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ANNUAL PROGRESS REPORT

Period Ending September 30, 1974

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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

For Period Ending September 30, 1974

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JANUARY 1975

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
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Preface

By all standards the Division enjoyed a good year. For example, two new research projects were begun: "Specialized Techniques for Energy-Related Research" and "In-Line Analysis for Energy-Related Research"; progress in these projects will be reflected in next year's report. The Division's involvement in nuclear energy programs increased markedly, with the devotion of five man-years to the High-Temperature Gas-Cooled Reactor Program (HTGR) and the resumption of the Molten-Salt Reactor Program (MSR) at the four-man-year level. Details of our contributions to those programs are best found in the monthly progress reports issued by the respective program offices. The support level also increased sharply, as evidenced by the addition of 17 technicians to the staff. The mass spectrometry work scope broadened even more during this period, with the addition of an ion microprobe mass analyzer. The continued impact of minicomputers in analytical chemistry and spectroscopy is quite obvious from this report. Both the Smoking and Health Program sponsored by the National Cancer Institute and the National Science Foundation Program on Ecology and Analysis of Trace Contaminants (EATC) continued at a substantial and productive level; significant advances were achieved in gas chromatographic profiling for mixtures of organic compounds and in trace metal analysis capabilities.

These developments are indicators of the progress that was made in the Division during this period. For next year we anticipate that these programs will continue, and we expect to become increasingly engaged in coal conversion technology programs as the nation's new energy program begins to take shape.

Part A. Analytical Research and Development

1. Instrumentation and Advanced Methodology

H. H. Ross, Head

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V. E. Norvell[5]

The increasing demand for improved analytical technology for environmental analysis has had a significant effect on the thrust of our work in both electrochemical and spectrochemical methods. In some cases, such as the analysis of organomercury compounds, we are reacting to the well-defined needs of various investigators; in others, we are trying to anticipate important problem areas only just emerging. General objectives in the field of environmental analysis are the lowering of detection levels and a simultaneous increase in the speed and number of analyses that can be carried out effectively. Although our work has been guided by these new environmental needs, we have not neglected the more basic aspects in our program. This year we completed a fundamental evaluation of Hadamard transform spectroscopy for application in the ultraviolet and visible spectral regions. Our mathematical model was compared with existing experimental data; the results led to an important change in our research directions.

We have continued our state-of-the-art development of new analytical instrumentation. A major project was completed by the design, fabrication, testing, and implementation of a new electronic and fusion package for fluorometric uranium analysis. This new system has been received with widespread interest throughout the analytical community. Of particular interest is the totally automatic operation of the electronic package. Other instruments that have been developed recently include a revised voltammeter and a battery-operated potentiostat-galvanostat; both of these units have wide application in electrochemical analysis.

---

1. Adjunct research participant.
2. ORAU graduate participant from the University of Tennessee, Knoxville, Tennessee.
3. GLCA participant from Kalamazoo College, Kalamazoo, Michigan.
4. ORAU summer research trainee from St. Andrews College, Laurinburg, North Carolina.
5. ORAU summer research trainee from the University of Tennessee, Knoxville, Tennessee.

Our work on computer applications has had a significant impact on the whole concept of analytical data acquisition and processing. We have initiated an effort in the development of pattern recognition techniques for complex analytical data. Although these methods will have general applicability, the first projected application will be to data developed in the ORNL Tobacco Smoke Research Program. Other important computer applications include a new interface for gas chromatography and an expanded program text for our computer-controlled atomic absorption spectrophotometer. For many analyses, significant time savings and increased capability have been realized.

We have investigated and perfected a variety of analytical schemes for the determination of organomercury compounds using our combined gas chromatograph–microwave emission spectrometer. This instrumental method has proved so successful that a second instrument has been built to accommodate a large number of routine samples. We have also devoted a portion of our development program to the extension of the use of this technique to the assay of arsenic, antimony, and selenium in environmental materials. In electrochemistry, we have devised a new procedure for the analysis of Cr(VI) in natural water by pulse polarography. The analysis is not degraded by the presence of Cr(III), a nontoxic form of the metal. Much of the above work has already been applied to practical analytical problems. Our work with the GeMSAEC fast analyzer has resulted in over a dozen analytical procedures that exhibit high sensitivity and good accuracy. These methods range from simple absorption procedures to the more exotic chemiluminescent techniques.

RESEARCH AND DEVELOPMENT IN SPECTROSCOPY

Hadamard transform spectroscopy (HTS). The development of multichannel or multielemental spectroscopic techniques, where analysis of several sample constituents can be carried out simultaneously, requires a highly specialized detector system. Historically, two approaches to the development of these detector systems can be discerned: multichannel or dispersive methods and multiplex methods. The dispersive approach has been characterized by a variety of mechanical rapid-scan spectrometers, quantometers, and array detectors. The multiplex approach first concentrated on interferometer techniques utilizing the mathematics of the Fourier transform. A more recent multiplex technique is based on the mathematics of the Hadamard transform. Spectrometers operating in this multiplex mode have been successfully applied to infrared spectroscopy. It has been suggested that HTS methods could, in principle, be applied to any spectral region. Since there is great demand for multielemental analyses, the application of HTS could significantly increase our efficiency and broaden our range in this field. The mathematical basis of the technique suggested that its merit could be evaluated theoretically by computer simulation. Thus, we have developed a mathematical framework within which the relative performance of singly multiplexed HTS and conventional spectrometers (SS) can be compared.[6]

The theoretical multiplex advantage, or Fellgett advantage (F), is defined as the ratio of signal-to-noise values for the HTS and SS modes. The theoretical F values were calculated for spectrometers operating in two spectral regions. For the low-energy region (infrared), our computer model shows that $F = \sqrt{N}/2$, where N is the number of slots in the Hadamard coded mask. This theoretical value for F is in excellent agreement with experimental data obtained by other spectroscopists. For the high-energy spectral region (uv to visible), we find that $F = (x/2\bar{x})^{1/2}$, where x is the intensity of the spectral element sought and $\bar{x}$ is the average intensity produced across the whole spectrum. Our theoretical calculations were verified by computer simulation of various characteristic spectra. We conclude that for the high-energy spectral range, HTS will be advantageous only for spectra characterized by a few well-defined and intense peaks on a very low-intensity background. Conversely, for spectra with high background (atomic emission and absorption), for dense spectra (atomic and molecular absorption), or for spectra with very weak spectral features, the HTS will be of no advantage over the conventional SS technique. On the basis of this study, we suggest that potential users of HTS systems, as well as other transform multiplex systems, carefully examine their instrumental

6. N. M. Larson, R. Crosmun, and Y. Talmi, "Theoretical Comparison of Singly-Multiplexed Hadamard Transform Spectrometers to Scanning Spectrometers," *Appl. Optics*, in press.

requirements before selecting these methods over the proven conventional scanning system.

Improved fluorometric analysis system. Last year we reported the development of new fluorometric instrumentation to replace the model Q-1165 fluorophotometer.[7] We placed the instrument, designated model Q-5198, into the General Analyses Laboratory in October 1973. Except for a short period after its installation, when a faulty connection was causing variations in exciter lamp intensity, the instrument has been used regularly for the fluorometric determination of uranium. Circuit schematics, drawings, and parts lists have been prepared for distribution. These include necessary engineering information to fabricate the electronics package, to modify the sample changer–photomultiplier assembly, and to fabricate the exciter-lamp housings. One instrument manufacturer has examined the photometer and is presently contemplating its manufacture on a commercial basis.

As part of the modernization of the equipment used for fluorometric determination, an effort was made to build an automatic furnace that would uniformly fuse NaF-LiF pellets. To this end, five slotted tube furnaces were mounted in tandem above a constant-speed drive chain that would transport the pellets for controlled-temperature drying and fusion. During the analysis, an organic extract of uranium is pipetted onto a 270- to 330-mg pellet of 2% LiF–98% NaF in a platinum dish, and the pellet and dish are placed on a carrier attached to the drive chain. The pellet, moving at the rate of 6 cm/min, enters the drying furnace, which is 20 cm in length and maintained at 575°C. After drying, the pellet is allowed to cool for 5 min before entering the fusion furnaces. The fusion furnace consists of four slotted tubular heating elements in a single continuous insulated shell. The first 15 cm of the furnace is maintained at 990°C, the second 15 cm at 960°C, the next 15 cm is simply an insulated tube section that reaches an equilibrium temperature of 580°C, and the final 15 cm is maintained at 870°C. When the system is running at constant speed, 20 min is required for a sample to complete the cycle. Space is provided for the transport of 29 samples sequentially through the furnaces. After the first 20 min, uniformly fused pellets are produced at the rate of 40 per hour.

The residence time and temperatures were determined empirically to produce the same, or slightly higher, sensitivity than that obtained by flame fusion of the pellets. A series of samples run by furnace and flame fusion indicated the same sensitivity, but an improvement in the relative standard deviation by a factor of 2 in the furnace-fused samples was observed. The furnace pellet does not melt like the flame-fused pellet but remains as a sintered mass about half the original volume. Attempts to melt the sample pellet by extended heating or higher temperatures resulted in reduced sensitivities due to dissolution of platinum into the melt. The temperature is monitored and controlled by Chromel-Alumel thermocouples. Signals from the thermocouples are fed to a solid-state amplifier, and the amplified signal is used to drive a meter and second cutoff amplifer that controls a solid-state power relay. The desired temperature in degrees centigrade is set by a direct-reading ten-turn potentiometer. To date, stability and control have been excellent. Testing against the standard flame fusion method is still under way.

New applications of the gas chromatograph–microwave-excited spectrometer (GC-MES). The GC-MES analytical system has been described previously.[8] Through the application of the system to the determination of volatile organomercury compounds, we have demonstrated the superiority of the MES over the widely used electron capture (EC) detector. The capability of the system to determine CH_3HgCl at the low-ppb level in relatively small biological samples (0.1 to 0.5 g) made possible the design of various experiments difficult to perform otherwise. In cooperation with workers from the Environmental Sciences Division, we have simultaneously determined the concentrations of CH_3HgCl and inorganic mercury in fish and insects at the baseline and at various contamination levels. We have also studied the possibility of mercury methylation by the fish itself, with the rather significant conclusion that it does not happen. These and similar studies required the construction of a second GC-MES system designed mainly for the routine determination of CH_3HgCl. This system will also be applied to the determination of selenium, arsenic, and antimony, using methods developed with the research instrument.

The GC-MES was also used to determine selenium in environmentally based samples.[9] The analysis is

7. H. H. Ross et al., "Analytical Instrumentation Design and Modification," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 9.

8. H. H. Ross et al., "Instrumentation and Advanced Methodology," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 1.

9. Y. Talmi and A. W. Andren, "The Determination of Selenium in Environmental Samples Using Gas-Chromatography with a Microwave Emission Spectrometric Detection System," *Anal. Chem.*, in press.

based on chelating Se(IV) with 4-nitro-*o*-phenylenediamine (PD) to form the thermally stable and volatile piaselenol complex. This is followed by its extraction into toluene, separation by the GC, and finally determination by the MES via monitoring of the emission intensity at the 204-nm selenium line. Various parameters affecting the formation and extraction of the piaselenol complex, such as time dependence, composition of digestion solution, selenium loss, and oxidation of the PD reagent, were studied along with some potential interfering parameters, such as matrix composition, oxidation state of selenium, and column deterioration. The detection limit for selenium was found to be 40 pg (relative sensitivity, 0.1 μg/liter) for water samples and 15 pg for solid samples. Various samples have been analyzed, including plant and animal tissues, coal, and fly ash. The relative error and relative standard deviation are in the range of 2 to 10%. The analytical method was applied, in cooperation with A. W. Andren, Environmental Sciences Division, to the physical-chemical characterization of selenium in emissions from a coal-fired steam plant (Allen Steam Plant, Memphis, Tennessee).

New methods for arsenic and antimony. Analytical procedures for the determination of arsenic and antimony were developed as a part of a larger study to determine the applicability of the GC-MES to multielemental analysis. The analytical procedure includes the following steps: (1) Samples are digested with HNO_3-$HClO_4$ mixture. (2) Aliquots of the digested sample (25 to 50 ml) are diluted to 100 ml and thionalide is added. (3) The As^{3+} (reduced from As^{5+} by ascorbic acid) is coprecipitated by the thionalide and collected on an 0.8-μm Millipore filter. (4) After drying in an oven (70°C), the precipitate is transferred from the filter to a 20-ml vial, dissolved in ether, and reacted with phenylmagnesium bromide. The triphenylarsine and triphenylstibine formed are separated by the GC column and quantitatively determined by monitoring of the emission intensities at the arsenic 228.8-nm and antimony 259.8-nm lines. With this procedure we have determined the arsenic content of various NBS standards (coal, fly ash, orchard leaves, and bovine liver). The accuracy involved in the determination of antimony is currently under investigation. The relative sensitivity for solid samples is approximately 30 ppb for arsenic and 40 ppb for antimony, and for water samples it is about 0.06 ppb for arsenic and 0.08 ppb for antimony.

Another avenue explored for the determination of selenium and arsenic was the injection of H_2Se or $(CH_3)_2HAs$ into a stream of helium in which a dc arc was burning and monitoring of the appropriate emission wavelength.[10] Direct injection proved unsatisfactory, however, since it unavoidably involved the simultaneous injection of air into the gas stream; nitrogen bands caused substantial spectral interference at the wavelengths used. An alternate method of introducing the sample into the gas stream without introducing spectral interferences was developed using a system similar to that of Braman et al.[10] Arsine generated in the sample solution is purged with a stream of helium and accumulated in a trap at liquid-nitrogen temperature. The AsH_3 is later released by simultaneous warming of the trap and purging with a stream of helium into the arc chamber window. A new chamber was designed, in which the gas stream enters near this window, flows toward the arc (away from the monochromator), and is then vented. To combat gas leaks inherent in the original design, gas-tight (hard wax-sealed) joints, a manometer, and a flow meter were installed in the high-pressure region. The rate of heating of the trap (a particularly sensitive parameter) was stabilized by immersion of the trap in an empty Dewar flask during the warm-up. The effects of heating rate, trap material, trap geometry, depth of packing, gas flow and composition, and addition rate of the reductant are being studied. Reproducibility of recovery is now ±7% at the 150-ng level; usable sensitivity is limited by arsenic and other impurities in the reagent ($NaBH_4$).

ELECTROCHEMICAL METHODS AND INSTRUMENTATION

Coulometry is a quantitative electrochemical tool that we have employed extensively for the accurate determination of uranium and plutonium. With highly radioactive solutions, where radiolysis products can cause positive errors, the accuracy of the method appears to be degraded. With such solutions we have in the past used predictive techniques to minimize the effects of radiolytic damage. We are studying ways to improve the predictive method, and possibly to increase the accuracy of the method when applied to lower concentrations of uranium or plutonium. To carry out our studies successfully will require the rapid accumulation of fairly large amounts of data, the ability to process the data rapidly, and a facility for examining the acquired data and for interacting with the experiment as it progresses. Therefore, we have completed the writing of a new general-purpose compiler, FOCULH, designed for

10. R. S. Braman, S. L. Justen, and G. C. Foreback, "Direct Current Discharge Spectral Emission-Type Detector," *Anal. Chem.* **40**, 95 (1968).

flexibility in data acquisition, processing, and control functions. For our proposed work in predictive coulometry, we have removed unnecessary functions from FOCAL and inserted the following:

1. a programmable clock routine for determining the sampling rate and elapsed time,
2. an analog-to-digital conversion (ADC) routine that acquires data and then stores them according to a fetch-put routine,
3. a fetch-put routine (FP), which either stores a datum in single or double precision or floating point notation in a selectable core location or retrieves the contents of an addressed core location,
4. a channel-select routine that determines the source of the next datum to be handled by the ADC routine,
5. a display function that can be used to display data on an oscilloscope or X-Y plotter,
6. an EXECUTE command that carries out the above routines without the assignment of variable space, and
7. a library call that permits use of disk storage and retrieval.

