and Ceramics	23,144	164	6,810	292	367	30,777
Neutron Physics	165		57	13	45	280
Operations	1,048	36	894	6,632	3,865	12,475
Physics	30	34	6	69	2	141
Plant and Equipment		610				610
Reactor	1,307		616	365	965	3,253
Solid State	1,549	10	168	4		1,731
Thermonuclear	60					60
Others						
K-25				1	7	8
Los Alamos Scientific Laboratory		88		18		106
Miscellaneous	1,372	2,647	92	94	353	4,558
Protective Coatings				138	296	434
Y-12	795	460	76	2		1,333
Total	72,356	19,124	27,036	43,748	61,487	223,751

[a] Average number in group, 2 scientists and 3 technicians.

[b] Average number in group, 1 scientist and 4 technicians.

[c] Average number in group, 4 scientists and 12 technicians.

[d] Average number in group, 12 scientists and 10 technicians.

[e] Average number in group, 8 scientists and 8 technicians.

7. General Analyses Laboratory

W. R. Laing, Head

Reflecting additional activity in several programs and the startup of a new program, the number of results reported this year increased from 11,500 to 27,000.

HTGR work included all phases of fuel preparation from uranium loading of ion exchange resin beads to cracked particle testing of carburized fuel sticks. Loaded ion exchange beads were checked for loss on drying and percent uranium. Carburized beads were analyzed for U, C, O, and N. After the addition of SiC and pyrolytic carbon coatings, the samples were checked for broken particles, coating density, mercury density, uranium, and nitrogen. The carburized fuel sticks were checked for broken particles.

The Environmental Sciences Division began a program to measure the sulfur balance in an ecological test area. Over 1100 samples of twigs, leaves, bark, stems, and soil were submitted for sulfur analyses. The Leco sulfur analyzer, standardized with NBS orchard leaves, was used for all determinations. It was found that the addition of 250 mg of MgO was an aid in the combustion of the soil samples.

In other Environmental Sciences work, 1200 samples were analyzed for C_2H_2 and C_2H_4 by gas chromatography. The conversion of acetylene to ethylene by bacteria was used to measure the bacterial population of soil plots.

Monitoring of Laboratory effluents to determine if they meet EPA requirements increased from 9 samples/week to 21 samples/week, with another 8 samples taken on a monthly basis. Twelve tests were made on these samples, using methods approved by EPA for this purpose. Additionally, special samples for dissolved oxygen were taken over a period of three weeks to check the performance of a new aerator.

Samples for the MSR Program included Li_2Te and $LiTe_3$ for purity measurements, neodymium and tellurium in fuel salt, and uranium valence studies in fluoride salts. Six samples of salt containing ^{233}U were analyzed for oxygen. A new method for F in $NaBF_4$, in which the salt is decomposed by $CaCl_2$ in the presence of ammonium vanadate and the CaF_2 separated and weighed, was placed in operation.

As in past years a number of materials preparations were performed, most of them for the Solid State Division. For the Neutron Diffraction Group a major project was the preparation of the mixed compound $^{154}Sm_{0.83}Y_{0.17}S$ for neutron scattering studies. Interest derives from the behavior of SmS, which is black at normal pressure but collapses to a gold phase of smaller lattice constant under 6.5 kilobars. The introduction of yttrium allows this transition to occur at atmospheric pressure. The collapse is associated with a change in valence of samarium which may vary from 2.0 to 2.7. The compound ^{154}SmN was also made for this group. Another major activity was the preparation of $NaBrO_3$ from 300 mg of NaBr prior to making isotopic $Na^{79}BrO_3$. The normal material was successfully prepared, but due to differences in purity, indicated between x-ray and laser examination, the study was not continued at this time. For the Isotope Target Preparation Group the isotopic fluorides $^{175}LuF_3$, $^{160}GdF_3$, and $^{140}CeF_3$ were made. Finally, for the Neutron Spectrometry Group a number of alloys were provided and treated in various ways such as by annealing: $Th_{0.2}Ce_{0.8}$, $Th_{0.266}Ce_{0.734}$, $Th_{0.29}Ce_{0.71}$, $CeAl_3$, $Ni_{0.7}Rh_{0.3}$, and $Ni_{0.65}Rh_{0.35}$.

For the Hyperfine Interactions Group of the Physics Division the three alloys AuAl, Au_2Al, and Au_4Al, and the three isotopic ferrites $Ni_{0.8}{}^{110}Cd_{0.2}{}^{56}Fe_2O_4$, $Ni_{0.5}{}^{110}Cd_{0.5}{}^{56}Fe_2O_4$, and $^{110}Cd^{56}Fe_2O_4$ were made. For the Electrochemistry Group of the Chemistry Division, 3 kg of the low-melting eutectic KCl-LiCl was prepared by fusion-filtration techniques. The recovery of several valuable isotopes from completed research studies was also accomplished for various groups.

New work for this year was in the area of coal conversion technology. A coal laboratory was established. Initially, procedures for the proximate and ultimate analyses of coal and char were set up. Later these procedures were adapted to tar and liquids. Gas chromatographic methods have been used for the measurement of hydrocarbons and permanent gases in off-gas streams. A Perkin Elmer elemental analyzer was used to measure C, H, and N on 1- to 3-mg samples. A Parr adiabatic calorimeter has been installed to measure the heat content of solids and liquids. Additional tests which have been provided are viscosity, density, forms of sulfur, solids, benzene, cyclohexane, nitromethane, cresol and acetone solubles, ash analysis, and methylene chloride extractions. Two chemists visited the Pittsburgh Energy Research Center during the year to observe procedures and techniques used there for these types of samples.

Seven technicians attended a 62-hr-training class, and one chemist and three technicians attended a 16-hr electronics class.

8. Radioactive Materials Analytical Laboratories

J. H. Cooper, Head

More than two-thirds of the results reported by the Radioactive Materials Analytical Laboratories were for the Chemical Technology Division in support of the LWBR Assistance and the Transuranium Production Programs.

The uranium dioxide powder from the LWBR program must meet certain requirements with respect to surface area before it is acceptable for blending with thoria. Our laboratory has purchased a rapid surface area analyzer from the Micromeritics Corporation. This instrument works on the principle of argon adsorption at liquid-nitrogen temperature. Initially, a sample aliquot is degassed at elevated temperature and allowed to adsorb argon at 0°C in an ice bath at preset pressure. The sample tube is immersed in a liquid-nitrogen bath, and more argon is adsorbed. The volume of argon changes to keep the preset pressure, and the change in volume is a measure of the surface area of the powder. The instrument is calibrated so that digital readout of the volume change is in square meters of surface area. A sample aliquot and a known standard aliquot can be analyzed on this instrument in about 1 hr. The previous method required more than 4 hr for the same analysis.

The Transuranium Analyses Laboratory assisted Chemical Technology Division personnel in studying the effects of zirconium on the solubility of plutonium and the effects of ruthenium on the oxidation states of plutonium. Plutonium and zirconium concentrations were determined by radiometric and spectrophotometric methods respectively. The various oxidation states of both plutonium and ruthenium were followed with time by scanning the absorbance of the samples on a Cary model 14 spectrophotometer.

The Operations Division submitted samples of sludge from the radioactive waste tanks for a variety of analyses. Density and percent solids were determined in the hot cells. Small aliquots (10 to 50 mg) were removed from the cells and prepared for analyses by the Nuclear and Physics Methods Group. The samples were dispersed by ultrasonic treatment and separated by zonal centrifugation. Portions were then examined by x-ray diffraction, x-ray fluorescence, and transmission microscopy. The samples were also analyzed for uranium, thorium, and fission products.

To test various metals for compatibility with molten salts, the Reactor Division irradiated small metal capsules filled with salt. Portions of these capsules (with salt) were submitted for analysis. The salt was melted out under an argon atmosphere, dissolved in nitric-boric acid, and analyzed for iron, chromium, and nickel. The remaining salt (adhering to the metal) was leached off in a mixture of sodium versenate, boric acid, and sodium citrate. The bare metal specimens were partially dissolved (approximately 1 mil of the surface removed) in aqua regia, and the resulting solutions were analyzed to measure the migration of fission products into the metal.

9. Environmental and Radiochemical Analyses Laboratories

R. R. Rickard, Head

Since a substantial mutuality of interest exists in the projects served, the Radiochemical Analyses Laboratory and the Environmental Analyses Laboratory were combined during the past year. In both of these laboratories, new instrumentation was acquired to extend or improve analytical capability.

Visitors from Spain, the Philippines, the University of Wisconsin, the University of Kentucky, and EPA Las Vegas worked one or more days in the laboratories to gain practical experience in environmental analyses. Both trace element and radiochemical methodologies were reviewed.

Radiochemical analyses. During the past year, obsolete counting equipment was either upgraded or replaced. Solid-state electronic systems were substituted for tube-operated units on the low-level beta counters, and new gas-flow proportional alpha counters were acquired. In addition, two new 6- by 6-in. well-type NaI gamma-ray detectors were obtained to expand the capability for low-level gamma-ray measurements.

In cooperation with members of the Nuclear and Physics Methods Group and with assistance from the Computer Sciences Division, a gamma-ray spectrum resolutions program used in neutron activation (program MONSTR) was adapted for general use. Both 7- and 9-track magnetic tape systems and a plotting routine were tested in conjunction with the resolution of Ge(Li) detector-derived gamma-ray spectra. Adoption of program MONSTR obviates the need for time-consuming calculation; thus a significant reduction in time for spectral analysis was realized.

Most of the gamma-ray analyses were performed in support of fuel recycle programs, waste management studies, and transplutonium element reprocessing. Special analyses included ^{129}I, ^{99}Tc, HTO, and protective coating decontamination studies. There has also been a continuing need to measure low concentrations of ^{90}Sr, ^{131}I, and ^{239}Pu in environmental samples.

Environmental analyses. Trace element and macronutrient analyses of environmental samples have continued, but as a result of a change in program emphasis, are fewer in number than in the preceding year. Generally, service was rendered toward a variety of specific projects of rather limited scope.

New instrumentation was acquired to upgrade or expand the capability in the area of trace constituent analyses. Two Technicon AutoAnalyzers with preplumbed cartridges were acquired to facilitate the analyses of nitrate-nitrite, phosphate, sulfate, and ammonia. AutoAnalytical procedures have been extended to the determination of nickel, chlorine, and chromium.

During the past year, continued use was made of group extractions of trace metals (Pb, Cd, Cu, Zn) with ammonium pyrolidine dithiocarbamate in methyl isobutyl ketone cyclohexane for atomic adsorption spectrophotometric measurements. General improvements in atomic absorption spectrophotometry have been realized with the acquisition of a Perkin-Elmer model 503 instrument with electrodeless discharge lamps and a model 2100 graphite furnace. The graphite furnace has been used to measure low concentrations of zinc, copper, chromium, manganese, cadmium, and lead in water and in dissolved tissue of small mammals.

Analyses for trace quantities of mercury in environmental samples continued to require the use of the "clean" laboratory. In addition to the Cherokee Lake and Holston River survey programs for the distribution of both organic and inorganic mercury in fish, sediment, and water, environmental samples from around the Almaden mercury mine in Spain were analyzed. Bird feathers, bird tissue, fish, and a variety of plant and tree foliage were analyzed to determine the degree of transport of mercury to the near and far regions surrounding the mine site.

A general paper describing the preparation and analysis of aquatic-related samples was written.[1] The paper was presented orally at a National Bureau of Standards Symposium.

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[1] N. M. Ferguson, J. R. Lund, R. R. Rickard, and L. T. Corbin, "Preparation and Analysis of Aquatic-Related Samples," presented at Symposium on Accuracy in Trace Analysis, National Bureau of Standards, Gaithersburg, Maryland, October 7–11, 1974.

10. Industrial and Radiation Safety

G. R. Wilson

The Analytical Chemistry Division had ten medical treatment cases in the 15 months covered by this report. One was a serious accident caused by failure of the gear shift on a three-speed bicycle. One of the medical treatment cases was listed as recordable, and as far as can be determined was an allergic reaction caused by fumes from organic compounds. When the employee was transferred to another laboratory, the rash disappeared. The rest of the cases were minor burns, cuts, and sprains.

Three new members have been appointed to the safety and housekeeping inspection team. Five safety and housekeeping inspections were held in the past 15 months, and each group within the Division holds quarterly safety meetings.

Two members of the Division are taking the National Safety Council Defensive Driving course and plan to instruct other divisional employees who wish to take the course.

11. Quality Control Program

G. R. Wilson

During the five quarters covered by this report, the number of control programs has remained about the same. The Environmental Analyses Group dropped the atomic adsorption method for determining iron, chromium, nickel, and cobalt; a copper control program was added to those of cadmium, lead, and zinc, which were already being analyzed by the atomic adsorption technique.

As more data became available, several fixed limits of error were changed; the low-level Leco sulfur was increased to a limit of error of 15%, and the low-level colorimetric thorium in the presence of low-level uranium was decreased to 4%. The thorium and uranium control used by the Radioactive Materials Analytical Laboratories contains high uranium and low thorium levels, requiring a separation to analyze for thorium; therefore, the fixed limit of error was changed to 5% for the thorium and to 0.5% for the uranium. At the same time, it was decided that if less than six results were obtained from a control program in a quarter, the statistical data would be reported to supervision but excluded from the Quarterly Statistical Control Report.

Following the recommendations of the Quality Assurance Committee, an addition to the Master Analytical Manual, containing procedures for the preparation of standards and controls, has been written. An assistant is being trained to handle the Quality Control Program in the absence of the Quality Control Officer.

Table 11.1 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 11.2.

Table 11.1. Distribution by laboratory of control tests for July 1974–September 1975

Laboratory	Number of control results		Quality level[a] (%)	
	Total	Outside fixed limits	1974	1975
Environmental Analyses	1094	60	93.92	94.52
Radioactive Materials Anal	887	127	96.69	85.68
General Analyses	1351	115	87.14	91.49
Total	3332	302		
Average			93.4	90.94

[a] Control results within 2S limits.

Table 11.2. Distribution by method of control results for July 1974–September 1975

Type of method	Constituent	No. of programs	No. of results	Total for method
Atomic absorption	Calcium	1	68	
	Cadmium	1	50	
	Cobalt	1	2	
	Copper	1	15	
	Lead	1	42	
	Magnesium	1	66	
	Potassium	1	54	
	Sodium	1	54	
	Zinc	2	73	424
Colorimetric	Beryllium	1	64	
	Chromium	2	82	
	Iron	2	109	
	Molybdenum	1	24	
	Nickel	2	83	
	Nitrogen	3	250	
	Phosphorus	1	132	
	Sulfate	1	176	
	Thorium	2	212	
	Uranium	1	209	1341
Coulometric	Uranium	3	586	586
Flame photometric	Lithium	1	40	
	Sodium	2	10	50
Fluorimetric	Uranium	2	116	116
Gravimetric	Carbon	2	169	169
Polarographic	Uranium	1	12	12
Infrared absorption	Carbon	1	161	161
Volumetric	Fluoride	1	59	
	Nitrate	1	87	
	Sulfur	1	67	
	Uranium	1	111	
	Thorium	2	149	473
Total		44		3332

Part C. Activities Related to Education

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, USERDA, and Professor of Chemistry, Iowa State University, Ames.

L. B. Rogers, Professor of Chemistry, University of Georgia, Athens.

CONSULTANTS

A. E. Cameron advises the Mass and Emission Spectrometry Group of the Division.

M. T. Kelley (Adjunct Research Participant) advises the Advanced Methodology and Instrumentation Group with particular emphasis on computer applications.

G. Mamantov, University of Tennessee, specializes in areas of electrochemistry and molten-salt research.

The Division continued its Seminar Program on a monthly schedule. The following specialists were brought to ORNL on short-term consulting bases this past year (details of seminars are listed in Part E of this report).

Dr. Thomas Aczel, Exxon Research and Engineering Company, Baytown, Texas.

Professor Robert S. Braman, Department of Chemistry, University of South Florida, Tampa.

Professor Maurice M. Bursey, Department of Chemistry, University of North Carolina, Chapel Hill.

Professor Stanley Deming, Department of Chemistry, University of Houston, Houston, Texas.

Professor Charles A. Evans, Department of Chemistry, University of Illinois, Urbana.

Professor Eli Grushka, Department of Chemistry, State University of New York at Buffalo.

Professor Gary M. Hieftje, Department of Chemistry, Indiana University, Bloomington.

Professor Donald E. Leyden, Department of Chemistry, University of Georgia, Athens.

Professor Harry B. Mark, Jr., Department of Chemistry, University of Cincinnati, Cincinnati, Ohio.

Professor L. E. Smythe, Head, School of Chemistry, The University of New South Wales, Kensington, New South Wales, Australia.

Professor John P. Walters, Department of Chemistry, University of Wisconsin, Madison.

Professor Lauren R. Wilson, Department of Chemistry, Ohio Wesleyan University, Delaware, Ohio.

GRADUATE THESIS RESEARCH PROGRAM

R. V. Crosmun. Dr. Crosmun was awarded the Ph.D. degree from the University of Tennessee. His research was on the application of the radio-frequency furnace to environmental trace analysis applicability of Hadamard transform spectroscopy to the uv-visible region under the direction of Y. Talmi and J. A. Dean.

Sandra T. Crosmun. Sandra, a student at the University of Tennessee, continued work toward her doctorate under the direction of T. R. Mueller and J. A. Dean. Her research in pulsed anodic stripping voltammetry with a wax-impregnated graphite electrode and in the computer-assisted coulometric titration of uranium is essentially complete.

SHORT COURSE ON "BASIC ANALYTICAL INSTRUMENTATION FOR CHEMISTS AND CHEMICAL TECHNICIANS"

H. H. Ross and T. R. Mueller of this Division organized and taught a short course covering the basic concepts of chemical instrumentation. Sixteen persons attended the sessions, which consisted of two 1-hr lectures per week for ten weeks. The primary objective of the course was to improve understanding of modern analytical instrumentation among the participants. The first half of the course was oriented toward basic electronics, while the second half concentrated on practical analytical systems. Homework assignments (problem sets) were given after each lecture, along with written supplementary material of general interest.

COOPERATIVE TRAINING PROGRAM WITH ORAU

A three-day laboratory and lecture series at ORNL for participants in an ORAU summer training program, "Trace Analysis for Environmental Pollutants," was held during August. W. S. Lyon arranged the ORNL program in cooperation with G. I. Gleason of ORAU. Lectures and lab demonstrations were presented by J. F. Emery, L. D. Hulett, J. M. Dale, J. S. Eldridge, and Y. Talmi of the Analytical Chemistry Division, and by N. E. Bolton of the Health Division. Subjects covered were activation analysis, scanning electron microscopy, low-level radioactivity measurements, gas chromatography, microwave emission spectroscopy, and industrial hygiene. The 12 ORAU student participants were chemistry and physics teachers at various colleges and universities in all sections of the U.S.

GREAT LAKES COLLEGES ASSOCIATION EDUCATION PROGRAM

This cooperative program is now in its sixth year. Three GLCA students were assigned to the Division during the fall 1974 semester: R. V. Buhl of Albion College, Albion, Michigan, to work with D. L. Manning on voltammetric studies in fluoroborate media, primarily; M. A. Freeman from Wabash College, Crawfordsville, Indiana, to H. H. Ross, assisting in constructing a nitrogen laser and testing its characteristics and exploring its analytical applications; R. H. Morse, Kalamazoo College, Kalamazoo, Michigan, to H. Kubota on analysis of polynuclear aromatic compounds. Two students were on assignment in the Division during the fall 1975 semester: L. A. Adler of Kenyon College, Gambier, Ohio, to work with J. F. Emery on activation analysis, J. B. Summers of Denison University, Lima, Ohio, to work with J. E. Caton on liquid chromatography.

IAEA FELLOWSHIP PROGRAM

D. A. Batistoni, IAEA Fellow, University of Buenos Aires, Argentina, was assigned to the Division in August 1975 for a one-year period to work with C. Feldman on evaluation of emission spectroscopy sources.

G. G. Thern, IAEA Fellow, CNEA, Buenos Aires, Argentina, was given a six-month extension of assignment to the Division in October 1974 to continue work on burnup analysis and postirradiation examination of nuclear fuel under the direction of W. S. Lyon. He left April 18, 1975.

P. S. Murty, IAEA Fellow, Bhabha Atomic Research Center, Bombay, India, was reassigned to the Division from the Physics Division in June 1975 for a one-year period. He is studying 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. N. A. Goeckner, Western Illinois University, Macomb, spent the summer working with W. H. Griest on the identification of polynuclear aromatic compounds in tobacco smoke condensate.

ORAU Summer Undergraduate Research Trainees

Mary S. Buren, Angelo State University, San Angelo, Texas, worked with J. E. Caton on identification and isolation of aryl-hydrocarbon hydroxylase enzyme from tissue extracts.

T. L. Croxton, Cumberland College, Williamsburg, Kentucky, worked with H. H. Ross on electrochemical correlation of heterogeneous electron transfer rates.

E. K. Chess, College of Idaho, Caldwell, worked with H. Kubota on estimation of benzo[*a*]pyrene in coal-related products.