The FP function adds considerable power to the compiler, in that it permits changes in machine language routines under keyboard or program control.

Analysis of natural water. The determination of hexavalent chromium in the presence of trivalent chromium in water is very important. Few, if any, waters contain chromium from natural sources. Hexavalent chromium resulting from pollution by industrial wastes appears to be relatively stable in natural water, since only a low concentration of reducing materials is present. There have been no reports of oral toxicity in the trivalent form; indeed, trivalent chromium is necessary for the maintenance of a normal glucose tolerance factor. The maximum permissible limit for Cr(VI) in potable water is 0.050 μg/ml. Therefore we were particularly interested in a method of determination that would distinguish chromium oxidation states.

There have been suggestions made for determining chromium in water samples by differential pulse polarography. At a dropping mercury electrode (DME), chromium presents a well-defined reduction wave in ammonium acetate buffer. Two common ions found in natural waters, Cu(II) and Fe(III), can be serious interferences when a DME is used for polarographic studies. We found that added Fe(III) has no effect on the chromium reduction wave and, consequently, creates no problem in the analysis of Cr(VI). By the addition of small amounts of ethylenediamine, the otherwise overlapping Cu(II) reduction wave is shifted negatively, eliminating Cu(II) interference. A tenfold excess of Cu(II) shows no effect on the Cr(VI) wave, even when the concentration of Cr(VI) is as low as 0.05 μg/ml.

Natural water samples containing Cr(VI) were buffered to approximately pH 7 with 0.1 *M* ammonium acetate and 0.005 *M* ethylenediamine and analyzed. Natural water samples of chromium content from 0.035 to 2.0 μg/ml can be analyzed directly without further preparation. Concentrations higher than 2.0 μg/ml exhibit polarographic waves with maxima that are not analytically useful. The detection limit of this method is 0.010 μg/ml. A paper describing these studies has been accepted for publication.[11]

Our work[12] on the simultaneous determination of lead, cadmium, and zinc at a thin-mercury-film wax-impregnated graphite electrode has been completed. The analyses were performed in the anodic stripping mode. Natural water samples containing the three elements were buffered to pH 5.7 with a solution of 0.1 *M* sodium acetate–0.012 *M* hydrochloric acid and analyzed. Concentrations ranged between 2 and 200 ng/ml for lead, 0.1 and 100 ng/ml for cadmium, and 10 and 100 ng/ml for zinc. Samples containing greater amounts must be diluted for accurate analysis. A paper describing these results has been prepared.[13]

Instrumentation. The Q-2943A voltammeter is a fast scan instrument designed so that the counter electrode, rather than the controlled electrode, is physically grounded. For this reason, the instrument is used extensively in the Molten-Salt Reactor Program when voltammograms are to be made using the reactor vessel or test loop plumbing as the counter electrode. These structures are usually at ground potential. We recently assisted the Instrumentation and Controls Division with the engineering revision of the Q-2943A into the Q-2943B, a less costly instrument. The Q-2943B utilizes the printed circuit boards and other components of the

11. S. T. Crosmun and T. R. Mueller, "The Determination of Hexavalent Chromium in Natural Waters by Differential Pulse Polarography," *Anal. Chim. Acta*, in press.

12. H. H. Ross et al., "Instrumentation and Advanced Methodology," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973*, ORNL-4930, p. 7.

13. S. T. Crosmun, J. A. Dean, and J. R. Stokely, "Pulsed Anodic Stripping Voltammetry of Zinc, Cadmium and Lead with a Mercury-Coated Wax-Impregnated Graphite Electrode," submitted to *Anal. Chim. Acta.*

A model without change, but the individual modules have been eliminated, allowing us to reroute some wiring. This change improves the bandwidth of the instrument and should eliminate a small, but sometimes significant, interaction between various circuits in the instrument. Three units are currently being fabricated with this design. Two will be used in the Energy Research Program of our division; the third is to be used by the Chemistry Division.

We designed a battery-operated potentiostat-galvanostat for A. L. Bacarella (Chemistry Division). Operating from four 6-V lantern batteries, the instrument features a drift-correcting circuit, current-handling capability to 300 mA, fabrication from plug-in printed circuit cards previously designed for other projects, and compactness. The use of a battery power supply provides isolation from commercial power lines and thus eliminates ac ground loops in some sensitive experimental setups. In the potentiostatic mode, potential control is ±10 μV; in the galvanostatic mode, worst-case current regulation is ±1 μA. When isolation from power lines is not required, or where currents near the maximum are to be drawn frequently, the addition of an ac-dc power supply (±12 or ±15 V) is possible. Parts cost is about $125.

APPLICATION OF COMPUTERS TO CHEMICAL ANALYSIS

Pattern recognition. In cooperation with the UCCND Computer Sciences Division, we have initiated a study of pattern recognition as a technique for solving complex analytical chemistry problems. The specific task under investigation is the analysis of high-resolution gas chromatographic profiles generated in the ORNL Tobacco Smoke Research Program. The objective is to determine which of the peaks in the chromatogram are correlated highly with biological activity and to select the peaks for which chemical compound identification would be worth while. Pattern recognition techniques involve the use of artificial intelligence and multivariate analysis to point out relationships present in multidimensional space. These relationships, or patterns, are not visualized readily by a human mind used to thinking in one-, two-, and three-dimensional space. Karhunen-Loeve transformation, cluster analysis, *k*th nearest neighbor selection, correlation, and least-squares methods are some of the mathematical procedures employed to classify and predict.

We obtained from C. F. Bender (Lawrence Livermore Laboratory) a FORTRAN IV pattern recognition program, RECOG, which has been modified to run on the IBM 360/91 computer using about 360K bytes of core memory. We also obtained from Dr. Ralph Gonzalez (University of Tennessee) a FORTRAN IV version of ISODATA, a program that originated at Stanford Research Institute. Both RECOG on the IBM 360/91 and the ISODATA version on the DEC system 10 have been executed successfully at ORNL. Our preference is RECOG, because of its greater flexibility. Raw analog data from the gas chromatograph are digitized and stored sequentially on magnetic tape (DECTAPE) by a dedicated minicomputer (8K PDP-8/E). The 12-bit raw data are transferred from the PDP-8 formatted DECTAPE to a DEC system 10 disk file. Further data processing on the DEC system 10 produces an array containing peak-area and retention-time information. This array for each of 23 cigarettes will be the input for RECOG. ORGRAPH, an ORNL program on the IBM 360, will be used to generate two-dimensional displays of clustered data. Programming to accomplish this CALCOMP display is under development.

Other applications. A major minicomputer application this year was the interfacing of an 8K PDP-8/E computer with a single DT8E DECTAPE unit to a PE-900 gas chromatograph. Preliminary work on this project was done by J. A. Kinsinger in the summer of 1973, and it was developed further when the installation was made early in 1974. The interface to the gas chromatograph was quite simple in principle but was complicated by the fact that the output signal from the chromatograph was not only smaller than anticipated but also more strongly contaminated with noise pulses from the control circuits of the chromatograph. The noise problem was solved with a three-section RC filter, followed by a 60-Hz parallel T. The signal magnitude was enhanced by the use of two operational amplifiers, one with a gain of 8 and one of unity gain. By feeding of these into two of the multiplexer channels of the computer's analog-to-digital converter, a range of gains from 1 to 64 can be selected automatically under program control.

Readings from the gas chromatograph are taken at 1-sec intervals and examined for peaks during the run. When multiple peaks are detected, peak areas are divided by the "perpendicular drop" technique and similarly printed, but marked by an asterisk. The raw data readings are stored in the computer core as acquired, but when a block of 512 points has been acquired, those data are transferred to DECTAPE. This transfer is effected without any disturbance of the data taking beyond a possible slight delay in the time at which some points are taken. The entire programming

system is based on the use of FOCAL with appropriate functions for controlling data acquisition and DECTAPE transfers. The program is written so that data can be read back from DECTAPE and reanalyzed.

The data on DECTAPE can also be read into the DEC system 10 computer and processed in a similar manner with a FORTRAN program that is essentially a translation of the FOCAL program used on the PDP-8/E. This, however, gives data that can be used in other computational work (such as the pattern recognition studies noted above).

The use of the PDP-8/E computer interfaced to a Perkin-Elmer 403 atomic absorption spectrophotometer has been expanded by some additions to the FOCAL interpreter in use in the computer. The addition of two additional functions and appropriate FOCAL program text permits the computer to be used for keeping a table of the backlog of analyses in the Environmental Sciences Laboratory and revising it daily. The computer can also be used for calculation of the results of mercury analyses, which are run in considerable numbers by this group.

The 8K PDP-8/I that was used in the Molten-Salt Reactor Program and later on one of the GeMSAEC units has now been installed on the iron-free beta spectrometer used for ESCA (electron spectroscopy for chemical analysis) spectra, replacing a 4K PDP-8 that seemed to have excessive program failures. The operating program was completely rewritten to use a FOCAL-based system with appropriate functions to read the data and operate the controls of the spectrometer. An X-Y plotter was installed to enable the operator to produce plots of the spectra while data acquisition was in process, and a Tennecomp TP-1371 cartridge tape unit was installed to permit the storage of spectra on magnetic tape for later retrieval. The 8K PDP-8/I has been much more reliable in operation, and the FOCAL-based program is much more flexible and has considerably increased capabilities as compared with the assembly language program in the 4K PDP-8 that was replaced.

A modification of the ALPHA-M least-squares program was written on the DEC system 10 to enable the processing of x-ray fluorescence spectra acquired on a multichannel analyzer in the Metals and Ceramics Division. When it proved not to be feasible to transfer such spectra into the newly acquired NS-880 system in the Division because of differences in energy scale and lack of a high-speed tape reader, the ALPHA-M program was adapted to process the 700 channels that constitute the significant portion of the spectra. Pure Gaussian peaks are generated as standards for the elements sought, and the least-squares fit is performed on three overlapping portions of the spectrum, since the memory space available in the DEC system 10 is insufficient to accommodate the entire spectrum at once. The least-squares procedure speeds up the calculation of peak areas very significantly and allows the calculation of element concentrations in the same program.

With small computers of limited word length, the problem of loss of significance in complex mathematical operations is a constant pitfall. Largely because of simplicity in programming, we have usually used the determinant solution technique for the simultaneous equations generated in least-squares fit procedures. We found in trying to generate calibration equations for efficiency in gamma spectral measurements that ill-conditioned determinants were generated, and their solution on a computer with 23- to 27-bit significance resulted in ridiculous answers. Use of the ALSQ (ALSQ-BLSQ, G. W. Stewart III) matrix reduction technique very much improves the results obtained, even with 23-bit significance (PDP-8 or PDP-11). A version of the ALPHA-M program has also been written with the matrix reduction (Householder reduction) instead of the matrix inversion used in the current version. The new version appears to open up the possibility of using the ALPHA-M program in minicomputers.

APPLICATIONS OF THE GeMSAEC FAST ANALYZER

As part of the ORNL/NSF(RANN) project on Ecology and Analysis of Trace Contaminants, we have continued to investigate applications of the GeMSAEC fast analyzer for performing analyses and solving problems of interest in evaluating environmental quality. Emphasis has been on the analysis of natural and potable waters. During the past year a major objective has been achieved – the development of hardware and software capabilities to implement most photometric methods of analysis. We can now employ spectrophotometric, turbidimetric, luminescence, and kinetic (including initial-rate, fixed-time, and variable-time) techniques; appropriate computer programs are available to process the data.

The implementation of luminescence techniques proved to be difficult because of the very short duration of the chemiluminescent light pulses (usually less than 5 sec). It was necessary to modify the machine-language data-acquisition function in the FOCAL compiler to enable a sufficient number of readings to be taken to define the shape of the pulse.

Since the shortest interval between readings on any individual cuvette is the time required for one rotor revolution, the modified data are collected at intervals defined in terms of rotor revolutions rather than clock time. In practice, the rotor is started from a stationary state, aligned so that the first cuvette is the first to pass the photomultiplier, and accelerated at a maximum rate of 1000 rpm. A clock is started at the beginning of the second revolution, and the first set of emission readings is taken for each of the 15 cuvettes. Each cuvette is read 16 times during a single pass under the photomultiplier, and the readings of each are averaged, stored, and treated as a single observation. After a specified number of rotor revolutions, a clock reading is again taken, followed by the second set of emission readings. As many as 21 sets of data can be taken in this way, each set consisting of a clock reading taken at the beginning of data collection and the averaged readings for each of the 15 cuvettes. A dark-current reading is taken after all the data have been collected and the individual cuvette observations have been corrected. These values are stored and can be recalled by FOCAL programs for further data processing.

A summary of the specific methods of analysis that have been adapted to the GeMSAEC analyzer to date is shown in Table 1.1. The methods for sulfur dioxide,

Table 1.1. Analyses adapted to the GeMSAEC fast analyzer

Substance	Method of analysis	Concentration range (mg/ml)	Relative standard deviation (%)
SO_2	West-Gaeke method (fixed-time kinetic)	$<1^a$	1
O_3	Reaction with eugenol (fixed-time kinetic)	$<1^a$	2
Ca(II)	As calcium oxalate (turbidimetric)	10–100	10
Cr(III), (VI)	Catalytic luminol method (chemiluminescence)	0.05–0.6	1
Cu(II)	Catalytic method (variable-time kinetic)	0.1–1	5
Fe(III)	Reaction with thiocyanate (spectrophotometric)	0.1–3	3
Mg(II)	As $Mg(NH_4)PO_4$ (turbidimetric)	5–70	5
Se(IV)	Catalytic method (variable-time kinetic)	0.1–1	5
Zn(II)	Reaction with 4-(2-pyridylazo)resorcinol (spectrophotometric)	0.2–1	3
Cl^-	Reaction with $Hg(SCN)_2$ (spectrophotometric)	5–75	2
I^-	Catalytic method (initial-rate kinetic)	0.02–0.1	10
NO_2^-	Diazotization and coupling (spectrophotometric)	0.1–1	1
PO_4^{3-}	Reduced phosphomolybdate method (fixed-time kinetic)	1–14	5
S^{2-}	Synthesis of ethylene blue (spectrophotometric)	0.1–1	1
SO_4^{2-}	Reaction with Ba(II) or CAD (turbidimetric)	5–50	2

[a]Dependent on sample collection time.

ozone, copper, iron, magnesium, selenium, zinc, iodide, phosphate, and sulfate were described previously,[14] and papers were recently published on ozone,[15] selenium,[16] and zinc[17] analyses. The following analytical methods were developed in the past year.

Calcium. A survey of photometric methods for calcium indicated that none was readily adaptable to the GeMSAEC analyzer, so we chose to develop a turbidimetric method based on precipitation of calcium oxalate. The sample (0.4 ml) containing 10 to 100 ppm of calcium is mixed with 0.3 ml of a 0.025 *M* phthalate buffer, pH 4, and saturated with ammonium oxalate, and the absorbance at 470 nm is measured after 5 min. The computer program written for spectrophotometry is also used for turbidimetry. Interfering elements, mainly the rare earths, are not likely to be present in natural waters. The precision of the method is not outstanding (about 10% relative standard deviation), because of variable rates of crystal growth. High concentrations of calcium (greater than 70 ppm) rapidly form large crystals, which tend to settle in the cuvette, while low concentrations (less than 10 ppm) form crystals very slowly, reaching maximum absorbance after 15 min. Measurement of absorbance after 5 min is a compromise to obtain the most nearly linear calibration curve. The calcium content of several natural water samples was in the range of 50 to 100 ppm, and a sample of well water contained 135 ppm.

Chloride. Chloride ion was determined by an adaptation of the standard mercuric thiocyanate method,[18] in which the chloride ion is reacted with mercuric thiocyanate to produce thiocyanate ion, which in turn combines with ferric ion to form red ferric thiocyanate. A 0.2-ml sample was added to 0.1 ml of a saturated mercuric thiocyanate solution in 1 *M* $HClO_4$ in one well of the transfer disk, and 0.4 ml of 2.5% ferric perchlorate in 2 *M* $HClO_4$ was placed in the other. Absorbance measurements were made at 460 nm, 10 sec after rotor start-up. Concentrations of chloride from 5 to 75 ppm were determined with a relative standard deviation of about 2%. Although the calibration curve became nonlinear above about 10 ppm, the chloride content of natural waters is usually less than that. Our natural and potable water samples had less than 5 ppm of chloride, and a sample of well water contained 15 ppm.