J. L. Hibbard, Gustavus Adolphus College, St. Peter, Minnesota, worked with L. D. Hulett on x-ray fluorescence methods for the determination of sulfur in coal.

W. D. Reents, Monmouth College, West Long Branch, N.J., worked with J. F. Emery on determination of uranium by neutron activation analysis.

ORNL Summer Employees

V. E. Norvell, graduate student at the University of Tennessee, Knoxville, worked with H. H. Ross on organometallic analysis, using the gas chromatographic microwave emission spectrometer, and on subsystem development in solid-state array detectors.

ORNL Sabbatical Employees

T. W. Gilbert, Professor of Chemistry, University of Cincinnati, Cincinnati, Ohio, spent a nine-month sabbatical period working in the area of liquid chromatography.

L. A. Knecht, Professor of Chemistry, Marietta College, Marietta, Ohio, spent a nine-month sabbatical period working on trace-metal studies of environmental and biological materials.

Part D. Supplementary 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.

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

Consultant:	Smoking and Health Program, National Cancer Institute

L. T. Corbin

1974 Recipient:	ASTM Award of Merit
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
Vice-Chairman:	Committee C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, ASTM
Chairman:	Subcommittee C5:05, Test Methods, Analytical Task Group, Committee C-26, 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

Cyrus Feldman

Member:	Committee E-2, Emission Spectrochemical Analysis, ASTM Subcommittee, Arsenic Committee, Medical and Biologic Effects of Environmental Pollutants, NAS-NRC
Fellow:	ASTM
Member:	Publications Committee, Society for Applied Spectroscopy
Scientific Editor:	*Optics and Spectroscopy* (English translation of Russian journal *Optika i Spektroskopiya*)

G. Goldberg

Member:	Committee D-1, Paint, Varnish, Lacquer, and Related Products Subcommittee D01.43, Coatings for Power Generation Facilities, ASTM Advisory Board of Utilities Nuclear Coating Work Committee

Gerald Goldstein

Member: Committee on Specifications and Criteria for Biochemical Compounds, NAS-NRC

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

President: Tennessee Institute of Chemists, AIC

M. R. Guerin

Consultant: Smoking and Health Program, National Cancer Institute

Chairman: Chemistry Subgroup, Tobacco Working Group, 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*

H. Kubota

Consultant: Smoking and Health Program, National Cancer Institute

W. R. Laing

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

Chairman: ASTM Subcommittee C26.01

Secretary: ASTM Subcommittee C26.05
Subcommittee C5:05, Test Methods, Analytical Task Group, Committee C-26, ASTM

Chairman: Subcommittee C5:01, Nomenclature, Committee C-26, ASTM

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
Committee N43-3, Equipment for Nonmedical Radiation Applications, United States of America Standards Institute

Regional Editor: *Journal of Radioanalytical Chemistry*

Associate Editor: *Radiochemical and Radioanalytical Letters*

H. S. McKown

Secretary: Instrument Society of America, Oak Ridge Section

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

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

Chairman:	Committee on Analytical Applications of Radiations and Isotopes, IRD, American Nuclear Society
Member:	Executive Committee, IRD, American Nuclear Society
Technical Chairman:	International Nuclear and Atomic Activation Analysis Conference and 19th Annual Meeting on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 14–16, 1975

H. H. Ross

Member:	ORNL Graduate Student Selection Panel ORNL Industrial Cooperation Committee Scientific Advisory Committee, International Conference on Liquid Scintillation Science and Technology, Alberta, Canada, 1975–76
Consultant:	Special Training Division, Oak Ridge Associated Universities

W. D. Shults

Coordinator:	ORNL-NSF(RANN) Ecology and Analysis of Trace Contaminants Program
Secretary:	Fellowship Committee, Analytical Division, ACS
Member:	Coal Technology Program Committee Panel on Chlorine and Vapor Phase Hydrogen Chloride, NAS-NRC Panel on Environmental Quality Indicators, NAS-NRC Environmental Quality Advisory Board, City of Oak Ridge Committee on Environmental Analytical Methodology, ACS

J. R. Stokely

Member:	Committee D-22, Methods of Sampling and Analysis of Atmospheres, ASTM Subcommittee on Characterization of Smoking Product Atmospheres, ASTM

J. C. White

Representative from ACS to:	Project N11, Basic Materials and Materials Testing for Nuclear Applications, Nuclear Standards Board United States of America Standards Institute (sponsored by ASTM) FACSS Governing Board
Member:	Editorial Board, *Analytical Letters* Analytical Chemistry Division Executive Committee, ACS Federation of Analytical Chemistry and Spectroscopy Societies Governing Board Analytical Specialists Group, Union Carbide Corporation Technology Subcommittee
Secretary:	IUPAC Division of Analytical Chemistry
Representative from Soc. for Appl. Spec. to:	American Chemical Society

Part E. 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 Books

AUTHOR(S)	TITLE	PUBLISHER
Bolton, N. E.,* J. A. Carter, J. F. Emery, C. Feldman, W. Fulkerson,* L. D. Hulett, W. S. Lyon	"Trace Element Mass Balance Around a Coal-Fired Steam Plant," pp. 175–87 in *Trace Elements in Fuel: Advances in Chemistry Series 141*, ed. by S. P. Babu	ACS, Washington, D.C., 1975
Carter, J. A., R. L. Walker, J. R. Sites	"Trace Impurities in Fuels by Isotope Dilution Mass Spectrometry," pp. 74–83 in *Trace Elements in Fuel: Advances in Chemistry Series 141*, ed. by S. P. Babu	ACS, Washington, D.C., 1975
Walker, R. L., J. R. Walton, J. A. Carter, D. R. Matthews	"Measurement System for Total Nitrogen and $^{15}N/^{14}N$ in Plant Tissue, Soil, and Water (IAEA-SM-191/25)," pp. 429–38 in *Isotope Ratios as Pollutant Source and Behavior Indicators*, ed. by R. A. Beck	IAEA, Vienna, 1975

Articles

Andren, A. W.,* D. H. Klein,* Y. Talmi	"Selenium in Coal-Fired Steam Plant Emissions"	*Environ. Sci. Technol.* 9, 856 (1975)
Apple, R. F., H. G. Davis, A. S. Meyer	"Analysis of Methyl Iodide, Methyl Nitrate, and Methyl Alcohol in 20 *M* Nitric Acid by Gas Chromatography"	*Anal. Lett.* 7, 671–74 (1974)
Bostick, D. T.	(See Talmi, Y.)	
Bowling, J. L.,* J. A. Dean,* G. Goldstein, J. M. Dale	"Rapid Determination of Chromium in Natural Waters by Chemiluminescence Using a Centrifugal Fast Analyzer"	*Anal. Chim. Acta* 76(1), 47–55 (1975)
Carter, J. A.	(See Klein, D. H.)	
	(See Thompson, G. M.)	
	(See Walker, R. L.)	

AUTHOR(s)	TITLE	PUBLISHER
Caton, J. E., D. W. Holladay,* N. G. Anderson*	"Immunosubtractive Electrophoresis on Gradient Polyacrylamide Gels"	*Anal. Lett.* 7, 483–96 (1974)
Caton, J. E.	(See Nettesheim, P.)	
Christie, W. H., D. H. Smith	"Ion Microprobe Analysis of Grain Boundary Impurity Segregation in an Alloy Failure"	*Trans. Am. Nucl. Soc.* 21 (3), 13 (1975)
	(See Gentry, R. V.)	
Crosmun, S. T.,* J. A. Dean,* J. R. Stokely	"Pulsed Anodic Stripping Voltammetry of Zinc, Cadmium and Lead with a Mercury-Coated Wax-Impregnated Graphite Electrode"	*Anal. Chim. Acta* 75, 421–30 (1975)
Crosmun, S. T.,* T. R. Mueller	"The Determination of Chromium(VI) in Natural Waters by Differential Pulse Polarography"	*Anal. Chim. Acta* 75, 199–205 (1975)
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Donohue, D. L., W. W. Harrison*	"Radiofrequency Cavity Ion Source in Solids Mass Spectrometry"	*Anal. Chem.* 47, 1528–31 (1975)
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Dunn, H. W.	(See Hulett, L. D.)	
Dyer, N. C.,* A. B. Brill,* W. S. Lyon	"Biomedical Studies Using Nuclear Activation Techniques"	*Trans. Am. Nucl. Soc.* 21, 95 (1975)
Eby, R. E.	(See Walker, R. L.)	
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Eldridge, J. S.	"Activities and Needs Related to Radioactivity Standards for Environmental Measurements"	Environ. Monit. Ser., EPA-670/4-75-006, US EPA, 56 pp. (1975)
Eldridge, J. S., G. D. O'Kelley,* K. J. Northcutt	"Primordial Radioelements and Cosmogenic Radionuclides in Rocks and Soils from Descartes and Taurus-Littrow"	Lunar Science VI, Lunar Sci. Instit., Houston, Tex. pp. 242–44 (1975)
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AUTHOR(S)	TITLE	PUBLISHER
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Emery, J. F.	(See Klein, D. H.)	
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	(See Klein, D. H.)	
Franklin, J. C.	(See Harrison, W. W.)	
Gentry, R. V.,* L. D. Hulett, S. S. Cristy,* J. F. McLaughlin,* J. A. McHugh,* M. Bayard*	"Spectacle Array of ^{210}Po Halo Radiocentres in Biotite: A Nuclear Geophysical Enigma"	*Nature* 252, 564–66 (1974)
Gentry, R. V.,* D. H. Smith, W. H. Christie, S. S. Cristy*	"Radiohalos in Coalified Wood: New Time Limits Suggested for Coalification and Introduction of Uranium"	*Eos* 56, 473A (1975)
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Guerin, M. R.	(See Nettesheim, P.)	
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Harrison, W. W.,* J. C. Franklin, J. A. McHugh*	"Workshop on Mass Spectrometric Analysis of Solids"	*Anal. Chem.* 47, 1059A–60A (Oct. 1975)
Hulett, L. D., H. W. Dunn, J. M. Dale	"Analysis of Solids – Approaching the Whole Problem"	*Trans. Am. Nucl. Soc.* 21(3), 12 (1975)
Jenks, G. H.,* E. Sonder,* C. D. Bopp,* J. R. Walton	"Reaction Products and Stored Energy Released from Irradiated Sodium Chloride by Dissolution and by Heating"	*J. Phys. Chem.* 79, 871 (1975)