Nitrite. Nitrite was analyzed by a standard method involving diazotization of sulfanilic acid, then coupling with naphthylamine hydrochloride.[19] A 0.4-ml sample was combined with 0.1 ml of sulfanilic acid solution in one well, and 0.2 ml of naphthylamine solution was placed in the other. The reactions proceeded rapidly after mixing, and absorbance measurements at 520 nm were made 10 sec after rotor start-up. Concentrations of nitrite ion from 0.1 to 1 ppm were determined with excellent precision; the relative standard deviation was about 1%. Natural and potable water samples were found to contain very little nitrite, less than 0.05 ppm.

Sulfide. The determination is based on the reaction of sulfide ion with *N,N*-diethyl-*p*-phenylenediamine, in the presence of $FeCl_3$ as a catalyst, to form ethylene blue,[20] which absorbs strongly at 670 nm. A 0.4-ml sample was placed in the larger well in the transfer disk, and 0.2 ml of the acidified amine solution in the smaller well. When the $FeCl_3$ catalyst was premixed with either the sample or amine solutions, results were unsatisfactory, so we used the mixing chamber in the disk for the catalyst. Color development is complete within 60 sec after mixing, and 0.1 to 1 ppm of sulfide can be determined with a relative standard deviation of less than 1%. Several water samples were analyzed, but none contained detectable quantities of sulfide ion. Sulfide spikes could be recovered quantitatively, however.

Chromium. Chromium was determined by a recently developed chemiluminescence method[21] based on the ability of Cr(III) to catalyze the reaction between hydrogen peroxide and luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) in basic medium, which produces chemiluminescence. When appropriate concentra-

14. H. H. Ross et al., "Instrumentation and Advanced Methodology," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 3.

15. J. L. Bowling, J. A. Dean, and W. D. Shults, "Determination of Atmospheric Ozone Using the Centrifugal Photometric Analyzer," *Anal. Lett.* 6, 933 (1973).

16. J. L. Bowling, J. A. Dean, and G. Goldstein, "Determination of Selenium in Natural Waters Using the Centrifugal Photometric Analyzer," *Anal. Lett.* 7, 205 (1974).

17. G. Goldstein, W. L. Maddox, and M. T. Kelley, "Spectrophotometric Analysis with the GeMSAEC Fast Analyzer. Determination of Zinc Using 4-(2-Pyridylazo)resorcinol (PAR)," *Anal. Chem.* 46, 485 (1974).

18. American Society for Testing and Materials, *Annual Book of ASTM Standards. Part 23. Water; Atmospheric Analysis,* Philadelphia, 1972, p. 25.

19. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 13th ed., Washington, D.C., 1971, p. 240.

20. T. D. Rees, A. B. Gyllenspetz, and A. C. Docherty, "Determination of Trace Amounts of Sulfide in Condensed Steam with *N,N*-Diethyl-*p*-phenylenediamine," *Analyst* 96, 201 (1971).

21. W. R. Seitz, W. W. Suydam, and D. M. Hercules, "Determination of Trace Amounts of Chromium(III) Using Chemiluminescence Analysis," *Anal. Chem.* 44, 957 (1972).

tions of the reagents are mixed in the presence of catalyst, a pulse of light is produced with a duration of about 2.5 sec. Using a parallel-mixing transfer disk for fast, efficient mixing and the modified data acquisition function previously described, concentrations of Cr(III) or, after reduction, Cr(VI) from 50 to 600 ppb were determined with a relative standard deviation of 1 to 2%. The method is very rapid, and only a small sample (0.3 ml) is required. In addition, since the method is selective for uncomplexed Cr(III) ions, comparison of results with analyses for total chromium and Cr(VI) by other methods provides information on the chromium species present in a sample and the presence or absence of complexing agents. A paper describing this method has been prepared.[22]

22. J. L. Bowling, J. A. Dean, G. Goldstein, and J. M. Dale, "Rapid Analysis of Chromium in Natural Waters by Chemiluminescence Using a Centrifugal Fast Analyzer," to be submitted to *Anal. Chim. Acta.*

Enzyme inhibition tests. Since most substances that are toxic in trace quantities severely inhibit or inactivate essential enzyme systems, we explored the possibility of screening for toxic materials in vitro via enzyme inhibition tests. Appropriate conditions were established for testing against *Escherichia coli* alkaline phosphatase enzyme, using *p*-nitrophenyl phosphate as the enzyme substrate. Some of the more potent inhibitors (and the sample concentration at which inhibition was detectable) were beryllium (1 ppb), phosphate (0.2 ppm), cadmium (1 ppm), and nitrilotriacetic acid (2 ppm). Tests were also made on the effect of water samples on the enzyme. Distilled water, well water, and spring water did not inhibit significantly. Three natural water samples from the Walker Branch Watershed caused a 10 to 15% inhibition, and similar results were obtained with samples collected over a period of several months.

2. Nuclear and Physics Methods

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The Nuclear and Physics Methods Group operates a variety of expensive, extremely sophisticated, most sensitive, and highly complementary facilities and equipment, primarily for elemental determinations. Concomitant with research programs devoted to exploring and improving nuclear and other physics techniques, we have adopted a policy of immediate translation of methodology to practical real-world problems. This procedure should stimulate and encourage the researcher, since the fruition of his work is immediately visible; at the same time, it channels the research itself, by feedback from the user, into areas where analytical problems exist. In a few endeavors where such practical application has not developed, we have directed our attention to new and different projects. At present, there are no facilities or equipment in active operation within this group where some special analytical services are not being performed.

Construction of the x-ray fluorescence analyzer system employing a pyrolytic graphite monochromator is completed, and the instrument is being used for qualitative identifications while calibration and programming for quantitative analysis proceed. The ESCA system (electron spectroscopy for chemical analysis) has been used to study surface problems submitted by researchers in several divisions, and we ourselves continue to look for new applications of ESCA and to develop expertise in the technique. Combinations of several quite different techniques are often used for problems involving surface characterization: for example, zonal centrifugation separation followed by scanning electron microscopy and/or x-ray diffraction.

Most of the engineering and mechanical problems at the HFIR neutron activation analysis (NAA) lab have finally been resolved, and this year large numbers of multielement determinations on very small samples have been completed. The activation analysis lab at the ORR continues to perform yeoman service to many projects: special samples have ranged from monkey hair to mosses to coal to soil. The PDP-15 computer program MONSTR, developed here, is being used successfully for instrumental quantitative NAA at both sites.

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Expertise in low-level radioactivity measurement built up over the years through participation in NASA projects is now being applied to problems of local radioactive wastes; the NASA projects continue at a reduced level of effort. Environmental studies being actively pursued include the Allen Steam Plant trace element balance, behavior of heavy elements in soil, water, and vegetation, development of improved methods for assaying radioactive contaminants, and pollution abatement of toxic materials through solvent extraction.

In our continuing effort to share expertise and to assist the AEC in critical areas – a tradition begun in the early days of research into properties and uses of radioisotopes and extended with the development of activation analysis – we have collaborated with the Region II Directorate of Regulatory Operations in assembling, testing, and using a mobile laboratory for on-site verification of uranium inventories.

X-RAY AND ELECTRON PHYSICS

X-ray fluorescence. The Analytical Chemistry Division has completed construction of an x-ray fluorescence analyzer system that employs an Si(Li) energy-dispersive spectrometer. A silver-target x-ray tube is used to produce the excitation radiation. The main innovation in our system is the use of a pyrolytic graphite monochromator to isolate the Ag $K\alpha$ energy from the scattered bremsstrahlung and focus it on the sample. Removing the scattered radiation greatly reduces the background in the fluorescence spectrum. The approach is patterned after that of Sparks et al.,[5] who set up a similar system using an Mo $K\alpha$ excitation source. Because of the better peak-to-background conditions, significant improvements in detection limits have been achieved for both systems. After experimenting with our system, we conclude that the following generalizations concerning detection limits can be stated.

For a small quantity of a given element to be detected by x-ray fluorescence, its cross section for excitation and its fluorescence yield must be favorable. Also, the background must be low in the energy range of the spectrum where the fluorescence peak occurs. For the case of Ag $K\alpha$ (22.1 keV) excitation used in our system, high cross sections and fluorescence yields occur for elements with fluorescence energies in the range of 10 to 20 keV; detection sensitivity should therefore be high for those elements. For biological or environmental samples, however, the energy range for high detection sensitivity is shortened to 10 to 15 keV, because the spectrum has a high background beyond 15 keV due to Compton scattering. Elements 33 (As) through 39 (Y) have K x-ray fluorescence energies in the range of 10 to 15 keV. Elements 75 (Re) through 94 (Pu) have L energies in this range. For these elements we have detection limits of 1 ppm or less for biological or environmental samples. For elements that have x-ray fluorescence energies in the region 5 to 10 keV, 23 (V) through 33 (Ge) and 58 (Ce) through 80 (Hg), detection limits are 1 to 10 ppm. For fluorescence energies below 5 keV, cross sections for excitation by Ag $K\alpha$ are very low, and detection limits are poor (1000 ppm or higher).

Detection sensitivities can be improved for elements with fluorescence energies below 5 keV by the use of lower-energy sources for excitation. We have studied the ^{55}Fe source, which produces Mn $K\alpha$ (5.4 keV) x rays. We have analyzed animal waste samples for Ti (4.5 keV fluorescence energy) and achieved a sensitivity of 15 ppm. We have also found that an ^{241}Am source, which produces 59.5-keV gamma rays, can very effectively excite the $K\alpha$ fluorescence peak of some of the heavier elements. For simulated fission-product samples containing elements 41 through 62, it appears that we will be able to achieve detectability limits of 20 to 50 ppm. Thus, using our x-ray fluorescence system with a variety of excitation sources (Ag $K\alpha$, ^{241}Am, ^{55}Fe), we have a capability of high-sensitivity analysis for almost all elements heavier than potassium. Detection limits are 50 ppm at worst, and 1 ppm or lower for many elements.

We have been able to use the system with Ag $K\alpha$ excitation for quantitative analysis also. It appears that for biological or environmental specimens in which the heavy-element concentrations are less than 1000 ppm, an absolute method can be developed; that is, it will not be necessary to standardize empirically for each matrix. We have mounted our system on a goniometer. The sample is positioned so that the entrance angle of the excitation radiation and the exit angle of the fluores-

5. C. J. Sparks, O. B. Cavin, L. A. Harris, and J. C. Ogle, *Trace Substances in Environmental Health – VII*, D. D. Hemphill, ed., University of Missouri, Columbia, Missouri, 1973.

cence radiation are precisely defined, allowing us to determine the self-absorption coefficients of each sample matrix accurately and to make calculations for quantitative results from first principles.

There are two special features of the Si(Li) detector used in our system that are worthy of mention. They represent improvements in state-of-the-art instrumentation: (1) internal collimation and (2) high-purity pyrolytic graphite window. The internal collimator is placed between the window and the Si(Li) crystal. It is of sandwich construction, with lead in front followed by tantalum and aluminum. Its purpose is to collimate the incoming x-ray beam so that it strikes only the central region of the crystal, which prevents edge effects of the Si(Li) crystal from introducing an artificial low-energy background. Other workers have reported the use of guard rings in Si(Li) detectors to reduce edge effects. It appears that internal collimation is just as effective and simpler in construction. The high purity of the graphite window eliminates vagaries in detector response. Beryllium windows, which are normally used, have heavy-metal impurities whose absorption edges cause abrupt changes at certain energies in the intensity of radiation transmitted to the detector. The graphite window is ultrathin (0.0002 in.) and is made by cleaving a single crystal. The high strength of the single-crystal graphite window allows it to withstand atmospheric pressure unsupported. The internal collimation and graphite window features were first explored by Sparks[6] in cooperation with a local electronics company.

X-ray photoelectron spectroscopy (ESCA). X-ray photoelectron spectroscopy has been used in two energy-related programs during the past year, both requiring surface analysis. The ESCA (electron spectroscopy for chemical analysis) technique involves the measurement of the energy spectrum of electrons photoejected from solids bombarded with x rays. The kinetic energies of the escaping electrons are in the range 100 to 1400 eV, which restricts the depth within the solid from which they can escape. Thus, the method samples only the surface of solids. For organic or other light-element matrices, the escape depth is about 100 Å; for heavy-element matrices it is 10 to 20 Å. The ESCA technique can be used for the analysis of all elements heavier than hydrogen. Each element has a set of peaks with unique energies, making interpretation of the spectra very easy. The oxidation states of elements can often be determined from small shifts (1 to 5 eV) in the energies of their peaks.

Supported catalysts are being studied at ORNL for use in the desulfurization and liquefaction of coal. We have used the ESCA technique to study the surface of cobalt oxide–molybdenum oxide adsorbed on alumina, with some commercially supplied samples and some prepared at ORNL. We were unable to detect cobalt on the surface of either type of sample, which suggests that it had diffused into the alumina matrix. The molybdenum was observed to have a binding energy about 2 eV higher than that for the pure MoO_3 state. This is tentatively interpreted as being due to the conversion of molybdenum to the $Al_2(MoO_4)_3$ state. When our characterization of the unreacted catalyst is finished, we will study catalysts that have been used in various reactions such as desulfurization processes. Our goal is to develop a routine expertise in the surface analysis of catalysts so that we can provide information useful for an understanding of their behavior in various applications.

In the Molten-Salt Reactor Project there is a severe problem of intergranular corrosion of Hastelloy. The corrosion is believed to be catalyzed by tellurium fission product adsorbed on the Hastelloy from the molten-salt medium. We are attempting to use ESCA to determine the chemical state of the absorbed tellurium. We have found that tellurium has measurable chemical shifts, in that one can easily distinguish between such states as TeO_3, TeO_2, and Te metal. When we examined such alloys as NiTe and Ni_3Te_2 we found that the surface was enriched in tellurium to the extent that no nickel was detected. Thus it appears that tellurium tends to segregate at the surface of Ni-Te mixtures. The surface-segregated tellurium was in three chemical states – metallic Te, TeO_2, and TeO_3. We attempted to study Hastelloy that had been exposed to tellurium vapor in a quartz capsule at high temperatures, but we found that the surface was grossly contaminated with silicon from the capsule walls; thus, the tellurium, nickel, and chromium were obscured and could not be studied. Work on another scheme for tellurium treatment is in progress.

Scanning electron microscopy, x-ray diffraction, and zonal centrifuge separations. The scanning electron microscope (SEM) is well known as a powerful tool in microanalysis. It provides a high-resolution photomicrograph of the specimen of interest, and measurement of the energies of x rays [Si(Li) spectrometer] induced by the electron beam as it strikes the specimen can provide elemental analysis. Details as small as 200

6. C. J. Sparks, Metals and Ceramics Division, private communication.

to 500 Å can be resolved in SEM photographs, and elemental analysis can be done on particles as small as 1000 Å (10^{-15} to 10^{-14} g).

We often use the combined techniques of scanning electron microscopy and x-ray diffraction to analyze complicated powder mixtures that contain many different compounds. X-ray diffraction is also a well-established technique, known for its ability to identify compounds, but diffraction patterns are sometimes ambiguous and difficult to interpret when the mixture is complicated. Thus it is desirable to have elemental analysis, which is conveniently supplied by the SEM, for supporting information. If, for example, the x-ray diffraction pattern indicates $FeSO_4$, we examine the sample with the SEM to determine whether the elements iron and sulfur are present and whether they are both present in the same particles.

Some mixtures are so complicated that separations must be performed before analyses are attempted. We have found the zonal centrifuge to be very effective for this purpose, and the technique has been exploited in the Environmental Sciences Division. Separation is done on the basis of density. Centrifuge tubes are filled with a fluid whose density increases continuously from bottom to top. Pure tetrabromoethane (TBE), with a density of almost 3, is used for the heavy fluid at the bottom, and ethanol, with a density of 0.95, is used for the light fluid at the top. Mixtures of TBE and ethanol are used for intermediate densities. For proper dispersion of the mixture to be separated in the density gradient fluid, it is dehydrated with absolute ethanol and treated with a surfactant, polyvinylpyrrolidone. The mixture is then deposited at the top of the density gradient tube and centrifuged at high speed. Components of the mixture separate at different heights in the tube according to their density.

Using the combined approach of zonal centrifugation, scanning electron microscopy, and x-ray diffraction, we have been able to analyze mixtures of large numbers of components. In the case of dust collected from a gas stream of the Peach Bottom Reactor, we identified ten compounds – Fe_2O_3, Fe_3O_4, $FeSO_4$, FeC, Fe, Fe_3C, Cr_2O_3, silicate glass, quartz, and cristobalite.

ACTIVATION ANALYSIS

Trace element balance at the Walker Branch Watershed by absolute multielement NAA. In collaboration with the Environmental Sciences Division, we have started a study on the balance of trace elements in the Walker Branch Watershed. A. Andren and E. Baes of that division obtained 2-liter samples from the watershed and filtered them through Nuclepore filters. We prefer these filters to the Millipore brand because the latter disintegrate during relatively short bombardments at the HFIR. Filtrates and blank filters (for purposes of background subtraction) were subjected to absolute multielement NAA at our High-Flux Laboratory. We found only ten elements in the Nuclepore filters, ranging from 0.73 μg (aluminum) to 2 ng (manganese) for a 47-mm-diam filter. Other than aluminum, the most significant impurities were sodium (0.60 μg), chlorine (0.68 μg), and zinc (0.35 μg).

We can regularly analyze the filtrates for 20 to 24 trace elements. Table 2.1 shows typical results corresponding to four sampling sites in the watershed. We have completed the methodology, so the analyses are being continued in the General Hot Analyses Laboratory.

Environmental baselines by absolute NAA of tree rings. We are involved with the Environmental Sciences Division in an interdisciplinary effort aimed at gaining information about environmental baselines and trace contamination levels in the Oak Ridge–Knoxville area.

Table 2.1. Water environmental reference levels (in μg/liter) for the Walker Branch Watershed, January 1974, determined by nondestructive absolute NAA[a]

Element	East 500 yd	East basin	West basin	West spring
Al	174	187	213	112
Cl	3.65	1.88	1.63	2.58
Ti	5.65	5.33	7.90	4.88
V	0.20	0.24	0.28	0.14
Na	0.89	0.36	0.45	0.42
K	19.9	21.8	28.8	14.8
Sc	0.33	0.034	0.037	0.023
Cr	0.99	1.27	1.02	0.97
Mn	0.39	0.48	0.42	0.32
Fe	62.5	68 5	80.8	41.3
Co	0.029	0.036	0.023	0.019
Ni	ND[b]	ND	ND	ND
Cu	ND	ND	ND	ND
Zn	0.67	ND	ND	ND
As	0.027	0.023	0.016	0.0098
Se	0.014	ND	ND	0.015
Br	0.026	0.024	0.032	0.020
Rb	0.12	0.17	0.19	0.084
Cs	0.10	0.014	0.017	0.0083
Eu	0.0011	0.0014	0.0015	0.0011
Lu	0.0012	0.0011	ND	0.0009
Hf	0.0060	0.0055	0.0068	0.0045
W	0.0080	0.0080	0.0083	0.010
Hg	0.025	0.015	0.020	0.028

[a]Counting errors for most determinations range from 0.32% (chromium) to 8.5% (bromine), with larger uncertainties (12.3 to 20.8%) for titanium, selenium, and tungsten.

[b]ND, not detected.

Instrumental absolute multielement NAA is currently providing data both on conditions of a century ago and on gradual atmospheric contamination, by analysis of rings from trees grown in a relatively unpolluted area and in a city.

D. E. Reichle and W. F. Harris of the Environmental Sciences Division obtained core samples from two similar shortleaf pines (*Pinus echinata*) over 100 years old located on the Walker Branch Watershed and in Knoxville. Soils are red-yellow podzolic derived from dolomitic bedrock. With a 12-mm-diam increment bore, three cores were obtained from each tree 4.5 ft (137 cm) above ground and at approximate intervals of 120° around the trunk. The cores were immediately stored, refrigerated in plastic bags, then cut into increments corresponding to successive five-year growth periods, and finally placed in clean corked Pyrex tubes until bombardment.

We analyzed the samples by nondestructive absolute multielement NAA at the High-Flux NAA Laboratory, where a pneumatic system conveys the samples (enclosed in polyethylene rabbits) to the bombardment site in the beryllium reflector of the HFIR. The thermal flux there is 6×10^{14} cm^{-2} sec^{-1}, and the thermal-to-resonance flux ratio is between 45 and 55. Usually, a 5-sec bombardment allows determination of Mg, Al, C, V, and Mn, which produce short-lived nuclides; a 5-min irradiation follows, which yields Na, K, Br, and W by counting 24 hr later and Cr, Fe, Co, Zn, Rb, and Ba after 7 to 10 days. Counting is done with a Ge(Li) detector of 12% relative efficiency and a Nuclear Data 50/50 system. This 4096-channel analyzer is coupled to an 8K PDP-15 computer. We use the MONSTR overlay system of programs to process the gamma-ray spectra.[7]

We have determined 13 elements simultaneously in four increments each of two cores of the Walker Branch Watershed tree. Increments analyzed were numbers 20, 8, 3, and 1, corresponding to time lapses 1872–76, 1932–38, 1958–63, and 1968–72 respectively. No clear trend was seen in the data, so no attempt will be made to draw conclusions now. We have separated, somewhat arbitrarily, sodium, chlorine, and potassium, because they might reflect natural tree components and/or sample-handling contamination; and perhaps aluminum (from the soil) and iron (from the bore) should be added to this group. Most of the remaining elements appear to show only small variations.

7. W. S. Lyon et al., "Activation Analysis Development," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 42.

Methodology of absolute high-flux NAA: Bombardment losses. We have continued our efforts at the High-Flux NAA Laboratory to meet the strict reliability and accuracy requirements of instrumental absolute NAA.

The very high flux (about 5×10^{14} cm^{-2} sec^{-1}) at which our samples are irradiated at the HFIR poses special problems. We have observed that polyethylene rabbits become almost black during a 10-min irradiation and dangerously brittle if bombarded further. Millipore filters are practically evaporated in only 5 min, and the gas released can cause plastic rabbit capsules to explode. Magnesium and graphite rabbits, instead, have proven useful and safe for longer (three-day) bombardments.

Because of the bombardment conditions at the HFIR, there was concern about possible loss of elements or radioactive products. To investigate this possibility, we bombarded five similar 0.1-g samples of kale under conventional conditions for increasing times of 5, 15, 31, 45, 61, 121, and 301 sec. Twelve nuclides were measured, and the concentrations of Na, Mg, Al, Cl, K, Ca, V, Mn, Zn, Br, Rb, and Sr were calculated and compared with values obtained in previous 5- to 301-sec irradiations. The variations observed are all compatible with the experimental uncertainties of the individual elemental determinations. Therefore, we conclude that there is no effect of the length of bombardment on analytical results, within the limits (5 min) of this experiment.

Methodology of absolute high-flux NAA: Rabbit near-core travel time. From the start we have assumed that the pneumatic rabbit spends a negligible travel time near the HFIR core with respect to bombardment lengths, but inconsistencies in flux determinations and systematic errors observed in the NAA of standards have shown this not to be the case. Table 2.2 shows variations observed in flux and monitor activity values in relation to bombardment times. The importance of flux determinations in absolute activation analysis cannot be overemphasized. It is clear from the table that thermal flux values are too high for short monitor bombardments, where the near-core travel time is more significant.

To calculate the near-core travel time τ, we consider the activity induced in the monitor:

$$A = \frac{N \ln 2}{T_{1/2}} (t + \tau) (\sigma_0 \phi_{th} + I_0 \phi_r) ,$$

where t is the bombardment time set on the timer and $t + \tau \ll T_{1/2}$; σ_0 and I_0 are the thermal cross section and

Table 2.2. Flux and monitor activity vs bombardment time at the High-Flux NAA Laboratory

Bombardment time (sec)	Thermal flux (10^{14} cm^{-2} sec^{-1})	Resonance flux (10^{13} cm^{-2} sec^{-1})	Flux ratio	Monitor activity	
				^{56}Mn (10^3 μg^{-1} sec^{-1})	^{198}Au (10^2 μg^{-1} sec^{-1})
1.0	9.01	2.04	44.1	10.1	11.0
3.0	6.32	1.43	44.2	21.2	23.2
5.0	5.60	1.63	34.3	31.5	36.6
7.0	5.20	1.50	34.7	41.0	47.6
9.0	5.20	1.51	34.4	52.6	61.3
11.0	5.10	1.53	33.3	63.2	74.1
15.0	4.92	1.58	31.1	83.4	100.0

resonance integral for production of either ^{56}Mn or ^{198}Au, and ϕ_{th} and ϕ_r are thermal and resonance flux. Since for any irradiation condition involving one nuclide over a short span of time the flux cross-section term is a constant, the equation reduces to $A = R(t + \tau)$. This is the equation of a straight line, from which the constant τ can be obtained by (1) plotting the values of Table 2.2 for A vs t, (2) finding the intercept $R\tau$ for t = 0, and (3) determining $R = A/t$ from the table for a long bombardment (e.g., t = 15.0 sec), where $T_{1/2} \gg t \gg \tau$. By using the ^{56}Mn activities of Table 2.2, we obtained R = 0.56 μg^{-1} sec^{-2} and τ = 0.94 sec. This value explains the above systematic error. With correction factors obtained from the data of Table 2.2, we are now correcting our former results for NBS orchard leaves and coal and for Bowen's kale. The new results, which indicate errors acceptable for absolute NAA, will mark the completion of our methodology study.

Applied NAA. Multielement determinations were made on a large variety of materials: coal, fly ash, creek and spring water, mosses, soils, aquatic insects, and monkey hairs. Arsenic was determined in samples from various stages in a zinc-processing plant, from the ore to the finished product, including all of the by-products. Gold was determined in more than a hundred samples of lead to be used in an experiment on convective mixing in a microgravity environment.

Several products of ^{237}Pu and ^{246}Pu were analyzed for use as tracers in environmental experiments. The Ge(Li) x-ray detector was used to determine ^{165}Er (its only emissions are holmium x rays) and ^{239}Pu in barley leaves. The limit of detection for ^{239}Pu using the L x rays is about 70 dis/min. Other nuclides measured were ^{146}Pm used in a cross-section experiment and ^{228}Ra in a ^{232}Th product.

MONSTR, the PDP-15 program for analyzing Ge(Li) gamma-ray spectra, has been used successfully to analyze x-ray spectra obtained from the Ge(Li) x-ray detector. MONSTR has also been modified for the DEC system 10 and is now being converted for the IBM 360s.

MEASUREMENT OF RADIOACTIVITY

Low-level gamma-ray spectrometry. The low-level gamma-ray spectrometry facility located in Building 4500N (Room G-4) contains three spectrometer systems: (1) a Ge(Li) system with 15% relative efficiency, (2) an intermediate-level NaI(Tl) system containing two 5- by 4-in. NaI(Tl) detectors mounted in a variable-geometry configuration within a 5-in. lead shield, and (3) an ultralow-level spectrometer developed for the Apollo lunar sample analysis program.[8]

The lithium-drifted germanium system has found widespread applications for the determination of low-concentration radionuclides in environmental samples as well as in complicated fission- and activation-product solutions. The spectrometer with the germanium detector is a modern 16K computer-based system containing automatic peak search software. The computer programs have simplified data-reduction procedures to the point that a 4096-channel spectrum can be resolved into its components in a matter of minutes, compared with the several hours required for previous spectrometers.

The intermediate-level NaI(Tl) system has been applied to the measurement of low-concentration ^{65}Zn in a unique Skylab experiment.[9] In the Skylab studies, ^{65}Zn radiotracer was used to study transport mecha-

8. J. S. Eldridge et al., "Nondestructive Determination of Radionuclides in Lunar Samples Using a Large Low-Background Gamma-Ray Spectrometer and a Novel Application of Least-Squares Fitting," *Nucl. Instrum. Methods* **112**, 319–22 (1973).

9. D. N. Braski, E. H. Kobisk, and F. R. O'Donnell, *Preparation, Testing, and Analysis of Zinc Diffusion Samples, NASA Skylab Experiment M-558*, ORNL-4956 (April 1974).

nisms of zinc atoms in molten zinc in unit-gravity and near-zero-gravity environments. Several microcuries of ^{65}Zn (range 7 to 17 μCi) were used in each of eight land-based and three Skylab experiments. The ^{65}Zn tracer transport was studied in a rod of 0.286 in. diameter by 1.84 in. length. After melting, the rods were cut into 50 or 60 segments for counting. Sample weights were necessarily small, ranging from 0.02 to 0.5 g. It was necessary to determine ^{65}Zn concentrations in each segment for all experiments. Concentrations of ^{65}Zn ranged from 6×10^{-5} to 3 μCi/g. The advantage of the intermediate-level spectrometer in these studies was the high efficiency for gamma-ray detection in such small samples, coupled with the ability to accommodate the five-orders-of-magnitude variation in the activity levels of the samples.

Experimental results from ^{65}Zn transport studies in the unit-gravity environment (earth) showed a uniform ^{65}Zn distribution (no concentration gradient). Near-zero-gravity tests (Skylab) showed distributions characteristic of simple diffusion. The unit-gravity tests showed that convection phenomena were the dominant factors influencing zinc transport.

The extreme sensitivity of the ultralow-level spectrometer was used to advantage in a search for the decay of ^{96}Zr,[10] which is one of 11 beta-unstable nuclides that are thermodynamically capable of radioactive decay but possess long half-lives compared with the age of the universe. We attempted to detect the beta decay of ^{96}Zr by the presence of its daughter nuclide, 23.4-hr ^{96}Nb, which has a large decay energy (about 3.1 MeV) and decays via a series of triple gamma-ray cascades. In our low-background spectrometer, this pattern of coincident gamma-ray transitions can lead to a high detection sensitivity as well as serving as a means of positive identification of the radionuclide.

Our sample, 9.64 g of zirconium enriched to 57.4% ^{96}Zr, was measured for 9573 min, with an additional measuring period of 6637 min for the background determination. The resulting experimental singles and coincident spectra were analyzed according to our general approach for studies of lunar samples. Analysis of the data resulted in a determination of 3.8 ppm thorium and 0.8 ppm uranium in the sample. These primordial radioelements are interferences in the measurement of ^{96}Nb disintegrations. However, we were able to set an upper limit of $\leqslant 0.13$ dis/min of ^{96}Nb, from which we compute a half-life of $\geqslant 3.56 \times 10^{17}$ years. This is possibly the longest half-life known for a beta-unstable nucleus.

10. E. Eichler, G. D. O'Kelley, J. S. Eldridge, and J. B. Ball, "A Search for the Decay of ^{96}Zr," *Phys. Rev. C*, in press.

Radionuclide characteristics and measurements. We continue to be concerned with measurements and standards for radionuclides, to study their properties, and, when asked, to advise local and outside workers on these topics. New and 30-year-old ^{226}Ra standards from NBS were compared and found to agree within less than 1%. Standards of ^{137}Cs from NBS and Amersham/Searle (British Radiochemical Centre) were found to differ by 4%, and this was confirmed by GE-Vallecitos. A number of standards were obtained for calibration of gamma spectrometers and other instruments. Advice was given to local, K-25, and Air Force personnel on standards, and reference material was furnished for radiochemical training at K-25. Three inquiries about growth and measurement of thorium daughters were answered. Information was given to the College of American Pathologists for use in a program described elsewhere,[11] contributions were made to a manual on standards,[12] and decay-scheme information was given to AEC and ASTM personnel.