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Klatt, L. N., J. B. Carraway*	"Study of Diffusional Shielding Effects of Micrometer Fed Capillary Mercury Electrodes"	*Anal. Chem.* 47, 761–63 (1975)
Klein, D. H.,* A. W. Andren,* J. A. Carter, J. F. Emery, C. Feldman, W. Fulkerson,* W. S. Lyon, J. C. Ogle,* Yair Talmi, R. I. Van Hook,* Newell Bolton*	"Pathways of Thirty-Seven Trace Elements Through a Coal-Fired Power Plant"	*Environ. Sci. Technol.* 9, 973 (1975)
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	"The Great Double-Barrelled Shotgun Uranium Hunt. I"	*Radiochem. Radioanal. Lett.* 22, 357 (1975)
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Lyon, W. S., J. F. Emery	"Neutron Activation Analysis Applied to the Study of Elements Entering and Leaving a Coal-Fired Steam Plant"	*Int. J. Environ. Anal. Chem.* 4, 125 (1975)
Maddox, W. L.	(See Diamond, L.)	
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Mueller, T. R.	(See Crossman, S. T.)	
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Northcutt, K. J.	(See Eldridge, J. S.)	
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O'Kelley, G. D.,* J. S. Eldridge, K. J. Northcutt	"Cosmogenic Radionuclides in Samples from Taurus-Littrow: Effects of the Solar Flare of August 1972"	Proc. Fifth Lunar Conf., Suppl. 5, *Geochim. Cosmochim. Acta* 2, 2139-47 (1974)
Pfuderer, P.,* S. Janzen,* W. T. Rainey, Jr.	"The Identification of Phthalic Acid Esters in the Tissues of Cyprinodont Fish and Their Activity as Heartrate Depressors"	*Environ. Res.* 9, 215-23 (1975)
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	See Singer, G. M.)	
Ross, H. H., T. R. Mueller	"Precision Logic Probe"	*Mach. Des.* p. 46 (Feb. 20, 1975)
Rubin, I.	(See Nettesheim, P.)	
Shults, W. D.	(See White, J. C.)	
Singer, G. M.,* W. Lijinsky,* W. T. Rainey, Jr.	"Mass Spectrometry of *p*-Toluenesulfonamides: Useful Amine Identification Derivatives"	*Org. Mass Spectrom.* 10, 473-79 (1975)

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Stokely, J. R.	(See Cowman, S. T.)	
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Talmi, Y., A. W. Andren*	"Determination of Selenium in Environmental Samples Using Gas Chromatography with a Microwave Emission Spectrometric Detection System"	*Anal. Chem.* 46, 2122-26 (1974)
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Talmi, Y., R. E. Mesmer*	"Gas Chromatography-Microwave Emission Spectroscopy for Measuring Volatile Organometallics"	Proc. NSF Trace Contaminants Conf., ORNL, Aug. 8-10, 1973; *Water Res.* 9, 547-52 (1975)
	"Studies on Vaporization and Halogen Decomposition of Methyl Mercury Compounds Using GC with a Microwave Detector"	*Water Res.* 9, 547-52 (1975)
Talmi, Y., V. E. Norvell*	"Determination of Arsenic and Antimony in Environmental Samples Using Gas Chromatography with a Microwave Emission Spectrometric System"	*Anal. Chem.* 47, 1510-16 (1975)
Thern, G. G.*	(See Moore, F. L.)	
Thompson, G. M.,* R. L. Walker, J. A. Carter, D. M. Lumsden*	"Uranium Series Dating of Stalagmites from Blanchard Springs Caverns, USA"	*Geochim. Cosmochim. Acta* 39, 1211-18 (1975)
Walker, R. L., R. E. Eby, C. A. Pritchard, J. A. Carter	"Simultaneous Plutonium and Uranium Isotopic Analysis from a Single Resin Bead - A Simplified Chemical Technique for Assaying Spent Reactor Fuels"	*Anal. Lett.* 7, 563-75 (1974)

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	(See James, L. M.)	
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Walton, J. R.	(See Jenks, G. H.)	
White, J. C., W. D. Shults	"Analytical Problem Solving in a Diversified Laboratory"	*Chem Technol* 4, 699 11 (1974)
Young, J. P., C. E. Bamberger,* R. G. Ross*	"Spectral Studies of *f-d* and *f-f* Transitions of Pa(IV) in Molten LiF-BeF$_2$-ThF$_4$"	*J Inorg Nucl Chem* 36, 2630 32 (1974)

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Crossman, Ronald V.	"The Application of the Radio-Frequency Furnace to Environmental Trace Analysis Applicability of Hadamard Transform Spectroscopy to the UV-Visible Region"	University of Tennessee, Knoxville, December 1974
Geist, Wayne H	"A Study of the Derivatization and Analysis of Nucleotides by Gas-Liquid Chromatography"	Vanderbilt University, Nashville, Tennessee, August 1975

REPORTS

AUTHOR(S)	TITLE	REPORT NUMBER AND DATE
Andren, A. W.,* S. E. Lindberg,* L. C. Bate	*Atmospheric Input and Geochemical Cycling of Selected Trace Elements in Walker Branch Watershed*	ORNL-NSF-EATC-13 (June 1975)
Burton, C. I.,* S. A. Reynolds	*Estimated Radiation Doses from Ingestion of Tritium-Containing Consumer Products Made with Hydrocarbons from Nuclearly Stimulated Natural Gas Wells*	ORNL-TM-4730 (Dec. 1974)
Carter, J. A.	*Report of Foreign Travel to Karlsruhe, Germany and Vienna, Austria, February 10 21, 1974*	ORNL-CF-74-3-25 (Mar. 15, 1974)
Carter, J. A., J. R. Walton, R. L. Walker, D. R. Matthews*	*Rapid* ^{15}*N Isotopic-Ratio and Total Nitrogen Analytical System for Environmental Samples*	ORNL-NSF-EATC-8 (Jan. 1975)
Corbin, L. T., G. R. Wilson	*Statistical Quality Control Report: Analytical Chemistry Division, July through September 1974*	ORNL-CF-74-10-70 (Oct. 21, 1974)
	October through December 1974	ORNL-CF-75-1-40 (Jan. 1, 1975)
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	April through June 1975	ORNL-CF-75-7-15 (July 14, 1975)
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Dahlman, R. C.,* S. A. Reynolds	*Plutonium in Aquatic and Terrestrial Environments*	ORNL-5016 (Mar. 1975)
Dickens, J. K.,* T. A. Love,* J. W. McConnell,* J. F. Emery, R. W. Peelle*	*Fission Product Beta and Gamma Energy Release Quarterly Progress Report for July September 1975*	ORNL-TM-5156 (Nov. 1975)

AUTHOR(S)	TITLE	REPORT NUMBER AND DATE
Dyer, F. F., R. P. Wichner,* W. J. Martin,* L. L. Fairchild,* H. J. deNordwall*	*Post Irradiation Examination of Peach Bottom HTGR Driver Fuel Element E06-01*	ORNL-TM-5190 (Nov. 1975)
Fulkerson, W.,* W. D. Shults, R. I. Van Hook*	*Ecology and Analysis of Trace Contaminants. Progress Report, October 1973 through September 1974*	ORNL-NSF-EATC-11 (Dec. 1974)
Goldberg, Gerald, D. A. Costanzo	*A Versatile Particle Size Analyzer*	ORNL-TM-5157 (Nov. 1975)
Guerin, M. R., P. Nettesheim*	*ORNL Tobacco Smoke Research Program. Summary Report*	ORNL-5008 (Mar. 1975)
Houtzeel, A.,* F. F. Dyer	*A Study of Fission Products in the Molten-Salt Reactor Experiment by Gamma Spectrometry*	ORNL-TM-3151 (Aug. 1972)
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 (Oct. 1975)
Mueller, T. R., D. J. Fisher, G. Goldberg, P. S. Gouge, H. H. Ross, J. E. Strain, W. D. Shults	*Summary Report. Electrochemical Ambient Air Monitor for Chlorine/Chloride*	ORNL-TM-4813 (Feb. 1975)
Shults, W. D., L. T. Corbin	*Analytical Chemistry Division Research and Development Summary — September and October 1974*	ORNL-CF-74-11-7 (Nov. 1, 1974)
	November 1974	ORNL-CF-74-12-22 (Dec. 1, 1974)
	December 1974 and January 1975	ORNL-CF-75-2-1 (F 1, 1975)
	February 1975	ORNL-CF-75-3-2 (Mar. 1, 1975)
	March 1975	ORNL-CF-75-4-3 (Apr. 1, 1975)
	April 1975	ORNL-CF-75-5-2 (May 1, 1975)
	May 1975	ORNL-CF-75-6-33 (June 1, 1975)
	June 1975	ORNL-CF-75-7-2 (July 1, 1975)
	July 1975	ORNL-CF-75-8-2 (Aug. 1, 1975)
	August 1975	ORNL-CF-75-9-5 (Sept. 1, 1975)
	September 1975	ORNL-CF-75-10-3 (Oct. 1, 1975)
Young, J. P.	*Report of Foreign Travel to Germany, Austria, France, and England*	ORNL-FTR-46 (Oct. 21, 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.

International Nuclear and Atomic Activation Analysis Conference
and
Nineteenth Annual Meeting on Analytical Chemistry
in
Nuclear Technology

This year's Gatlinburg Conference was an international meeting on activation analysis. Minor cosponsorship was supplied by the American Nuclear Society's Isotopes and Radiation Division and the Oak Ridge ANS Local Section. Three full days of activities took place at the Riverside Motor Lodge in Gatlinburg October 14–16. Forty-eight papers were presented in six sessions: Neutron Activation Analysis in Biology, Charged-Particle and Photon Activation Analysis, Atomic and Nuclear Excitation Methods, Neutron Activation Analysis in Environmental Science, Special Developments and Applications of Neutron Activation Analysis, and X-Ray Fluorescence Techniques. In addition, a panel discussion, "Environmental Activation Analysis – Are We Asking the Right Questions?" was held Wednesday evening. The international flavor of the meeting was enhanced by the presence of 32 foreign attendees.

Co-General Chairmen were L. J. Brady and W. Lyon. Technical Program Chairman was Enzo Ricci; A. L. Harrod was Treasurer and Exhibits Coordinator.

At Meetings of Professional Societies, Conferences, and the Like

AUTHOR(S)	TITLE	PRESENTED AT
Bate, L. C., S. E. Lindberg,* A. W. Andren*	"Elemental Determination of Water and Air Particulates by Use of Neutron Activation Analysis"	International Conference on Heavy Metals in the Environment, Toronto, Canada, Oct. 27–31, 1975
	"Elemental Analyses of Water and Air Solids by Neutron Activation Analysis"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 14–16, 1975
Bolton, N. E.,* W. Fulkerson,* W. S. Lyon, J. F. Emery, A. W. Andren,* R. I. Van Hook,* C. Feldman, L. D. Hulett, H. W. Dunn, J. A. Carter	"Coal in the Environment"	Conference on Coal in the Environment sponsored by Bituminous Coal Res., Inc., Louisville, Ky., Oct. 22–24, 1975
Bostick, Deborah	"Biological Applications of Chemiluminescence"	Chemical Technology Division Biochemical Technology Seminar, ORNL, Dec. 17, 1974
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"	Ninth Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia, Mo., June 10–12, 1975
	"Multi-Element Isotope Dilution Spark Source Mass Spectrometry"	American Society for Mass Spectrometry 23rd Annual Conference on Mass Spectrometry and Allied Topics, Houston, Tex., May 28, 1975

AUTHOR(S)	TITLE	PRESENTED AT
Carter, J. A., R. L. Walker, R. E. Eby, C. A. Pritchard	"A Simplified Separation Method for Simultaneous U and Pu Isotopic Analysis with a Two-Stage Mass Spectrometer"	International Symposium on the Safeguarding of Nuclear Materials, Vienna, Austria, Oct. 20–24, 1975
Costanzo, D. A.	"Analytical Chemistry Requirements and Problems"	High-Temperature Gas-Cooled Reactor Analytical Information Exchange Meeting, Allied Chemical Co., Idaho Falls, Idaho, Sept. 26, 1974
	"Reactor Program Coordination — HTGR"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Feb. 5, 1975
	"Analytical Chemistry Support to the GB-10 Experiment"	Technical Review of the Gas-Cooled Fast Reactor Program, ORNL, Aug. 21, 1975
	"Overview of Analytical Chemistry for HTGR"	High-Temperature Gas-Cooled Reactor Analytical Information Exchange Meeting, General Atomic Co., San Diego, Nov. 4–5, 1975
Caton, J. E.	"Exposure Chemistry as Non-Invasive Dosimetry of Individual Smoke Constituents During Inhalation Bioassay"	Tobacco Working Group Meeting, Bethesda, Md., Feb. 18–19, 1975
	"Immunological Reagents as Analytical Chemistry"	ORAU Traveling Lecture, Maryville College, Maryville, Tenn., Jan. 21, 1975
	"Polyacrylamide Gel Electrophoresis"	ORAU Traveling Lecture, Agnes Scott College, Decatur, Ga., Feb. 26, 1975
	"Polyacrylamide Gel Electrophoresis"	ORAU Traveling Lecture, Langston University, Langston, Okla., Dec. 5, 1974
	"Polyacrylamide Gel Electrophoresis"	ORAU Traveling Lecture, University of Oklahoma, Norman, Dec. 4, 1974
	"The Potential of Polyacrylamide Gel Electrophoresis in Bioanalytical Chemistry"	Chemical Technology Division Biochemical Technology Seminar, ORNL, Dec. 3, 1974
Caton, J. E., J. R. Stokely, M. R. Guerin	"Depletion of Constituents in Contained Smoke Aerosols for Inhalation Exposure Dosimetry"	Twenty-Ninth Tobacco Chemists' Research Conference, University of Maryland, College Park, Oct. 8–10, 1975
Christie, W. H.	"Ion Microprobe Mass Analysis: A Description with Applications in Metallurgy"	Metals and Ceramics Seminar, ORNL, Aug. 8, 1975
	"Ion Microprobe Mass Analysis — Surface Profiling"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Feb. 5, 1975
	"Mass Spectrometry and Ion Microprobe Mass Analysis"	ORAU Traveling Lecture, Bethune-Cookman College, Daytona Beach, Fla., Oct. 31, 1974
	"Mass Spectrometry and Ion Microprobe Mass Analysis"	ORAU Traveling Lecture, University of North Carolina, Chapel Hill, Mar. 6, 1975
	"Mass Spectrometry and Ion Microprobe Mass Analysis"	ORAU Traveling Lecture Program, University of Puerto Rico, Mayaguez Campus, Apr. 29, 1975
	"Mass Spectrometry and Ion Microprobe Mass Analysis"	ORAU Traveling Lecture Program, University of Puerto Rico, Rio Piedras Campus, Apr. 28, 1975
	"Mass Spectrometry and Ion Microprobe Mass Analysis"	ORAU Traveling Lecture, Rice University Department of Geology, Houston, Tex., Nov. 19, 1975
Christie, W. H., L. N. Klatt	"Overview of the Analytical Chemistry Division at ORNL"	Lawrence Livermore Laboratory, Chemistry Department, Livermore, Calif., Sept. 11, 1975

AUTHORS	TITLE	PRESENTED AT
Christie, W. H., D. H. Smith	"Ion Microprobe Analysis of Grain Boundary Impurity Segregation in an Alloy Failure"	International Nuclear and Atomic Activation Analysis Conference and 19th Annual Meeting on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 14–16, 1975
Christie, W. H., D. H. Smith, H. Inouye*	"An Ion Microprobe Investigation of the Tensile Failure of a Pt-Rh-W Alloy Caused by Segregation of Silicon to Grain Boundaries"	Seminar on Quantitative Techniques in Secondary Ion Mass Spectrometry, Honolulu, Hawaii, Oct. 15–17, 1975
Corbin, L. T.	"Service Activities of 1974"	Analytical Chemistry Division Annual Information Meeting, ORNL, Feb. 1975
Costanzo, D. A.	"Analytical Chemistry Support to the GB-10 Experiment"	Technical Review of the Gas-Cooled Fast Reactor Program, ORNL, Aug. 21, 1975
	"Gas-Cooled Reactor Analytical Chemistry Development Programs"	ORNL Gas-Cooled Reactor Programs Bimonthly Information Meeting, Nov. 21, 1974
Dyer, N. C.,* A. B. Brill,* W. S. Lyon	"Biomedical Studies Using Nuclear Activation Techniques"	American Nuclear Society 1975 Annual Meeting, New Orleans, La., June 9–13, 1975
Eldridge, J. S.	"Low Level Measurement in the Environment"	ORAU Special Training Division Course on "Trace Analyses for Environmental Pollutants," Oak Ridge, Tenn., Aug. 21, 1975
	"Mobile Assay Laboratory for Nuclear Safeguards Instruments"	18th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 22–24, 1974
Eldridge, J. S., W. S. Lyon, F. L. Clay*	"Mobile Assay Laboratory for ^{235}U Safeguards Measurements"	Institute of Nuclear Materials Management, New Orleans, La., June 18–20, 1975
Eldridge, J. S., G. D. O'Kelley,* E. Schonfeld*	"Solar and Galactic Cosmic-Ray Activation of Lunar Samples"	International Nuclear and Atomic Activation Analysis Conference and 19th Annual Meeting of Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 14–16, 1975
Emery, J. F., E. F. Dyer	"Multielement Determinations by Absolute Neutron Activation Analysis"	18th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 22–24, 1974.
	"Replacement of Chemistry in Isotope Calibration, Activation Analysis, and Fuel Element Analysis by Instrumental Gamma-Ray Spectrometry"	Third Latin American Meeting on Radiochemistry, Sao Paulo, Brazil, Dec. 2–6, 1974
Emery, J. F., J. H. Cooper, J. C. Franklin	Panel Member – Multielement Analysis	18th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 22–24, 1974
Fellows, R. L.,* J. R. Peterson,* J. P. Young, R. G. Haire*	"Absorption Spectroscopic Studies of ^{253}EsCl$_3$ and ^{253}EsBr$_3$"	1975 South-Southwest Combined Meeting, American Chemical Society, Memphis, Tenn., Oct. 29, 1975
Ferguson, N. M., J. R. Lund, R. R. Rickard, L. T. Corbin	"Preparation and Analysis of Aquatic-Related Samples"	7th Materials Research Symposium on Accuracy in Trace Analysis, U.S. Bureau of Standards, Washington, D.C., Oct. 7–11, 1974
Franklin, J. C.	"Multi-Element Isotope Dilution by SSMS"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Feb. 5, 1975

AUTHOR(S)	TITLE	PRESENTED AT
Franklin, J. C., J. A. Carter, D. L. Donohue, R. W. Stelzner	"Multi-Element Isotope Dilution Spark-Source Mass Spectrometry"	23rd Annual Conference on Mass Spectrometry and Allied Topics, Houston, Tex., May 11–16, 1975
Franklin, J. C., J. A. Carter, J. R. Sites	"Spark-Source Mass Spectrometric Analysis of Nuclear and Fossil Fuels"	18th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 22–24, 1974
Gentry, R. V.,* D. H. Smith, W. H. Christie, S. S. Cristy*	"Radiohalos in Coalified Wood: New Time Limits Imposed on Coalification Time and Geological Age"	American Geophysical Union Annual Meeting, Washington, D.C., June 16–19, 1975
Goldberg, G.	"Testing of Protective Coatings (Paints) for the Nuclear Industry"	Utilities Nuclear Coatings Work Committee (UNCWC) Annual Meeting, San Francisco, Calif., July 15–18, 1975 (Seminar – Testing Laboratories) ASTM Subcommittee Meeting
Guerin, M. R.	"Role of ORNL Tobacco Smoke Chemistry Project in NCI Smoking and Health Program"	NCI Smoking and Health Program Contractors' Meeting, Atlantic City, N.J., July 16–18, 1975
	"Chemical Fractionation and Multicomponent Gas Chromatographic Analysis of Coal-Derived Liquids"	"Coalab '75, Fossil Fuel Chemistry and Energy," Laramie, Wyo., July 22–26, 1975
	"Analytical Chemistry in Experimental Chemical Carcinogenesis"	Seminar, Exxon Research Center, Baytown, Tex., Sept. 30, 1975
	"Analysis of Cigarette Tobacco Smokes and Condensates"	ORAU Traveling Lecture, Georgia State University, Atlanta, May 22, 1975
	"Discussion – Identification of Carcinogens, Tumor Promoters, and Cocarcinogens in Tobacco Smoke"	3rd World Conference on Smoking and Health, New York, June 2–5, 1975
Guerin, M. R., W. H. Griest, J. E. Caton	"Tobacco Smoke as an Environmental Pollutant"	ORAU Biological Considerations of Environmental Pollutants, Oak Ridge, Tenn., Aug. 18–22, 1975
Guerin, M. R., W. H. Griest, C.-h. Ho, W. D. Shults	"Chemical Characterization of Coal Conversion Pilot Plant Materials"	Third ERDA Environmental Protection Conference, Chicago, Ill., Sept. 23–26, 1975
Guerin, M. R., W. H. Griest, H. Kubota, C.-h. Ho, I. B. Rubin	"Chemical Characterization of Coal Conversion Pilot Plant Materials"	Third ERDA Environmental Conference, Chicago, Ill., Sept. 23–25, 1975
Guerin, M. R., I. B. Rubin, W. H. Griest, H. Kubota	"Chemical Fractionation and Multicomponent Gas Chromatographic Analysis of Coal-Derived Liquids"	Government, Industry, and Academic Technical Conf. on Fossil Fuel Chemistry and Energy, Laramie, Wyo., July 21–25, 1975
Guerin, M. R., G. Olerich, R. B. Quincy	"Multialiquot Determination of Phenol, Cresols, Glycerol, Catechol, Nicotine, and Free Fatty Acids"	28th Annual Tobacco Chemists' Research Conference, Raleigh, N.C., Oct. 28–30, 1974
Harrison, W. W., J. C. Franklin, J. McHugh*	Workshop on Mass Spectrometric Analysis of Solids	Houston, Tex., May 1975
Higgins, C. E., J. R. Stokely, M. R. Guerin, T. L. Roberts*	"Application of 'Blind Assay' Methodology to Organic Gas Phase Constituents in Tobacco Smoke"	28th Tobacco Chemist's Research Conference, Raleigh, N.C., Oct. 28–30, 1974