Activation of NaI(Tl) detector aboard the Apollo 17 flight. Preliminary measurements[13] of induced radionuclides in the Apollo 17 detector-activation experiment resulted in qualitative identifications for ^{24}Na, ^{123}I, ^{124}I, ^{125}I, ^{126}I, ^{128}I, and possibly ^{22}Na and ^{127}Xe. We have calibrated the measurement system with accurate replicas of the flight detector filled with radioactivity standards of ^{22}Na, ^{24}Na, ^{124}I, and ^{126}I dispersed in a matrix of elemental tin. The standard radionuclide spectra were used as the library for a least-squares analysis of the original data. The sodium isotopes were available at ORNL, but the iodine isotopes had to be synthesized at the ORIC. Proton bombardment of enriched ^{124}Te and ^{126}Te targets resulted in pure ^{124}I and ^{126}I for these calibrations.

Results from this experiment have been used to help interpret some characteristics of the Apollo 15 and 16 orbiting spectra. In addition, this experiment serves as a guideline for planning of the Apollo-Soyuz joint flight in July 1975. An expanded detector-activation experiment is planned for that flight.

Cosmogenic radionuclides from Taurus-Littrow: Effects of the solar flare of August 1972. Cosmogenic radionuclide concentrations in a suite of 13 rock and 13 soil samples from the Apollo 17 collection were

11. "Reducing the Health Hazard of Poor Radioactivity Measurements," *Dimensions/NBS* 58, 44 (1974).

12. R. H. Herber, *Users' Guides for Radioactivity Standards*, AEC report NAS-NS-3115 (1974).

13. W. S. Lyon et al., "Radioactivity Measurements for the Apollo Program," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973*, ORNL-4930, p. 45.

determined nondestructively by use of gamma-ray spectrometers with high sensitivity and low background. Cosmogenic radionuclides determined in this study were ^{22}Na, ^{26}Al, ^{46}Sc, ^{48}V, ^{54}Mn, ^{56}Co, and ^{7}Be.

The pattern of radionuclide concentrations observed in the Apollo 17 samples is quite distinct from that of any previous lunar sampling mission, due to proton bombardment by the intense solar flares of August 4–9, 1972. This intense proton irradiation made it possible for us to identify ^{7}Be in a lunar sample for the first time. Data on the ^{56}Co and ^{54}Mn contents of thin surface samples were used to calculate the proton flux and rigidity of the August 1972 solar flare. We determined the integrated proton flux J_i (>10 MeV) = 1.9×10^{10} cm^{-2}; and for an energy spectrum expressed as the function $E^{-\alpha}$, the shape parameter α was found to be $1.9^{+0.2}_{-0.1}$. Thus, the solar cosmic-ray event of August 1972 exhibited a much higher proton energy than other flares of cycle 20, which had characteristic values of $\alpha \approx 3.0$. This is a cooperative project with G. D. O'Kelley of the Chemistry Division, and we are publishing a more detailed account of the work.[14]

Primordial radioelement concentrations in rocks and soils from Taurus-Littrow. Primordial radioelement (potassium, thorium, and uranium) concentrations were determined nondestructively by gamma-ray spectrometry in 13 rock and 13 soil samples collected at various sample sites in the Taurus-Littrow landing zone by Apollo 17 astronauts. Concentrations of the three elements in the soil samples were found to have a narrow range of values for seven light-mantle soils, and the values were distinctly different from those for the other six soils in this study. The thorium content of the light soils was the same as that found from orbiting gamma-ray spectrometer determinations. Little or no variation of primordial radioelement content was observed as a function of depth, color, or texture in trench samples.

Variations of Th/U and K/U ratios were observed in three types of basaltic rocks. These observations lend geochemical evidence to the speculation that two or three subfloor basalt units were sampled at the Taurus-Littrow site. Basalt samples have Th/U ratios distinctly lower than the usual lunar and terrestrial value of about 3.8. Medium- and coarse-grained basalts were found to have K/U ratios of about 4300, differing greatly from the previously observed lunar average of about 2500. These geochemical differences indicate that the basalt flows filling the Taurus-Littrow valley are not only different in themselves but also different from previously sampled basalts from other Apollo sites.

This is a cooperative project with G. D. O'Kelley of the Chemistry Division, and we are publishing a more detailed account of the work.[15]

Rapid separation of thorium from other elements. We have recently developed a new, simple, rapid method for the separation of thorium from many other elements. The method is based on the solvent extraction of thorium from dilute nitric acid solution with a tertiary amine dissolved in xylene. Subsequent stripping of the thorium from the organic phase with hydrochloric acid achieves very high selectivity with essentially quantitative recovery. The method is particularly suitable for the purification and determination of small amounts of thorium isotopes in uranium and protactinium solutions and in the preparation of ^{234}Th tracer. A paper describing this work has been accepted for publication.[16]

POLLUTION STUDIES

Trace-element profiles through a coal-fired steam plant. This NSF(RANN) project is now in its final stages; recent results have been reported in another ORNL report,[17] a final report is in preparation, and several open literature publications either have been submitted or are being written. A great wealth of information on element concentrations in coal and ash at the Allen Plant has been accumulated, and the balance now appears satisfactory (±20%) with the exception of a few elements – primarily the volatiles. Molybdenum is still the worst, with a +100% imbalance. Molybdenum results obtained by neutron activation analysis consistently check themselves, as do those obtained by a conventional wet chemical technique (ignition, fusion, dissolution, and spectrophotometric

14. G. D. O'Kelley, J. S. Eldridge, and K. J. Northcutt, "Cosmogenic Radionuclides in Samples from Taurus-Littrow: Effects of the Solar Flare of August, 1972," *Geochim. Cosmochim. Acta,* in press.

15. J. S. Eldridge, G. D. O'Kelley, and K. J. Northcutt, "Primordial Radioelement Concentrations in Rocks and Soils from Taurus-Littrow," *Geochim. Cosmochim. Acta,* in press.

16. F. L. Moore and G. G. Thern, "Rapid Separation of Thorium from Other Elements by Liquid-Liquid Extraction," *Radiochem. Radioanal. Lett.,* in press.

17. N. E. Bolton et al., *Trace Element Measurements at the Coal-Fired Allen Steam Plant – Progress Report February 1973–July 1973,* ORNL-NSF-EP-62 (June 1974).

determination by the thiocyanate method). Unfortunately, the latter method gives results about twice as high as those obtained by activation, and, more unfortunately, both sets of data show the same high positive imbalance. Attempts to resolve the discrepancy by use of other analytical techniques have so far been unsuccessful. Other elements showing poor balance are arsenic (+33%) and antimony (+41%). A partitioning effect has been observed: 17 elements primarily deposit in the slag (Al, Ba, Ca, Ce, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Th, and Ti) 6 elements concentrate in the precipitator inlet and outlet (As, Cd, Pb, Sb, Se, and Zn); Hg and Br remain in the gas phase; and Co, Cr, Cs, Mo, Na, Ta, U, and V seem to be intermediate between slag and precipitator.

During this project, virtually every tool of modern inorganic analytical chemistry has been used. We have learned a lot, but there are still many unresolved problems concerning the behavior of trace elements in a steam plant. The effect of ash particle size, furnace type, electrostatic precipitator efficiency, composition of particulate as a function of depth, and reactions of elements in particulate formation – these are some of the problems that should be studied.

Pollution abatement of toxic materials. We have continued our project on pollution abatement of toxic materials by solvent extraction. This work is supported by the ORNL/NSF(RANN) project on Ecology and Analysis of Trace Contaminants. Our technical objective is to perform research and development studies leading to new, practicable industrial separation methods for pollution abatement. A detailed account of this project is included in another ORNL report.[18]

Quaternary amines are unique in their ability to extract metal cyanides from highly alkaline solutions. Zinc cyanide is extracted essentially quantitatively at both the subnanogram and macro levels. Because they readily extract free cyanide as well as anionic metal cyano complexes, the high-molecular-weight quaternary amines show considerable promise for industrial pollution abatement applications. A paper describing this work has been prepared.[19]

18. F. L. Moore et al., *Ecology and Analysis of Trace Contaminants Semiannu. Progr. Rep. Sept. 1973,* ORNL-NSF-EATC-6, p. 333.

19. F. L. Moore, "Liquid-Liquid Extraction of Zinc with High-Molecular-Weight Amines from Alkaline Cyanide Solutions," submitted to *Separat. Sci.*

^{235}U DETERMINATIONS FOR SAFEGUARD INVENTORIES

Inventory accountability requirements for ^{235}U stockpiles in the growing nuclear power industry have recently been strengthened due to concern over possible theft or unlawful diversion of fissionable materials. It is proposed[20] that organizations with such materials in their possession be able to ascertain their fissile inventories periodically with sufficient accuracy that the measured limit of error for material unaccounted for be no greater than ±0.5% of their inventories.

The USAEC Region II Directorate of Regulatory Operations conducts on-site inventory verification inspections at several licensee facilities within its jurisdiction. To perform on-site determinations of ^{235}U, a mobile laboratory system was assembled and tested. We became involved with the calibration and testing of the system through our contacts with the Instrumentation and Controls Division. Last year[21] we reported initial field operations in which only data collection was possible at a licensee facility. Since that report, development activities have proceeded to improve both hardware and operating techniques.

Difficulties in transporting the 600-lb lead shield to a field location were encountered in most instances, mainly caused by scheduling problems with motor freight carriers and with licensee facilities for the return. It was thus desirable to transport the shield with the mobile laboratory (weight restrictions prevented the transport of the shield within the laboratory). A surplus commercial rental trailer was acquired and modified to carry the lead shield behind the mobile laboratory. Figure 2.1 shows the mobile laboratory with the trailer attached. The laboratory has been dubbed "Safeguards Mobile Assay System" (SMAS).

Fluctuating line voltages were encountered at two previous field inspection sites. To correct problems caused by the fluctuations and to improve the overall system stability, an Elgar line conditioner was installed. Temperature effects are apparently the major factors influencing the system operation at the present time.

An extended field inspection was performed at a nuclear fuel plant of the General Electric Company in Wilmington, North Carolina. On the basis of experience gained during previous field trips and calibrations

20. U.S. Code of Federal Regulations 10 CFR 70; *Fed. Regist.* **38**, 3077 (1973).

21. W. S. Lyon et al., "Special Measurements; Fission Product and Radioactive Release Studies," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 38.

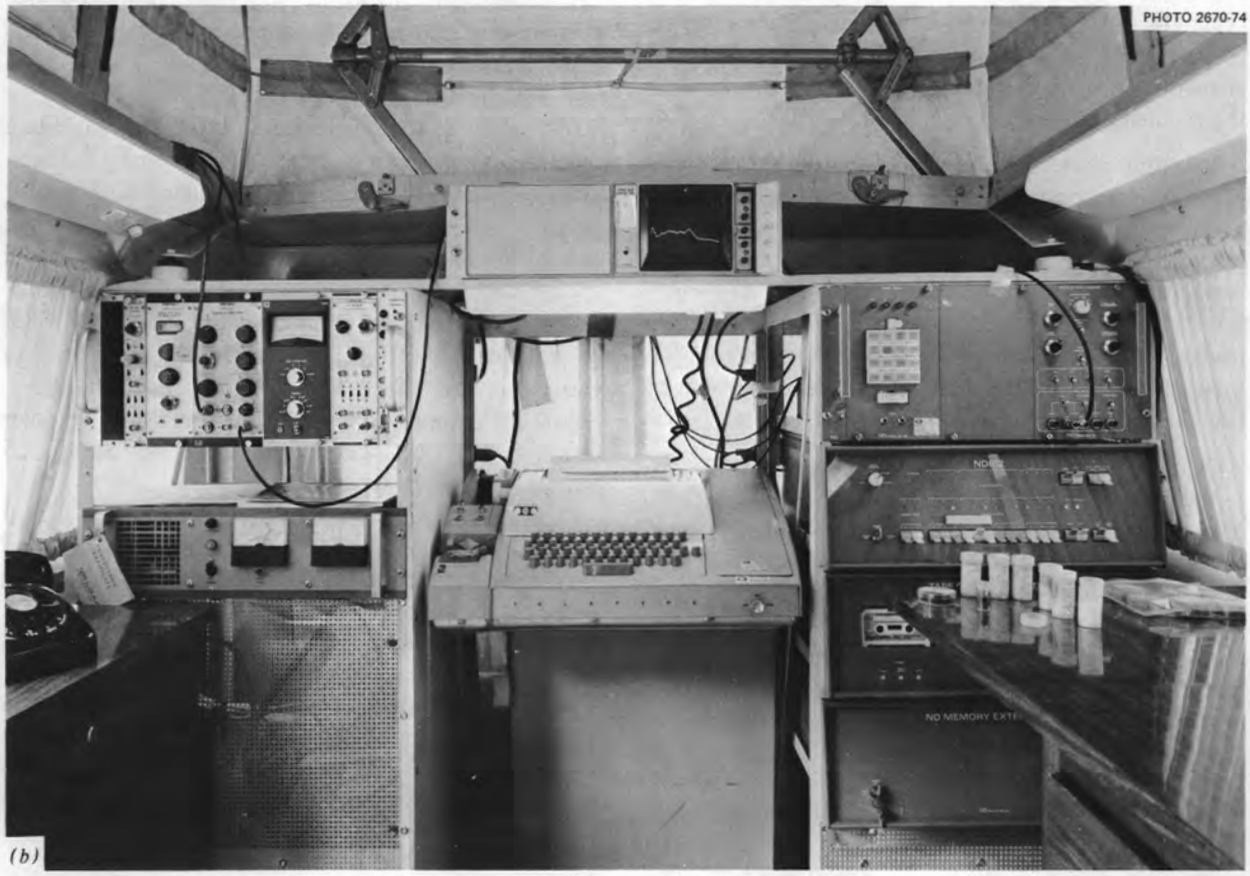

Fig. 2.1. Safeguards Mobile Assay System (SMAS). (*a*) SMAS in readiness for a field trip. The trailer carries the lead shield, and the air conditioning system is housed in the module above the cab. (*b*) Interior view of SMAS. The computer-analyzer is housed in the four modules on the right of the Teletype. Amplifier, high-voltage, and line-conditioner modules are mounted in the rack on the left. Supports for the extended roof can be seen at the top of the photograph.

performed at ORNL, it was possible to make quantitative determinations of ^{235}U in 49 pellet samples (about 11 g of UO_2, with ^{235}U varying from 1.2 to 3%). Internal standardization was performed; that is, three selected pellets were accepted as being correct, and other measurements were performed relative to those. Calculations were performed and quantitative results were obtained immediately after the measurements. Archive samples were collected from duplicate determinations to serve as standards for future measurements at this facility.

Seventy UO_2 powder samples were assayed with the SMAS, and quantitative results were calculated for each sample while the next sample was being counted. Calibration standards were available from previous archive samples, and results obtained were therefore independent of any General Electric calculations. The utility of the SMAS containing a computer-based spectrometer system was demonstrated by the ease of data collection and analysis.

Development efforts are under way to improve measurement techniques for other fuel types and enrichments. Preliminary results for finished fuel materials with 97% ^{235}U indicate that the quantitative measurement of 186-keV gamma rays is more accurate than that for lower-enrichment samples.

RADIOANALYSIS OF ENVIRONMENTAL MATERIALS

We are conducting a program of research and special analyses with the Environmental Sciences Division that emphasizes the determination of plutonium and transplutonic elements in environmental materials. Earlier plans had involved moderate levels in simulated environmental systems, but a "change in direction" has resulted in a substantial shift to field work, for example, in an old waste pond bed, involving low levels and increased demand on analytical techniques and facilities, since care must be taken to separate the desired elements from natural radioelements, whose activities are often much higher.