AUTHOR(s)	TITLE	PRESENTED AT
Higgins, C. E. J. R. Stokely, M. R. Guerin	"Organic Gas Phase Composition of Contained Smoke Aerosols Used for Inhalation Testing"	29th Tobacco Chemists' Research Conference, University of Maryland, College Park, Oct. 8–10, 1975
Ho, C.-h., W. H. Griest, M. R. Guerin	"Studies on a Terpene-Rich Fraction of Cigarette Smoke"	29th Tobacco Chemists' Research Conference, University of Maryland, College Park, Oct. 8–10, 1975
Holmberg, R. W., J. R. Stokely, M. R. Guerin	"Electron Microscope Measurement of Methyl Cyanoacrylate Fixed Tobacco Smoke Particles"	29th Tobacco Chemists' Research Conference, University of Maryland, College Park, Oct 8–10, 1975
Horton, A. D.	"A Survey of Analytical Methodology Suitable for Application to Coal Conversion Processes"	Engineering Section Assigned to Coal Conversion Project, Chemical Technology Conf. Room, Oct. 18, 1974
Horton, A. D., C.-h. Ho, M. R. Guerin	"Organosulfur and Sulfur Gases in Cigarette Smoke and Coal-Derived Samples Studies Using the Flame Photometric Detector"	9th Conference on Trace Substances in Environmental Health, University of Missouri, Columbia, June 10–12, 1975
Hulett, L. D.	"Photoelectron Spectroscopy Applied to Catalysis and Corrosion Problems"	First Annual Meeting of Federation of Analytical Chemistry and Spectroscopy Societies, Atlantic City, N.J., Nov. 18–22, 1974
	"Electron Spectroscopy for Chemical Analysis"	ORAU Training Lecture, ORNL, Aug. 20, 1975
	"Scanning Electron Microscopy"	ORAU Training Lecture, ORNL, Aug. 20, 1975
Hulett, L. D., J. A. Carter, K. D. Cook, J. F. Emery, D. H. Klein,* W. S. Lyon, G. A. Nyssen,* W. Fulkerson,* N. E. Bolton*	Trace Element Measurement at the Coal-Fired Allen Steam Plant – Particle Characterization"	Conference on Coal and the Environment, Louisville, Ky., Oct. 22–24, 1974
Hulett, L. D., J. M. Dale	"Progress Report on the Development of Position-Sensitive Detectors at ORNL"	Electron Spectroscopy Workshop, Pinawa, Manitoba, Canada, July 10–11, 1975
Hulett, L. D., J. M. Dale, T. A. Carlson*	"Progress Report and Future Plans for Electron Spectrometer Position Sensitive Detector Development"	Workshop on Photoelectron Spectroscopy, Pinawa, Canada, July 10–11, 1975
Hulett, L. D., H. W. Dunn, J. M. Dale	"Analysis of Solids – Approaching the Whole Problem"	International Nuclear and Atomic Activation Analysis Conference and 19th Annual Meeting on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 14–16, 1975
Hulett, L. D., M. T. Kelley*	"Hadamard Transform Spectroscopy: A Study of Its Limitations and Capabilities by Monte Carlo Calculations"	Chemical Instrumentation Award Symposium, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., Apr. 6–11, 1975
Hulett, L. D. G. A. Nyssen*	"Catalyst and Corrosion Studies by Photoelectron Spectroscopy"	First Annual Meeting of Federation of Analytical Chemistry and Spectroscopy Societies, Atlantic City, N.J., Nov. 18–22, 1974
Hurst, G. S.,* M. G. Payne,* M. H. Nayfeh,* J. P. Judish,* C. H. Chen,* E. B. Wagner,* J. P. Young	"Resonance Ionization Spectroscopy on $He(2^1S)$"	28th Annual Gaseous Electronics Conference, Rolla, Mo., Oct. 21–24, 1975

AUTHOR(S)	TITLE	PRESENTED AT
Kelley, M. T.*	"Analytical Instruments and How They Grew"	Chemical Instrumentation Award Symposium, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., Apr. 6–11, 1975
Klatt, L. N.	"Application of Electroanalytical Techniques to the Study of Reaction Mechanisms"	University of Tennessee, Knoxville, Feb. 11, 1975
	"Voltammetry of Pyrazine"	Symposium on Recent Advances in Analytical Voltammetry at the 169th National Meet. of the Am. Chem. Soc., Philadelphia, Pa., Apr. 6–11, 1975
Klatt, L. N., W. H. Christie	"Overview of the Analytical Chemistry Division at ORNL"	Chemistry Department, Lawrence Livermore Lab., Livermore, Calif., Sept. 11, 1975
Klatt, L. N., D. R. Sens,* P. W. Carr*	"Application of Enzymes to the Determination of Contaminants in Water"	Fifth Annual Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Jekyll Island, Ga., May 19–21, 1975
	"Determination of Nitrate at the Parts Per Billion Level Via an Enzyme Catalyzed Reaction"	Second Annual Meeting of Federation of Analytical Chemistry and Spectroscopy Societies, Indianapolis, Ind., Oct. 6–10, 1975
Klein, D. H.,* A. W. Andren,* J. A. Carter, et al.	"Trace Element Measurements at the Coal Fired Allen Steam Plant — Mass Balance and Concentrations in Fly Ash"	American Chemical Society, Philadelphia, Pa., Apr. 6-11, 1975
Kubota, H.	"Analysis of Tobacco Smoke"	ORAU Traveling Lecture, Georgia State University, Atlanta, May 22, 1975
	"Analysis of Cigarette Tobacco Smokes and Condensates"	ORAU Traveling Lecture, Tennessee State University, Nashville, Jan. 17, 1975
Kubota, H. W. H. Griest, M. R. Guerin	"Determination of Carcinogens in Tobacco Smoke and Coal-Derived Samples — Trace Polynuclear Aromatic Hydrocarbons"	9th Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia, June 11, 1975
Lackey, W. J.,* D. A. Costanzo, M. W. Waddell*	"Understanding Defective Coatings on HTGR Fuel Particles"	American Ceramic Society 77th Annual Meeting and Exposition, Washington, D.C., May 3–8, 1975
Lackey, W. J.,* J. D. Sease,* D. A. Costanzo, D. E. LaValle	"Improved Coating Process for High-Temperature Gas-Cooled Reactor Fuel"	American Nuclear Society Meeting, San Francisco, Calif., Nov. 17–21, 1975
Laing, W. R.	"Analytical Services for Coal Conversion Technology"	Coal Conversion Program, ORNL, Apr. 11, 1975
	"Review of Analytical Chemistry Programs at Oak Ridge National Laboratory	Whiteshell Nuclear Station Seminar, Pinawa, Manitoba, Canada, Mar. 14, 1975
Lindberg, S. E., A. W. Andren,* L. C. Bate	"Heavy Metal Transport Through a Forested Watershed"	International Conference on Heavy Metals in the Environment, Toronto, Canada, Oct. 27–31, 1975
Lyon, W. S.	"Neutron Activation Analysis Applied to Energy and Environment"	Conference on Nuclear Power and Applications in Latin America, Mexico City, Mexico, Sept. 28–Oct. 1, 1975.
	Panel Member: "Environmental Activation Analysis — Are We Asking the Right Questions?"	International Nuclear and Atomic Activation Analysis Conference and 19th Annual Meeting on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 14–16, 1975
Lyster, M. A.,* R. L. Fellows,* J. P. Young	"Search for Plutonium Fluorescence"	Fifth International Conf. on Plutonium and Other Actinides, Baden-Baden, West Germany, Sept. 10–13, 1975

AUTHOR(s)	TITLE	PRESENTED AT
Malinauskas, A. P.,* H. J. de Nordwall,* F. F. Dyer, R. P. Wichner,* W. J. Martin,* J. O. Kolb*	"Fission Product Behavior During Operation of the Second Peach Bottom Core"	IAEA-OECD (NEA) International Symposium on Gas-Cooled Reactors, Julich, Germany, Oct. 13 17, 1975
Manning, D. L.	"Electrochemical Measurement of BF_3OH^- in Fluoroborate Melts"	MSRP Review Meeting, ORNL, Dec. 5, 1974
Moore, F. L., W. S. Groenier*	"Pollution Abatement by Solvent Extraction: Removal and Recovery of Zinc, Cadmium, and Cyanide from Industrial Metal-Finishing Effluents"	AIChE Meeting, Chicago, Ill., May 4 8, 1975
Mueller, T. R.	"Considerations in the Application of LSI Calculator Circuits to Analytical Instrumentation"	American Chemical Society Meeting, Chicago, Ill., Aug. 24 29, 1975
Mueller, T. R., S. T. Crossman	"Computer-Assisted Controlled-Potential Coulometry in the Determination of Uranium"	Second Annual Meeting, Federation of Analytical Chemistry and Spectroscopy Societies, Indianapolis, Ind., Oct. 6 10, 1975
Mueller, T. R., H. H. Ross, J. E. Strain	"The Fluorometric Determination of Uranium: Development of the Procedure and Recent Improvement in the Method and Instrumentation"	169th National Meeting of the American Chemical Society, Philadelphia, Pa., Apr. 6 11, 1975
Nettesheim, P.,* M. R. Guerin, J. Kendrick,* J. Caton, W. Dalbey,* R. Griesemer*	"Acute and Chronic Inhalation in Rats"	3rd World Conference on Smoking and Health, New York, June 2 5, 1975
Rainey, W. T., Jr.	"Advances in Organic Mass Spectrometry"	Chemical Technology Division Biochemical Technology Seminar, ORNL, Mar. 18, 1975
	"Organic Mass Spectrometry as Applied to Coal Problems"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Feb. 5, 1975
Reents, W. D.,* J. F. Emery, K. J. Northcutt	"Sampling, Preparation, and Analytical Problems Associated with the Determination of Low Levels of Uranium in Water and Sediment"	Chemistry Department Seminar, Monmouth College, West Long Branch, N.J., Fall 1975
Reynolds, S. A.	"Progress in Environmental Actinide Analysis at Oak Ridge National Laboratory"	18th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 22 24, 1974
Ricci, E.	"Particle Reflection"	Thermonuclear Division Program Review Meeting, ORNL, May 14, 1975
	"Methodology for High-Flux Absolute Multielement NAA"	1975 Annual Meeting of the American Nuclear Society, New Orleans, La., June 8 13, 1975
	Moderator: "Environmental Activation Analysis: Are We Asking the Right Questions?"	International Nuclear and Atomic Activation Analysis Conference and 19th Annual Meeting on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 14 16, 1975
Ross, H. H.	"Liquid Scintillation Spectroscopy"	ORAU Meeting on Fundamentals of Nuclear Medicine, Oak Ridge, Tenn., Sept. 8 26, 1975
	"Principles of Liquid Scintillation Counting"	ORAU Meeting on Fundamentals of Nuclear Medicine, Oak Ridge, Tenn., Oct. 20, 1975; Nov. 7, 1975

AUTHOR(S)	TITLE	PRESENTED AT
	"Preparation of Samples for Liquid Scintillation Counting"	ORAU Meeting on Fundamentals of Nuclear Medicine, Oak Ridge, Tenn., Oct. 26, 1975; Nov. 7, 1975
Senn, D. R.,* L. N. Klatt	"The Effect of the Reaction $B + C \rightleftarrows A + D$ upon the Controlled Potential Electrolysis of the ECE Mechanism"	26th Southeastern Regional Meeting of the American Chemical Society, Norfolk, Va., Oct. 1974
Shults, W. D.	Session Chairman, "General Spectrophotometry"	Second FACSS Meeting, Indianapolis, Ind., Oct. 1975
	Program Chairman: M. T. Kelley Award Symposium (Instrumentation Award)	ACS Meeting, Philadelphia, Pa., Apr. 1975
	"Research and Development Activities"	Analytical Chemistry Division Information Meeting, ORNL, Feb. 6, 1975
Smith, D. H., R. Fiehler,* A. Muhl*	"Collecting and Processing Isotopic Mass Spectrometric Data with a Small, Non-Dedicated Computer"	DECUS Users Meeting, Zurich, Switzerland, Sept. 1974
Smith, D. H.	Panel Member, ASMS Secondary Ion Mass Spectrometry Workshop	Houston, Texas, May 1975
Smith, D. H., W. H. Christie	"Quantification Studies Using IMMA: Results from the NBS Iron Standards"	ASMS Secondary Ion Mass Spectrometry Workshop, Houston, Tex., May 1975
Stieff, L. R.,* R. B. Walton,* T. D. Reilly,* L. W. Fields,* R. L. Walker, W. T. Mullins,* J. I. Thomas*	"Neutron Measurements of ^{234}U Isotopic Abundance in UF$_6$ Samples"	16th Annual Meeting of Institute for Nuclear Materials Management, New Orleans, La., June 18–20, 1975
Stelzner, R. W., H. S. McKown, J. R. Sites	"Computerized Spark-Source Mass Spectrometer Densitometry"	169th National American Chemical Society Meeting, Philadelphia, Pa., Apr. 6–11, 1975
Stokely, J. R.	"Inhalation Chamber Chemistry in Support of Bioassay Studies"	NCI Smoking and Health Program Contractors' Meeting, Atlantic City, N.J., July 16–18, 1975
Stokely, J. R., J. H. Moneyhun, M. R. Guerin	"Chemical Indicators and Methods for Determination of Tobacco Smoke Concentration in Inhalation Exposure Systems"	29th Tobacco Chemists' Research Conference, University of Maryland, College Park, Oct. 8–10, 1975
Talmi, Y.	"The Applicability of a Gas Chromatograph with a Microwave Emission Spectrometric Detector (GC-MES) to Trace Analysis"	International Conference on Heavy Metals in the Environment, Toronto, Canada, Oct. 27–31, 1975
	"The Application of Solid-State Array Imagers to UV-Visible Spectrometry"	22nd Spectroscopy Symposium, Spectroscopy Society of Canada, Mt. Royal, Quebec, Canada, Oct. 26–29, 1975
	"Microchannel Plate Intensifier – Solid State Imager Spectrum Scanning Systems"	27th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, Mar. 1–5, 1976
Walker, R. L.	"Pu and U Analysis Employing Resin Bead Technique"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Feb. 5, 1975
Walker, R. L., R. E. Eby, C. A. Pritchard, J. A. Carter	"Use of Resin Beads as a Carrier for Nanogram Size Samples of Dissolved Irradiated Reactor Fuel"	IAEA Headquarters Seminar, Vienna, Austria, Nov. 14, 1974

AUTHOR(s)	TITLE	PRESENTED AT
	"A Simple Resin Bead Separations Method for the Simultaneous Isotopic Analysis of Pu and U"	Analytical Chemistry Division Seminar, ORNL, Sept. 23, 1975
Walker, R. L., J. R. Walton, J. A. Carter, D. R. Matthews*	"Measurement System for Total N and $^{15}N/^{14}N$ in Plant Tissue, Soil, and Water"	Symposium on Isotope Ratios as Pollutant Source and Behavior Indicators, Vienna, Austria, Nov. 18–22, 1974
White, J. C.	"Analytical Chemistry in Federal Laboratories Atomic Energy Commission Programs"	Symposium on "Analytical Chemistry in Federal Labs," 169th Meeting of the American Chemical Society, Philadelphia, Pa., Apr. 6–11, 1975
	"The Analytical Chemist and the Energy Crisis"	East Tennessee Section, American Chemical Society Meeting, Oak Ridge, Tenn., Apr. 4, 1975
	"Management of Laboratories: Budget Controls"	1975 Analytical Specialists Meeting, Union Carbide Corp., Niagara Falls, N.Y., Apr. 21–22, 1975
	"Union Carbide Management System"	Orientation Conference, Non-Supervisory Staff, ORNL, Aug. 5, 1975
Young, J. P.	"Spectral Studies of Actinide Halides at Oak Ridge National Laboratory"	Seminar at Department of Inorganic and Nuclear Chemistry, Technische Hochschule, Darmstadt, Germany, Sept. 19, 1975
Young, J. P., R. G. Haire,* R. L. Fellows,* M. Noe,* J. R. Peterson*	"Spectroscopic and X-Ray Diffraction Studies of the Bromides of Californium-249 and Einsteinium-253"	4th International Transplutonium Element Symposium, Baden-Baden, West Germany, Sept. 13–17, 1975

SEMINARS

The Division continues to sponsor seminars covering a wide variety of topics in its commitment to keep current with new developments in analysis and measurement and to keep informed in related fields of interest. Listed below are Analytical Chemistry Division seminars for the current period.

SPEAKER(S)	TITLE	DATE
Aczel, Thomas, Exxon Research and Engineering Company, Baytown, Tex.	"Applications of Mass Spectrometry to the Analysis of Coal Liquefaction Products"	Mar. 13, 1975
Berkau, K. U., Purchasing Division, UCND Graves, W. O., Finance and Materials Division ORNL	"The Purchasing and Receiving Functions"	Oct. 29, 1974
Bursey, Maurice, M. Department of Chemistry, Univ. of North Carolina, Chapel Hill	"Some Newer Methods of Ionization in Organic Mass Spectrometry"	June 26, 1975
Das, H. A., Reactor Centrum, The Netherlands	"Activation Analysis"	Nov. 5, 1974

SPEAKER(s)	TITLE	DATE
Deming, Stanley N. Department of Chemistry, Univ. of Houston, Tex.	"Simplex Optimization and the Automated Development of Analytical Chemical Methods"	Feb. 18, 1975
Evans, Charles A., Department of Chemistry, Univ. of Illinois, Urbana	"Comparison of Different Techniques for Surface Analyses"	Nov. 3, 1975
Goldberg, Gerald, ORNL	"Testing of Coatings for the Nuclear Industry"	Oct. 30, 1975
Grushka, E., Department of Chemistry, State University of New York at Buffalo	"Mechanistic Studies of Several Liquid Crystals as Stationary Phases in Gas Chromatography"	Oct. 31, 1974
Holmes, John M., ORNL Chem. Tech. Div.	"Coal Liquefaction"	Nov. 12, 1975
Hieftje, G. M., Department of Chemistry, Indiana Univ., Bloomington	"Computer Control of Experiments"	Dec. 16, 1975
Leyden, D. E., Department of Chemistry, Univ. of Georgia, Athens	"Preconcentration of Cations and Selected Anions Using Reagents Immobilized Via Silylation: Applications to X-Ray Fluorescence	Nov. 21, 1975
Mark, Harry B., Jr., Chemistry Department, University of Cincinnati	"Some Problems in the Chemical Analysis of the Environment"	May 20, 1975
Reynolds, S. A., ORNL	"Alpha Emitters in Environmental Materials"	Oct. 28, 1975
Shultz, Hyman, Analytical Research and Services Sect. PERC, Pittsburgh	"The Role of the Analytical Research and Services Section at the Pittsburgh Energy Research Center"	Dec. 10, 1974
Smythe, L. C., University of New South Wales, Australia	"Some Improved Methods for the Determination of Metals at the Ultra-Trace Level"	June 18, 1975
Walker, R. L., ORNL	"A Simple Resin Bead Separations Method for the Simultaneous Isotopic Analysis of Pu and U"	Sept 23, 1975
Walters, John P. University of Wisconsin, Madison	"Research-Generated Development of Spectrochemical Methods"	Jan. 9, 1975

SPEAKER(S)	TITLE	DATE
Wehry, E. L., Department of Chemistry, Univ. of Tenn., Knoxville	"New Methods in Infrared and Fluorescence Spectroscopy: Projected Applications to Analysis of Particulate Polycyclic Organic Matter"	Nov. 19, 1974
Wilson, Lauren R., Ohio Wesleyan University, Delaware, Ohio	"Inorganic Chemistry Aspects of Nitrogen Fixation"	July 28, 1975
Young, J. P., ORNL	"Recent Spectral Studies of Actinide Halide Crystals: Techniques and Results"	Apr. 29, 1975

IN-HOUSE SEMINAR PROGRAM

To increase communication between staff members and Division management, a dual program of in-house seminars was begun. The Division Director met bimonthly with the staff to discuss pertinent items of interest and to answer questions. In-house seminars, presented on a group basis and intended primarily to inform management, were scheduled about three times a month. The following presentations were made under this second phase of the communication exchange program.