Aqueous behavior of actinides. We recognized a need to study the behavior of actinide elements in aqueous solutions, including sorption losses and, for plutonium, possible valence changes, in view of inconsistent results from earlier work. The stabilities of 10^{-3} to 10^{-4} *M* nitrate solutions of Pu(IV) and Am(III) were investigated, as affected by pH, complexers, and container materials. Substantial sorption losses occurred above pH 2 for 7×10^{-9} *M* plutonium and pH 3 for 2×10^{-10} *M* americium in containers of polyethylene, polypropylene, borosilicate glass, and Teflon. The first two exhibited the least sorption, which was prevented or reversed by addition of HNO_3 (0.1 to 1 *M*) or complexing agents such as EDTA, DTPA, humic acid, and citric acid. The desorption rates of the two actinides were quite similar. At 2.5×10^{-11} *M*, plutonium sorption loss was much less pronounced than at 7×10^{-9} *M*. This concentration effect, plus ready desorption, led to the conclusion that the hydrolytic behavior of plutonium at low concentrations is quite different from the polymer formation familiar at higher levels. Plutonium remaining in solution or desorbed as above was found to have remained tetravalent, rather than undergoing disproportionation as some investigators have predicted.

Analytical methodology. Chemical manipulations often involve destruction of an organic or mineral matrix, separation of the actinides from other constituents, concentration, and preparation in a thin deposit for alpha counting or spectrometry. Gamma- and x-ray spectrometry are also used for sufficiently high levels, about 100 or more disintegrations per minute for ^{238}Pu, ^{239}Pu, and ^{240}Pu and a few disintegrations per minute for ^{241}Am. Portions of a standard solution of ^{242}Pu from the AEC Health and Safety Laboratory (HASL) are sometimes added to determine recovery of plutonium (by alpha spectrometric measurement), and ^{243}Am will be used for analysis of americium when available from NBS.

We prefer wet ashing to ignition of organic materials, because of the possibility of forming refractory compounds at high temperature. For plant samples, protracted treatment with H_2O_2 (ref. 22) followed by concentrated HNO_3 has been used, and for animal tissue direct digestion with concentrated HNO_3. Hydroxide precipitation was at first used for concentrating the actinides, followed by fluoride carrying if necessary, then TTA extraction of plutonium and reprecipitation of hydroxide and fluoride for transplutonic elements. Recently we have begun tests with carrying initially on CaC_2O_4 at pH 3 to 4 in the presence of a large excess of $(NH_4)_2C_2O_4$,[23] after which oxalate is decomposed, and hydroxide, TTA, and fluoride are employed as above.

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22. B. Sansoni et al., "Rapid Assay of Environmental Radioactive Contamination with Special Reference to a New Method of Wet Ashing," pp. 487–500 in *Environmental Contamination by Radioactive Materials,* IAEA, Vienna, 1969.

23. L. C. Henley, Health Physics Division, personal communication.

It was necessary to evaluate the suitability of some of the methods in the *ORNL Master Analytical Manual* under conditions different from those specified, such as volumes, acidities, and presence of complexing agents. For example, PrF_3 carrying was found useful for actinides other than uranium, with sample volumes up to 40 ml and HNO_3 concentrations as high as 4 *M*, and it was unaffected by realistic concentrations of acetate, EDTA, citrate, and DTPA. Calcium in excess of 1 mg coprecipitates, but this can be avoided by an initial $Pr(OH)_3$ precipitation. TTA-xylene extraction from 1 to 2 *M* acid is highly selective for Pu^{4+} and has been used to determine this species in experimental samples and also as a final step in preparation of "weightless" mounts for counting. Good recoveries were obtained up to 3 *M* $HClO_4$ and from humic acid and citric acid. However, 0.006 *M* oxalic acid, 0.001 *M* fulvic acid, and 0.001 *M* DTPA caused interference. The latter two interfere by slowing the rate of extraction, thus requiring much longer than the usual 10 min.

Analyses of samples of vegetation from the waste pond bed indicated plutonium levels of 0.05 to 0.03 dis min^{-1} g^{-1} (dry), with about tenfold less transplutonics, and White Oak Lake fish samples contained plutonium at an average of 0.005 dis min^{-1} g^{-1} (wet), plus a comparable amount of transplutonics. Leaves of barley grown in nutrient solution containing plutonium had much higher levels, permitting comparison of wet ashing and alpha counting with direct x-ray counting. Results differed by 5 to 40%, probably because of variability in the sample material.

Facilities. Alpha contamination of environmental samples in the laboratory must of course be as low as possible, but many samples contain substantial beta-gamma activity, so that they cannot be handled in a typical low-level facility. Part of a radiochemistry laboratory in Building 4500S has been used for most of the work described above. Even though nanocurie levels of plutonium and americium were handled early in the program, our precautions with the low-level samples have resulted in apparently negligible "blanks" at subpicocurie concentrations. We had insufficient low-level instruments for handling the low-level samples submitted and so have used those in L. C. Henley's group in the Health Physics Division, particularly the ZnS-Mylar counter.[24] Several of the latter type have been requested, and a low-background surface-barrier spectrometer has recently been put into service in J. H. Cooper's group. Additional spectrometer detectors are needed, since overnight counts are common in this work.

Special studies. A number of radiochemical and multidisciplinary problems have arisen in the past year. The nitrate solutions of ^{238}Pu and ^{239}Pu obtained from the Isotopes Division were found by TTA extraction to contain species other than the desired Pu^{4+}, and studies were made to determine the nature of the species and how to convert it (or them) to Pu^{4+}. It was found that repeated evaporation with concentrated HNO_3 would accomplish this, and partial complexing by a trace of fluoride was postulated.

Before selecting a rare earth for fluoride carrying of actinides, a sample of $Pr(NO_3)_3$ and several of $La(NO_3)_3$ were examined by gamma spectrometry. The praseodymium salt contained only about 1 ppm thorium and was chosen for use, since all the lanthanum salts contained actinium-series nuclides.

Another interesting study concerned plutonium-bearing particles isolated from a soil sample. Two alpha-active particles of about 100 μm size were located by autoradiography. They were then placed in a scanning electron microscope, and the x-ray fluorescence spectrum was taken, showing the presence of common mineral constituents. However, the plutonium content appeared to be less than 10^{-14} g in the portion of the specimens (about 2 μm depth) accessible to the exciting electrons. Examination was continued by radiometric methods. The alpha spectrum was highly degraded, and the emission rate was estimated as 300 min^{-1}. By gamma spectrometry, the ^{241}Am content was found to be about 145 dis/min, and the plutonium content was estimated from *L* x rays to be 1500 dis/min, or about 10^{-8} g as ^{239}Pu. The various techniques indicated that plutonium was concentrated within the particles, perhaps under a coating, and thus not available for excitation in the scanning electron microscope.

Determination of ^{89}Sr and ^{90}Sr. The simultaneous radioassay of ^{89}Sr and ^{90}Sr is tedious and time-consuming when carried out by conventional counting techniques. Since both of the strontium isotopes and the ^{90}Y daughter are virtually pure beta emitters, the assay is most often made by beta counting of the mixture over a long period with subsequent resolution of the experimental decay curve. We have recently completed the development of a new and faster procedure for carrying out this analysis, taking advantage of the large differences in the observed detection efficiencies of the above isotopes when they are counted via a Cerenkov process. A general assay scheme includes the following steps. A conventional liquid scintillation

24. J. H. Harley, *HASL Procedures Manual,* HASL-300 (1972).

counting system is used to determine the counting efficiencies of ^{89}Sr, ^{90}Sr, and ^{90}Y standards in aqueous solution by the Cerenkov process. (After these factors have been determined for a particular counting system, they need to be rechecked only at very infrequent intervals.) The strontium nuclides are separated from other nuclides in the selected sample by any convenient method and are then counted by a procedure identical to that used for the standardization. The counting sample is retained, and the ^{90}Y daughter of ^{90}Sr is allowed to grow into the mixture, either for a specific waiting period or until equilibrium is reached. The sample is then recounted in the same manner. From the two experimental counts and the previously determined single-nuclide counting efficiencies, a set of simple equations can be solved for the individual strontium activities. Key factors that permit the use of this procedure are the known genetic relationship between ^{90}Sr and ^{90}Y and the very small Cerenkov counting efficiency of ^{90}Sr. Our development work shows that ratios of ^{89}Sr to ^{90}Sr between 1:10 and 10:1 can be determined with errors less than 5%. This cooperative effort with the Instrumentation and Advanced Methodology Group is being prepared for publication.

14-MeV neutron generator application. During the past year, the 14-MeV neutron generator facility in Building 2001 has been used in a variety of analytical problems. These include the determination of oxygen in such reactive compounds as WS_2, Li_3N, TcF_4, and Li metal. In addition, the compositions of coal, slag, and fly ash have been studied (Fe, Si, P, Al, O, and Mg). Fluorine has been determined in a series of 22 samples of leaves, grasses, and soils. The results (based on resolution of β^+ decay curves) were nonspecific and were expressed as a maximum concentration of fluorine that could be present.

The radionuclides produced by 14-MeV neutron bombardment of electrical insulating materials (epoxy-fiberglass) intended for use in the thermonuclear program were investigated. The total neutron dose used was 10^{12} neutrons/cm^2. This experiment will be repeated later with a Van de Graaff and a 14-MeV neutron dose of $>10^{15}$ neutrons/cm^2.

3. Energy Programs: Molten-Salt Reactor Program

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The MSBR Analytical Chemistry Research and Development Group was reestablished in March 1974 to provide analytical support for the revitalized Molten-Salt Reactor Program (MSRP), which had been terminated early in 1973. A program plan has been prepared to align the analytical effort over the next ten years more closely with other aspects of the MSRP. The long-term objective of the analytical program is to provide the chemical devices and methods for the analyses required to achieve a safe and efficient molten-salt breeder reactor (MSBR). To this end, the strongest emphasis will be assigned to demonstration of the feasibility of in-line methods for constituents or properties of reactor streams that are deemed essential for power reactor operation. Essential determinations will include the redox condition of the fuel, oxide and bismuth contamination, corrosion indicators in the fuel and coolant, and measurements of tritium distribution throughout the system. Because of the importance of such determinations, a diversity of approaches will be investigated, including electroanalytical, spectrophotometric, and chemical (transpiration) methods.

A second important objective is to develop the analytical devices and methods required by the MSRP to conduct meaningful studies and experiments on technology development in diverse areas, including development of materials for the reactor's primary circuit, fuel processing, and the distribution and containment of tritium. Such developments will, as far as possible, be timed to coincide with the needs of the MSRP and may in many cases precede the design of perfected transducers for reactor application. Experience in this and other reactor technology programs has generally demonstrated the value of in-line methods both in more economical analyses and in more timely and frequently more meaningful results. The nature of MSBR salt streams (sensitivity of samples to atmospheric contamination, equilibrium shifts on cooling, and importance of oxidation state of constituents) further enhances the value of in situ analysis. Therefore, the analytical research and development program will be directed largely to the development of in-line or in situ methods. Development of methods for the analysis of discrete salt samples will be considered individually as the need arises.

At present, we are performing in-line measurements in fuel systems and experimental studies on the electroanalytical chemistry of bismuth and tellurium in fuel salt and of oxygenated and protonated species in fluoroborate melts. Spectral and electrochemical

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research in actinide chemistry, which is in part associated with the MSRP, is being carried out at the Transuranium Research Laboratory. We are also providing limited support to other programs through special gas-chromatographic analyses and methods development, in-line gas analyses, and application of computers to analytical methods and data resolution.

IN-LINE ANALYSIS OF MOLTEN FLUORIDE SALTS

The performance of in-line analyses promotes the objectives of the Analytical Chemistry Research and Development Program by providing the MSRP with data not attainable by chemical analysis of discrete samples, and by furnishing practical experience that will aid us in achieving our ultimate goal of developing in-line analytical methods for reactor streams. Electroanalytical chemistry of molten fluorides has progressed to the point at which trivalent uranium, a very important constituent that is sensitive to atmospheric contamination, can be determined with confidence. Also, relative concentrations of ionic corrosion products that cannot be determined by wet chemical methods can be estimated. Since in-line electroanalytical methods, specifically voltammetry, can usually be applied to molten-salt streams with only nominal modifications to facilities, it is planned to perform in-line voltammetric measurements in every major installation and many minor facilities of the MSRP. Other methods, such as spectrophotometry, will be similarly applied when in-line devices are developed.

The first installation to resume operation was FCL-2b, a forced-convection loop in which fluoroborate coolant had been circulated. This loop, which is designed for studies of corrosion of structural materials under ΔT operations simulating reactor flow and temperature increments, had been modified to provide a single penetration for electrodes. We provided an electrode assembly consisting of two iridium electrodes in a ¾-in. shield tube, and we have recorded several thousand voltammograms from the initial filling of the loop and throughout controlled reduction of the fuel by beryllium additions. These measurements have provided our initial experience in electrochemical measurements in breeder fuel compositions. The solvent for the initial runs, $LiF\text{-}BeF_2\text{-}ThF_4$ (68-20-12 mole %), will later be replaced with a reference fuel composition (72-16-12 mole %). Measurements in FCL-2b will, therefore, provide a comparison of the electroanalytical properties of the reference fuel with those of the more familiar MSRE compositions ($LiF\text{-}BeF_2\text{-}ZrF_4$) and, at least qualitatively, the effects of variations in composition in the region of the reference fuel. Also, because the conditions of measurement are far from ideal (the electrodes are located in an auxiliary vessel that is closely coupled with a vibrating pump), we are gaining experience in measurement under unfavorable conditions. At present, diffusion-limited voltammograms can be obtained only when the pump is stopped and measures are taken to disrupt convective flow patterns within the electrode shield. A novel electrode assembly is being fabricated to contain five assorted electrodes within a ½-in. shield tube that can be heated above the melt level to minimize convection.

We have made measurements of several hundred electroanalytical waves, including peak heights and potentials and parameters for the assessment of ideality of wave shapes. Quantitative interpretation of these measurements is now in progress but is somewhat involved because both the temperature of the melt and the area of exposed electrode change continually after the pump is turned off. These values are expected to be sufficient to permit a comparison of the electroanalytical properties of the present and reference fuels, and some qualitative observations can be made.

Because of the absence of zirconium, the thorium-bearing fuel exhibits a higher cathodic limit than MSR compositions, allowing the observation of the $U^{3+} \rightarrow U^0$ reduction wave as well as the useful $U^{4+} \rightarrow U^{3+}$ wave. The measurements confirm the validity of the voltammetric U^{4+}/U^{3+} ratio method in this fuel. As expected, the initial charge was quite oxidizing: $U^{4+}/U^{3+} \approx 10^5$. Additions of beryllium metal in increments of 8 to 60 mg (made by loop technicians under the direction of W. R. Huntley, engineer in charge of the loop) reduced the uranium in an expected manner. In the midrange reductions, the yield of trivalent uranium reached a value equivalent to about 90% of the added beryllium metal. In earlier additions, a substantial fraction of the beryllium metal was consumed by FeF_2 and other oxidants, whereas in the more reducing melts some CrF_2 was reduced. Reductions were continued until about 2% of the uranium was converted to UF_3 and a significant reduction in the height of the $Cr^{2+} \rightarrow Cr^0$ wave was observed. We hope the data will be sufficient to estimate the equilibrium coefficient, Q, for the reaction

$$2U^{4+} + Cr^0 \rightarrow 2U^{3+} + Cr^{2+}.$$

The measurements have also served to point out problems in the application of stripping techniques to practical systems – even small variations in flow must be eliminated – and have revealed interesting anomalies in the behavior of Cr^{2+} in this melt. The chromium reduction wave is generally better separated from the uranium wave than in $LiF\text{-}BeF_2\text{-}ZrF_4$ melts. Stripping measurements have indicated that the plating of chromium virtually ceases when reductions are made at potentials several hundred millivolts more negative than the reduction wave (see Fig. 3.1). Earlier we had postulated that such an effect could occur as a result of homogeneous precipitation of Cr^{2+} by U^{3+} diffusing from the working electrode, but we were unable to demonstrate it in MSRE-type fuel or to find reference to similar phenomena, at least for inorganic systems. When the temperature of the fuel is increased, we have noted decreases in the height of chromium waves, followed by slow recovery. This behavior is unexpected, because higher temperatures tend to favor increased dissolution of chromium, and it has generally been assumed that reaction rates are quite rapid in the molten fuels.

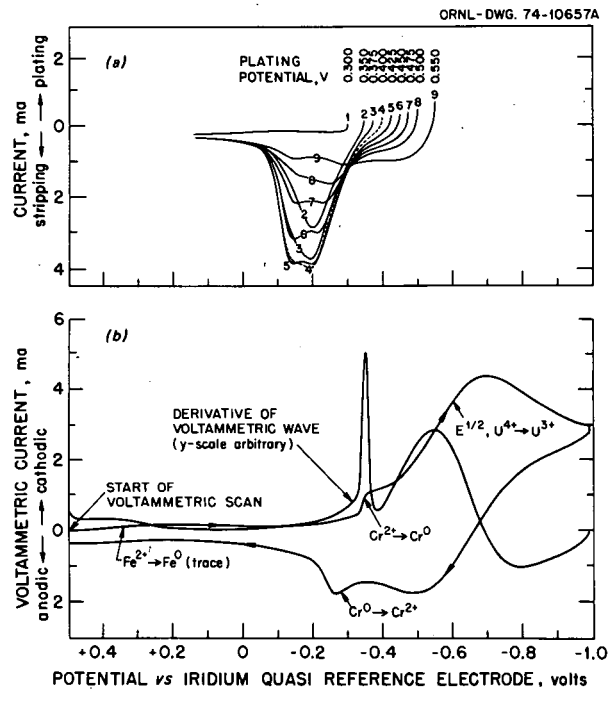

Fig. 3.1. Electroanalytical behavior of chromium in fuel solvent. (*A*) Stripping waves for chromium and Fe-Cr alloys. Plating: 40 sec at indicated potentials. Stripping scans: 0.1 V/sec. (*B*) Voltammetric wave. Scan rate: 0.1 V/sec. Fuel solvent: $LiF\text{-}BeF_2\text{-}ThF_4$ (68-20-12 mole %). Melt temperature: ~615°C. Uranium concentration: 1.4 wt %. U^{4+}/U^{3+} ratio: ~10^4. Total chromium concentration: ~100 ppm. Electrodes: 18 gage iridium, ~1 mm diameter, ~1 cm insertion.

Work is now in progress to examine the fuel during reoxidation by NiF_2 and to prepare for the in-line measurement of protonated species and corrosion products in the coolant salt, $NaF\text{-}NaBF_4$ eutectic, in the Coolant Salt Technology Facility.

ELECTROANALYTICAL STUDIES IN MOLTEN $NaBF_4$-NaF EUTECTIC

We have resumed electroanalytical studies in a fluoroborate coolant melt prepared from materials purified during the earlier program. Planned studies of the free proton wave have been delayed by the failure of our only remaining hollow palladium electrode. While awaiting materials for the fabrication of new electrodes, we have started studies of corrosion products. The $Fe^{2+} \rightarrow Fe^0$ reduction has been observed to conform to a soluble species reduction at a gold electrode and to a partially soluble species reduction at an iridium electrode, as demonstrated by chronopotentiometric measurements, which serve as useful indicators of the nature of the electroreductions. For the soluble species case, the ratio of the forward to the reverse transition time is 3:1, but for the insoluble case it is 1:1. For both electrode materials the observed ratio is approximately 3:1. It was noted earlier,[4] on the basis of wave positions and slopes, that chromium alloys with gold but not with iridium or pyrolytic graphite electrodes.

It is of practical analytical interest to establish the nature of the electrodeposition reactions. Generally, alloying is favorable for direct voltammetric measurements, because the position of the waves does not change with concentration and such soluble systems are amenable to square-wave voltammetry, which offers increased sensitivity and stability.[5] We have applied this technique (typically a 400-Hz, 50-mV square wave superimposed on a 0.1-V/sec linear ramp) and obtained well-defined waves with current enhancement in close agreement with theoretical predictions.

After chromium is added as Na_3CrF_6 to the melt, the iron and chromium waves are resolved without difficulty. The peak potentials are separated by about 350 mV, which is adequate for analytical purposes. However, at slow scan rates (<0.5 V/sec), the chromium

4. A. S. Meyer et al., "Analysis of MSRP Coolant Salt," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 26.

5. D. L. Manning and G. Mamantov, "Studies on the Electroreduction of Uranium(IV) in Molten $LiF\text{-}BeF_2\text{-}ZrF_4$ by Square Wave Voltammetry," *Electrochim. Acta* **19**, 177 (1974).

wave in the presence of iron is not as well defined as in the absence of iron. This is probably caused in part by the predeposition of iron on the gold electrode, which alters the surface characteristics of the electrode by the time chromium is deposited. At faster scan rates this distortion for the most part disappears and the waves are well defined. Linear plots of i_p vs $v^{1/2}$ were obtained for both species. A calculation of the iron concentration from the slope of the line agreed well with the value (about 300 ppm) from chemical analysis. A similar calculation for the concentration of chromium revealed a value of 130 ppm. This is low compared with the amount of chromium (about 260 ppm) added to the melt but in agreement with the value of about 125 ppm obtained from chemical analysis. The melt, therefore, is probably saturated in chromium at about 125 ppm at 500°C. We will make measurements and take a sample at 600°C to observe the effect of temperature on the chromium solubility. Concentration values from square-wave voltammograms recorded at 400 and 900 Hz agreed with the linear scan results. As expected, the addition of chromium exhibited no effect on the chronopotentiograms for the iron wave, which conforms to a soluble species reduction at a gold electrode.

Voltammetric studies were also carried out for an anodic wave seen at a gold electrode at about +1.5 V vs an iridium quasi-reference electrode (Ir QRE). We are reasonably sure that this wave is related to the $NaBF_3OH$ content of the melt, the electrode reaction probably being $OH^- \rightarrow H^+ + \frac{1}{2} O_2 + 2e^-$. The wave is reasonably well defined; noise is encountered on the diffusion-current plateau, which is indicative of gas formation at the electrode surface. However, the wave is irreversible; no reverse current is seen even at relatively fast (20 V/sec) scan rates. In nonrecrystallized "as is" $NaBF_4$, which was found to be 16 m*M* $NaBF_3OH$ by infrared spectroscopy, the wave height was about 1.5 mA. In a recrystallized batch of $NaBF_4$, about 120 m*M* in $NaBF_3OH$, the wave height increased to about 30 mA. The wave height varied in proportion to the ratio of known mixtures of the nonrecrystallized and recrystallized salt used to prepare the melt, and it appeared to be stable with time. Additional calibration will be required, but it appears that this anodic wave will prove valuable for the investigation of the effect of BF_3OH^- on corrosion and on tritium containment by coolant salt.

ELECTROANALYTICAL STUDIES IN MOLTEN $LiF\text{-}BeF_2\text{-}ZrF_4$ (65.6-29.4-5.0 MOLE %)

While awaiting delivery of the thorium-containing MSR fuel salt, we set up two cells for electrochemical studies on tellurium and bismuth in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ left over from the earlier program.

Electroanalytical studies of tellurium are of interest, since tellurium occurs in nuclear reactors as a fission product and recently has been considered a prime cause of stress corrosion cracking in structural metals and alloys.[6] For the tellurium studies, the melt was contained in a pyrolytic boron nitride cup, and the holder for a small tellurium pool electrode (1/8-in. diam) was fabricated from hot pressed BN. Contact to the molten tellurium pool was made with iridium wire.

Cathodic polarization curves on the tellurium pool electrode immediately after the electrodes were dipped into the melt at 500°C revealed a prewave at about −0.6 V vs an Ir QRE, followed by the limit at about −0.75 V. The anodic limit occurred at about 0.9 V. After about 24 hr, the anodic limit remained the same; however, the prewave shifted to about −0.8 V and the cathodic limit was seen at about −0.9 V. After this initial shift, the potentials of the prewave and cathodic limit remained stable.

The anodic limit is believed to be due to the oxidation of tellurium, and the cathodic limit corresponds to the reaction $2Li^+ + Te + 2e^- \rightarrow Li_2Te$. The voltage span from anodic to cathodic limit of about 1.6 V (fresh tellurium surface) and 1.8 V (aged surface) can be compared with 1.2 V in LiCl-KCl at 450°C reported by Bodewig and Plambeck;[7] however, they did not report a prewave prior to the cathodic limit as observed in the molten $LiF\text{-}BeF_2\text{-}ZrF_4$.

The cause of this prewave is unknown. It was not seen on background scans, and the wave height did not change significantly with time after the tellurium electrode was dipped in the melt. One possibility is the reduction to a lower-valence species, such as $LiTe_3$, by some impurity route. Bamberger, Young, and Ross[8] have reported the existence of such Li_mTe_n species in molten fluorides on the basis of spectral studies.

Chronopotentiograms recorded for this wave at the tellurium pool electrode, although not well defined in all cases, did reveal a ratio of forward to reverse transition times (τ) of about 3:1. Adsorption of the tellurium species at the electrode was also indicated from the chronopotentiometric data, since the $i\tau^{1/2}$

6. H. E. McCoy, "Materials for Salt-Containing Vessels and Piping," *The Development Status of Molten-Salt Breeder Reactors*, ORNL-4812 (August 1972), p. 195.

7. F. G. Bodewig and J. A. Plambeck, "Electrochemical Behavior of Selenium and Tellurium in Fused LiCl-KCl Eutectic," *J. Electrochem. Soc.* **117**, 618 (1970).

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

product consistently increased with increasing current density.

Adsorption of the supposed tellurium species was also noted at gold and iridium electrodes, as indicated by voltammetric and chronopotentiometric data. The chronopotentiometric results best fit the equation pertaining to the simultaneous reduction of diffusing and adsorbed species,[9] which is given as

$$i\tau = \tfrac{1}{2}\, nF\pi^{1/2}\, AD^{1/2}\, C\tau^{1/2} + nAF\Gamma,$$

where Γ is the surface excess (moles/cm^2) and the other terms have their usual significance. Calculation of the Γ term assuming an n value of 2 (probably the limiting case) gave a value of about 4×10^{-9} mole/cm^2, which can be compared with about 10^{-10} mole/cm^2 seen in aqueous systems.[9]

These observations are believed to support other work[6] that points to tellurium stress corrosion cracking. Adsorption of tellurium compounds would provide a reservoir of tellurium at the surface. The adsorbed Li_mTe_n species may disproportionate to more stable tellurides and elemental tellurium. Elemental tellurium in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ is more difficult to reduce than Ni^{2+} or Fe^{2+}, being comparable with Cr^{2+} and more easily reduced than U^{4+}. As known Li_mTe_n species become available, we plan to make standard additions to the fuel salt for electroanalytical studies. Provided the electrode reactions are reversible, we hope to extend the limits of detection by pulsed voltammetric techniques.

Bismuth, because of its use in salt stream purification systems,[10] is a possible impurity in a reactor fuel salt. For our previous work on bismuth,[11] the melt was contained in graphite or copper cells. Bismuth (added as BiF_3) was slowly lost from the molten $LiF\text{-}BeF_2\text{-}ZrF_4$ at 500°C. The two main routes for the loss would appear to be the reduction of the Bi^{3+} by the container material and volatilization of the BiF_3. For further investigation of this problem, a cell containing Bi^{3+} was set up; the melt was contained in a glassy carbon cell.

Well-defined voltammograms and chronopotentiograms were obtained in a melt approximately 10 m*M* in BiF_3 at gold, iridium, and glassy carbon electrodes. The peak potential for the $Bi^{3+} \rightarrow Bi^0$ reduction occurs at about −0.1 V vs the Ir QRE (prior results[11] showed that this reduction occurs at about +0.1 V vs an Ni(II)-Ni reference electrode). For the chronopotentiograms, the ratio of the forward and reverse transition times was essentially unity at the three indicator electrodes. Again, however, the bismuth was slowly lost from the melt, as revealed by a gradual decrease in the peak height of the voltammograms with time. For a check of volatilization, a cold finger was placed in the cell for a few days, and an x-ray fluorescence analysis of the deposited film indicated that the major constituent was indeed bismuth. Thus it now appears that bismuth is slowly lost from molten $LiF\text{-}BeF_2\text{-}ZrF_4$ primarily by volatilization, in agreement with the work of Cubicciotti.[12]

We will continue these studies to determine the lower limits of detection by voltammetry and stripping techniques. We believe that meaningful analytical results from on-line measurements can still be obtained, because the rate of bismuth loss is slow. Nickel constitutes a primary interference, so studies will be made on melts containing both bismuth and nickel.

SPECTROPHOTOMETRIC RESEARCH

Spectral techniques are being applied to the area of transuranium element research to provide information for the identification and characterization of various oxidation states of these ions in the liquid or solid state. This work provides basic information that is useful for analytical applications to other interests of the Division, particularly the MSRP, and has generated a potentially valuable family of radioisotopic light sources.

Further experimental work on the *f-d* and charge-transfer absorption spectra of trivalent lanthanide and actinide halides has demonstrated that charge-transfer band position can be predicted by the theory of Vander Sluis and Nugent,[13] but as postulated in the last report,[14] the prediction of *f-d* band positions seems to require knowledge of *d*-level splitting. In conjunction with L. J. Nugent and K. L. Vander Sluis, a paper describing these results is being written.

9. S. V. Tatwawadi and A. J. Bard, "Chronopotentiometric Measurement of Adsorption," *Anal. Chem.* **36**, 2 (1964).

10. L. E. McNeese, "Fuel Reprocessing," *The Development Status of Molten-Salt Breeder Reactors,* ORNL-4812 (August 1972), p. 331.

11. J. S. Hammond and D. L. Manning, "Studies on the Electroreduction of Bismuth(III) in Molten $LiF\text{-}BeF_2\text{-}ZrF_4$ by Voltammetry and Chronopotentiometry," *High Temp. Sci.* **5**, 50 (1973).

12. D. Cubicciotti, "Thermodynamic Properties of Bismuth Trifluoride," *J. Electrochem. Soc.* **15**, 1138 (1968).

13. K. L. Vander Sluis and L. J. Nugent, "Relative Energies of the Lowest Levels of the $f^q ps^2$, $f^q ds^2$ and $f^{q+1} s^2$ Electron Configurations of the Lanthanide and Actinide Neutral Atoms," *Phys. Rev. A* **6**, 86 (1972).

14. A. S. Meyer et al., "Spectrophotometric Research," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 31.

A study of the effect of temperatures from 25 to about 700°C on the spectra and x-ray diffraction of microgram amounts of crystalline $CfBr_3$ has been carried out. Spectroscopic evidence indicated that $CfBr_3$ undergoes reduction to produce Cf(II) with increasing temperature, with about 15 to 30% reduction at 600°C. Despite the ingrowth of Cf(II) into the $CfBr_3$ with increasing temperature, powder diffraction patterns exhibited only the monoclinic $AlCl_3^-$-type structure characteristic of $CfBr_3$, confirming this structure type as the high-temperature one. A mechanism involving a reversible shift of electron density from the Br(I) ions to the Cf(III) ions with increasing temperature is postulated to explain satisfactorily the experimental observations made in the present study. Californium triiodide is predicted to undergo thermal reduction to Cf(II) more easily than $CfBr_3$. A paper on this subject has been submitted for publication.[15]

Certain crystals doped with actinide ions exhibit an orange radioluminescence when freshly annealed and warm, which differs from the bluish radiation they emit when aged or cooled. As part of a general study of the properties of such doped crystals, the radioluminescence of ^{253}Es- and ^{244}Cm-doped $SrCl_2$ was studied as a function of time after annealing and of temperature over the range of 77 to 700°K. Prior to this investigation, radioluminescence studies apparently have been made on crystals at room temperature or below. It was demonstrated that the color changes seen as the temperature is raised from 300 to 700°K are not due to annealing of radiation damage but are due generally to changes in host emission. Particularly in the case of ^{253}Es-doped $SrCl_2$, there is also a longer-term effect, darkening of the crystal, which is caused by radiation damage and can be removed by annealing. The luminescence properties of ^{253}Es- and ^{244}Cm-doped $SrCl_2$ are similar below room temperature and appear to be associated with *F*-center formation. The high-temperature (>500°K) luminescence is due to another as yet unidentified center. The luminescence is quite stable, since the long-term darkening of the crystal is eliminated. The high-temperature, stable emissions of these and future radioluminescent crystals have been proposed as solid-state radioisotopic light sources for use in high-temperature applications, such as in the MSRP for precise colorimetric analyses according to the technique described by Ross.[16] A paper describing these radioluminescence studies is being written.[17]

We are continuing to investigate molten salts as a medium for the electrochemical generation and spectral characterization of unusual oxidation states of transuranic ions.[14] Molten KF-HF mixtures continue to appear as a good general solvent system for these and related studies. Molten hydroxides and oxides have not totally been eliminated for specific applications, but work in these systems is not presently under way.