April 11, 1975: Bio-Organic Analysis

M. R. Guerin: "Coal-Derived Samples."

I. B. Rubin: "Chemical Subfractionation."

A. D. Horton: "Multicomponent Gas Chromatographic Profiling."

April 18, 1975: Advanced Methodology and Instrumentation

H. H. Ross: "The Architecture and Application of Large-Scale Integrated Circuits to General Instrumentation Problems."

May 9, 1975: Gas-Cooled Reactor Programs

D. A. Costanzo: "Status of the HTGR and GCFR Programs."

May 16, 1975: Nuclear and Physics Methods

W. S. Lyon: "R&D Associated with Energy Program."

W. S. Lyon: "Prospects: NURE, Coal."

J. F. Emery: "Fission: Fission Heat."

L. D. Hulett: "Fossil: Studies with ESCA and SEM."

E. Ricci: "Fusion: Six Months in CTR."

May 23, 1975: Molten-Salt Breeder Reactor Program

A. S. Meyer: "Status and Projections of the MSBR Program."

D. L. Manning: "Voltammetry of Oxide in MSBR Fuel Solvent."

J. P. Young: "Resonance Ionization Spectroscopy."

May 30, 1975: Quality Control

L. T. Corbin, G. R. Wilson: "Quality Control Program."

June 27, 1975: Mass and Emission Spectrometry

D. C. Canada: "Organic Mass Spectrometry."

D. L. Donohue: "Multielement Isotope Dilution and New SSMS Sources."

D. H. Smith: "Ion Microprobe Measurements."

J. A. Carter: "NURE Program – Uranium and Trace Metals Results."

W. H. Christie: "IAEA Mass Spectrometer Status."

July 11, 1975: General Analyses Laboratory

L. J. Brady: "Coal Conversion Program."

W. R. Laing: "Reactor and Associated Programs."

July 18, 1975: Radioactive Materials Analytical Laboratories

J. H. Cooper: "The Westinghouse Program."

J. M. Peele: "The TRU Program."

J. H. Cooper: "Testing of Coatings for Nuclear Applications."

July 25, 1975: Environmental and Radiochemical Analyses Laboratories

R. R. Rickard: "Introduction."

N. M. Ferguson: "Selected Environmental Projects."

J. M. Shaboskie: "Program MONSTR."

R. R. Rickard: "Summary."

August 8, 1975: Advanced Methodology and Instrumentation

J. E. Strain: "In-Line Monitoring: the Development of New Monitoring Systems for In-Line, Real-Time Applications. Projected Applications Are Varied."

Deborah Bostick: "Sulfate Analysis: Research on New Methods for the Analysis of Sulfates in Particulate Materials. A Unique Enzyme Approach May Have General Appeal."

August 15, 1975: Gas-Cooled Reactor Programs

D. A. Costanzo: "Status of the HTGR Program."

D. A. Costanzo: "A Continuous Monitoring System for Tritium in the GB-10 Capsule Irradiation Experiment."

D. A. Lee: "In-Line Monitoring of the HTGR Fuel Particle Process Effluent Streams Using a Time-of-Flight Mass Spectrometer."

August 22, 1975: Bio-Organic Analysis

M. R. Guerin: "Chemical Characterization – Introduction and Background."

C.-h. Ho: "Terpenoids in Cigarette Smokes."

W. H. Griest: "Polynuclear Aromatic Hydrocarbons in Smoke and Coal-Derived Materials."

August 29, 1975: Bio-Organic Analysis

M. R. Guerin: "Bioassay Systems – Introduction and Background."

R. W. Holmberg: "Particle Size Methodology and Significance."

J. E. Caton: "Inhalation Dosimetry from Chemical Analysis of Exposure Environment."

September 26, 1975: Nuclear and Physics Methods

L. D. Hulett, J. M. Dale: "ESCA Laboratory."

F. L. Moore: "Mini-Plant."

J. F. Emery: "ORR Laboratory."

October 3, 1975: Pattern Recognition Studies (joint with Computer Sciences Division)

Nancy Larsen: "Technique and Results Obtained."

R. W. Stelzner, J. R. Stokely: "Chemical and Biological Measurements Involved."

October 24, 1975: Mass and Emission Spectrometry

R. L. Walker: "Introduction."

J. C. Franklin: "Installation and Performance of the High-Resolution MS-50 Mass Spectrometer."

W. T. Rainey: "GC-MS Modifications, TOF Mass Spectrometry, and Data Evaluation."

R. E. Eby: "Gas Analysis for the Coal Program."

October 31, 1975: Mass and Emission Spectrometry

J. A. Carter: "Introduction."

R. L. Walker: "NUREP Activities and Nd for MSRE."

W. H. Christie: "Ion Microprobe Mass Analyzer R/D for M&C Programs."

H. S. McKown: "Construction of the Two-Stage Mass Spectrometer for IAEA Status Report."

November 14, 1975: General Analyses Laboratory

W. R. Laing: "Activities of the General Analyses Laboratory."

November 21, 1975: Radioactive Materials Analytical Laboratories

J. H. Cooper: "Programs of the Radioactive Materials Analytical Laboratories."

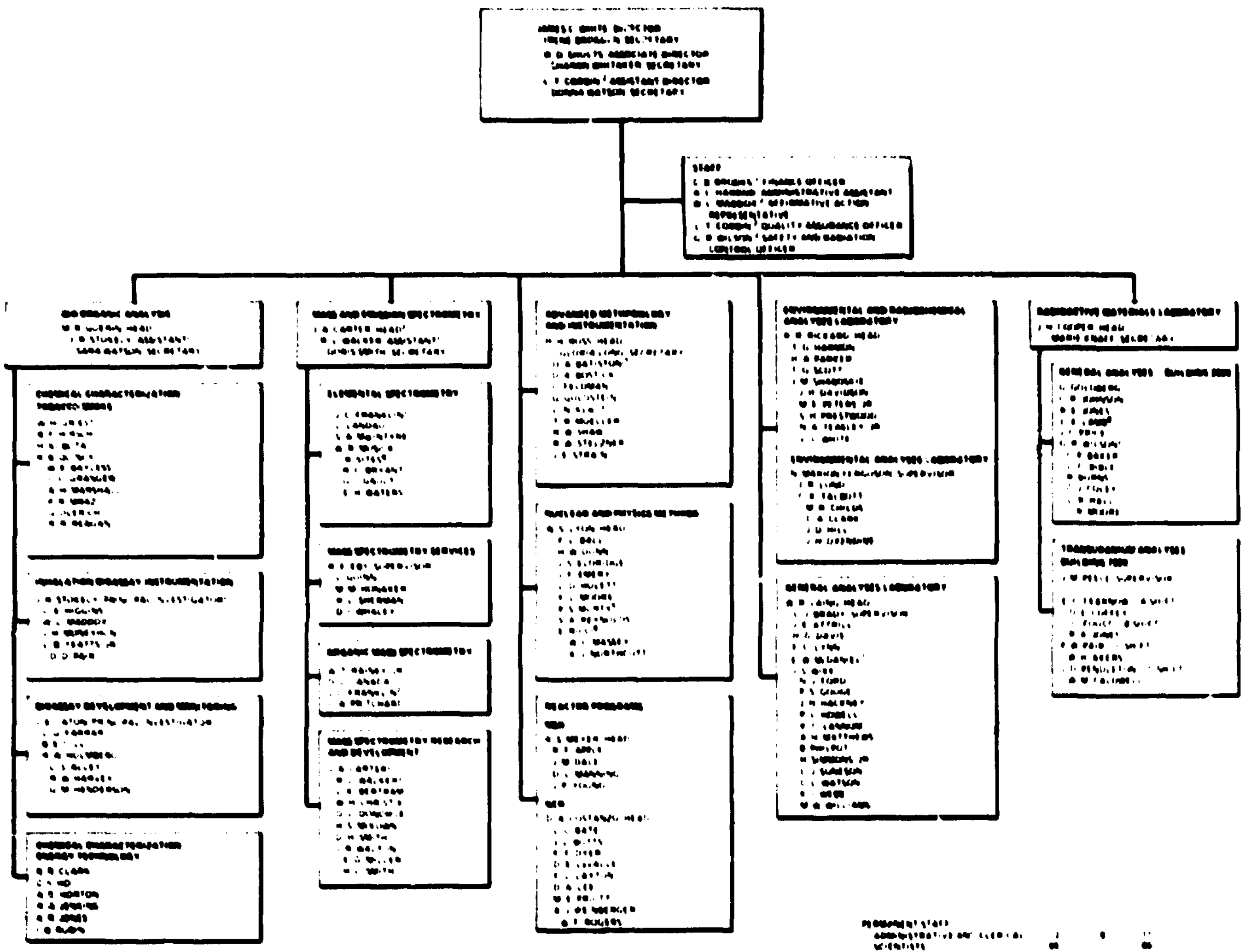
PATENTS

AUTHOR(s)	TITLE	PATENT NO.	DATE ISSUED
Dietrich, W. C., D. L. Manning	"Uranium-Sensitive Electrode Membrane"	3,864,233	Feb. 4, 1975

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

Reviewer or referee	Number of articles reviewed or refereed for indicated periodical																
	Anal. Biochem.	*Anal. Chem.*	*Anal. Lett.*	*Arch. Environ. Health*	ASTM Methods	*Clin. Chem.*	*Geochim. Cosmochim. Acta*	IEEE	*J. Agric. Food Chem.*	*J. Chem. Educ.*	*J. Environ. Qual.*	*J. Natl. Cancer Inst.*	*Radiochem. Radioanal. Lett.*	*Science*	*Tob. Sci.*	Proposals	Total
Bate, L. C.		1															1
Canada, D. C.																1	1
Carter, J. A							1										1
Christie, W. H.		1															1
Clark, B. R.			1														1
Eldridge, J. S.							1										1
Emery, J. F.		1															1
Feldman, C.		3									3			1			7
Goldstein, G.	1																1
Guerin, M. R.				1								4			1	4	10
Hulett, L. D.																1	1
Klatt, L. N.		2								1				1		1	5
Kubota, H.		1														1	2
Lyon, W. S.		6											9			1	16
Manning, D. L.																1	1
Meyer, A. S.			1													1	2
Moore, F. L.		3														1	4
Mueller, T. R.		1															1
Rainey, W. T.		1				2			1								4
Reynolds, S. A.					8		1	1									10
Ross, H. H.																2	2
Shults, W. D.																2	2
Smith, D. H.									1								1
Stokely, J. R.																1	1
White, J. C.																6	6
Young, J. P.		3															3
Total	1	23	2	1	8	2	3	1	2	1	3	4	9	2	1	23	86

ANALYTICAL CHEMISTRY DIVISION



[illegible]

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