Apparatus has been designed and fabricated for electrochemical and spectral studies of KF-HF mixtures of varying and controlled compositions under approximately isothermal conditions. The spectral-electrochemical (S-E) cell consists of three compartments (working, counter, and reference) separated from each other by an insertable plug that contains a porous Teflon film separator.[18] The cell and plugs are made of Teflon, and sealable windows made from Al_2O_3 are on opposite sides of the working compartment, so that spectral and visual observations of the compartment can be made. The furnace is designed so that the cell is located in a cavity of a massive nickel cylinder heated by cartridge-type heaters. The lid to this furnace body is nickel and is sealed to the body by a Teflon O-ring. The electrodes are molded into a ¾-in.-diam Teflon rod, and this electrode assembly, when in place for study of the melt, provides a gas-tight seal directly above the melt so that the required pressure of HF gas, added to or generated by the melt, is maintained essentially isothermally. The body of the furnace contains Al_2O_3 windows sealed by Teflon O-rings. The furnace, because of the Teflon seals, is limited to use at temperatures below about 260°C, but this is adequate for the KF-HF melts of interest. The complete assembly is vacuum tight, for use with HF or ClF_3 gas, and air-cooled. The entire apparatus is used with a glove box of special design, which fits in the sample space of a Cary spectrophotometer, model 14H. The glove box is required for work with transuranic elements.

A few preliminary electrochemical studies have been carried out in the S-E cell, but since no previous cyclic voltammetric studies of KF-HF melts have been per-

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(II)," submitted to *J. Inorg. Nucl. Chem.*

16. H. H. Ross, "New Concept in Precision Photometric Analysis Using a Radioisotopic Light Source," *Anal. Chem.* **38**, 414 (1966).

17. J. P. Young and C. B. Finch, "The Effect of Temperature on the Radioluminescence of $SrCl_2$ Doped with ^{253}Es or ^{244}Cm; Observation of Host Defect Emissions," to be submitted for publication.

18. Available from W. L. Gore and Associates, Inc., Newark, Delaware 19711.

formed, such studies are being carried out with the melt held in a Teflon crucible within the furnace. Electrode systems studied to date include combinations of graphite, amorphous carbon, copper, nickel, and platinum. There appears to be a span of approximately 5 V from H_2 evolution to, probably, F_2 evolution at a carbon electrode. Hydrogen gas is evolved at about −0.9 V relative to a copper reference electrode. No well-defined reproducible wave has been seen for the oxidation of O^{2-} (or OH^-), but at times a small oxidation wave at 1.9 V relative to copper appears, which might be due to this process. At a platinum electrode with scan rates greater than 20 V/sec, reversible H_2 waves are obtained. At medium or fast voltage scan rates at a carbon electrode, essentially no anodic currents are observed prior to the limit. If this is not an indication that the electrodes are passivated – and they do not appear to be – the solvent in this region will be ideally suited for the oxidation of the transuranic ions that we wish to study. Although graphite electrodes seem stable to fluorine evolution by voltammetry, they are decomposed to powder in the presence of ClF_3, which we have used in the purification of KF-HF salt prior to melting. There is some indication that copper electrodes become passivated when used anodically, but the mechanism is not understood at present.

Spectrally, KF-HF melts seem ideally suited as a transparent solvent. The melt is transparent from 220 to 1900 nm. It was observed, however, in the experiment in which graphite was destroyed by ClF_3, that the subsequent melt became opaque at 1380 nm, possibly due to absorption by some product formed by the reaction of ClF_3 with the solvent salt, graphite, or some other unknown reactant. The addition of praseodymium metal to the melt causes the evolution of hydrogen, and the spectrum of Pr(III) grows into the melt. It is interesting to note that the *f-f* transitions of Pr(III) in molten KF-HF at 250°C are more like those seen in aqueous solution than those seen in either molten LiF-NaF-KF, LiF, or even LiCl-KCl.

R. L. Fellows, a postdoctoral fellow, and J. R. Peterson, University of Tennessee, are cooperating in the above study.

ANALYSIS OF OFF-GAS SCRUBBER SOLUTION

A method for the determination of methyl iodide, methyl nitrate, and methyl alcohol in 20 *M* nitric acid solutions by gas chromatography was developed. This method was needed to provide support for studies of the scavenging of organic iodides from reactor off-gas streams. The separation and subsequent determination depend on proper conditioning of the column with water. A complete discussion of the method has appeared elsewhere.[19]

19. R. F. Apple, H. G. Davis, and A. S. Meyer, "Analysis of Methyl Iodide, Methyl Nitrate, and Methyl Alcohol in 20 *M* Nitric Acid," *Anal. Lett.*, in press.

4. Energy Programs: Gas-Cooled Reactor Programs

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During midyear, a Gas-Cooled Reactor (GCR) Analytical Chemistry Development Program was initiated. This program can be loosely grouped into two areas of activity – methods development and technical assistance.

The purpose of the methods development and evaluation program is to ensure adequate capabilities for the complete chemical characterization of high-temperature gas-cooled reactor (HTGR) fuel as required by the specifications shown in Table 4.1. The

Table 4.1. Specifications for HTGR fuel

Process stage	Specification	Method of analysis
Uranyl nitrate feed solution	Total uranium content	Potentiometric titration
	Uranium isotopic content	Mass spectrometry
	Impurities content	Mass spectrometry
	Nitrate content	Kjeldahl
	Acidity, conductivity, density	Conventional
Dried loaded resin	Uranium content	Potentiometric titration
	Impurities content	Mass spectrometry
Carbonized microspheres	Uranium-to-carbon ratio	Combustion-gravimetric
Converted microspheres	Carbon content	Combustion-gravimetric
	Oxygen content	Inert gas fusion–gravimetric
Inner LTIP-coated microspheres[a]	Carbon content	Combustion-gravimetric
	Inner LTIP coating density	Gradient density
	Particle density and porosity	Mercury penetration
SiC-coated microspheres	SiC coating density	Gradient density
Outer LTIP-coated microspheres	Outer LTIP coating density	Gradient density
	Particle density and porosity	Mercury penetration
	Carbon content	Combustion-gravimetric
	Impurities content	Mass spectrometry
	Uranium contamination of surface	Gas-flow proportional counting
Green rods	Filler content of matrix	Dissolution-gravimetric
Fired rods	Uranium content	Potentiometric titration
	Thorium content	Volumetric EDTA titration
	Impurities content	Mass spectrometry
	Broken-particle fraction	Chlorination

[a]LTIP, low-temperature isotropic pyrocarbon.

majority of the recommended methods of analysis listed represent analytical capabilities that have existed at the Laboratory for many years and have been applied to the analysis of a wide variety of reactor fuels and materials. However, due to the uniqueness of the HTGR fuel, it will be necessary either to modify and adapt these methods or to develop new ones and then evaluate them to ensure that they are adequate for the accuracy and precision of the fuel specification. Our initial efforts are to evaluate these methods for fresh fuel containing ^{235}U and then adapt them for glove-box and/or remote operation for analysis of aged recycle fuel containing ^{233}U and several hundred ppm ^{232}U. The presence of gamma-emitting decay products of ^{232}U in the aged recycle fuel requires that these analyses be performed in shielded glove boxes or hot cells.

The purpose of the technical assistance program is to ensure that the technical requirements of the various tasks and activities of the GCR program are being met by the analytical facilities of the Laboratory. To accomplish this purpose effectively, a continued effort is made to foster a close working relationship between analytical chemists and fuel-process chemists, material scientists, reactor engineers, and related experimentalists. At present, the emphasis of our work varies with the immediate needs and technical requirements of the various tasks and activities of the GCR program. The analytical assistance program includes activities in support of the GCR Base, Thorium Utilization, and Safety Programs conducted by the Metals and Ceramics, Chemical Technology, and Reactor Divisions.

DETERMINATION OF BROKEN-PARTICLE FRACTION

The determination of the number of broken particles in a fuel rod is one of the most important specifications for qualification of HTGR fuel, because particles with damaged coatings and exposed fuel release fission products to the reactor system. The specification for the broken-particle fraction in a fuel rod is 10^{-4}, or approximately one broken fuel particle in a fuel rod containing 10,000 to 15,000 particles.

The methods currently used are slow and at best semiquantitative, especially for fuel rods containing thoria particles. They involve either (1) the deconsolidation of the fuel rod, aqueous acid leaching of the separated particles for many hours (>50 hr for thoria kernels), and spectrophotometric measurement of the dissolved heavy metal; (2) high-temperature treatment of the fuel rod to convert exposed heavy metal to the carbide, pyrohydrolysis of the carbide, and gas-chromatographic measurement of the released ethane; or (3) neutron irradiation of the fuel compact and measurement of the released fission-product gases.

We continued our effort to develop and use the chlorine leach method for the determination of damaged fuel particles consisting of ThO_2 and/or uranium oxides or carbides.[1] Essentially, the method consists of passing chlorine over coated fuel particles at high temperatures. The chlorine reacts through cracks in the coatings to form the volatile chlorides, which deposit in the cool zone of the furnace tube and can be washed out for analysis to give a measure of the number of damaged microspheres.

We first developed a method in which chlorine is passed over the microsphere contained in a porous carbon boat heated in a resistance furnace to 1050°C. For loose particles, chlorination of exposed fuel was effected in 6 to 8 hr. For fuel rods, however, up to 50 hr was required to remove the exposed fuel completely by chlorination. To reduce the time required to effect quantitative chlorination and removal of the exposed fuel, the reaction temperature was increased to 1500°C. The fuel rods were held vertically in a graphite holder within a water-cooled quartz furnace tube and heated by induction to 1500°C. At this temperature, complete removal was effected in about 8 hr. To reduce the analysis time further, the chlorination apparatus was modified so that chlorine was forced through rather than over the fuel rod. With the flow-through system and a temperature of 1500°C, the time required to remove the exposed fuel completely was reduced to 2 hr.

The above methods were developed for the so-called "biso" microspherical particles, which consist of a kernel of thorium oxide or carbide coated with a porous layer of pyrocarbon and a layer of low-temperature isotropic pyrocarbon. We are evaluating this method for the "triso" particles, which consist of a

1. D. A. Costanzo et al., "Determination of Damaged Particles in HTGR Fuel Compacts," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973*, ORNL-4930, p. 57.

kernel of uranium or thorium oxide or carbide coated with a layer of porous pyrocarbon and a layer of silicon carbide sandwiched between two layers of low-temperature isotropic pyrocarbon.

DETERMINATION OF URANIUM AND THORIUM IN PYROCARBON- AND SILICON CARBIDE-COATED FUEL PARTICLES[2]

We participated with five other chemistry laboratories and three nondestructive assay laboratories in an interlaboratory evaluation program for the purpose of determining state-of-the-art measurement for uranium and thorium in pyrocarbon- and silicon carbide-coated uranium and thorium carbide particles. The program was conducted by the New Brunswick Laboratory.[3]

Accurate analyses of the coated fuel particle for heavy metal are made extremely difficult by the successive layers of chemically inert pyrocarbon and silicon carbide coatings surrounding the kernel. Conversion of the coated particle to the solution form amenable to analysis is the most difficult part of the heavy-metal assay, and because of the number of chemical treatments required to convert the particles to the solution, high precision and accuracy are difficult to obtain.

We employed classical sample pretreatment, which involves igniting the particles to remove the pyrocarbon, fusion of the residue with sodium carbonate to convert the silicon carbide to the soluble form, dissolution of the fission melt with nitric acid, and filtration of the acid solution to remove the silica. Uranium was determined by the potentiometric titration method of Davies and Gray,[4] and thorium was determined by oxalate precipitation and gravimetric measurement. With the above methods, the relative standard deviation of the mean for thorium and uranium was approximately 0.1%; however, in comparison with results of all participants for phase I of the interlaboratory comparison, our results for both thorium and uranium indicated a bias in our measurements.

In phase II of the interlaboratory evaluation program, we are evaluating a different method for pretreatment of the sample, in which the tedious and time-consuming fusion step is eliminated. In this method the sample will be crushed and ignited to 900°C to remove the pyrocarbon, the ignition residue will be leached with nitric acid, and the solution will be filtered to remove the silicon carbide residue. To ensure that all of the heavy metal has been removed from the silicon carbide residue and recovered, the residue will be fused with sodium carbonate, and the negligible amount (<0.5% of total heavy metal) will be determined by less precise methods of measurement.

DETERMINATION OF OXYGEN BY INERT GAS FUSION

An apparatus for the gravimetric determination of oxygen in HTGR fuel particles containing an oxycarbide kernel was assembled and evaluated using NBS standard 950a U_3O_8 and UO_2 microspheres. The procedure was similar to that of Holt and Stoessel.[5] A sample containing 30 to 40 mg of oxygen is weighed into a platinum capsule, which is placed in a carbon crucible. Additional platinum is added to the crucible to serve as a bath. The sample is heated by induction in a stream of argon for 10 min each at temperatures of 1690, 1820, and 2000°C. The evolved CO is oxidized to CO_2 by passage through hot copper oxide, collected on Ascarite, and weighed. Even though our data indicate that approximately 80% of the CO is evolved at 1820°C, it is necessary to heat the sample initially at lower temperature to prevent the rapid evolution of gas and entrainment of the unreacted sample. It was also found that an increase to 2000°C was necessary to extract the last 1 to 2% of the oxygen. The precision and accuracy of this method were found to be on the order of ±2%.

We studied the effect of glove-box atmosphere on the oxygen contamination of pyrophoric fuel kernels. Oxygen was determined by the Leco method, which also employs inert gas fusion. However, much smaller

2. Cooperative program with the General Analyses Laboratory.

3. C. D. Bingham and J. Whichard, *Evaluation of an Interlaboratory Comparison Involving Pyrocarbon and Silicon Carbide-Coated Uranium-Thorium Carbide Beads,* New Brunswick Laboratory Report NBL-269 (November 1973).

4. A. R. Eberle et al., *Titrimetric Determination of Uranium in Product, Fuel, and Scrap Materials after Ferrous Ion Reduction in Phosphoric Acid: Part I. Manual Titration; Part II. Automatic Titration,* New Brunswick Laboratory Report NBL-252 (July 1970).

5. B. D. Holt and J. E. Stoessel, "Macrodetermination of Oxygen in Metal Oxide by Inert Gas Fusion," *Anal. Chem.* 36, 1320–24 (1964).

amounts of oxygen (0 to 500 μg) are measured by gas chromatography. The results of this study have been reported by D. R. Johnson and F. L. Layton.[6]

DETERMINATION OF SURFACE CONTAMINATION OF HTGR FUEL PARTICLES

Gas-flow proportional alpha counting was evaluated for the determination of surface contamination of HTGR fuel particles. To measure the amount of surface activity by direct counting of the particles, we determined the counting efficiency for HTGR particles as follows. One-gram test portions of undamaged biso-coated thoria particles were counted as a monolayer in a gas-flow proportional alpha counter to determine surface background contamination. The particles were then leached to remove any loose graphite debris, recounted, and soaked in a solution of ^{233}U. After filtering and drying, the contaminated particles were counted and then leached to remove the contamination. The leach solution was collected and made to a known volume, after which the disintegration rate per milliliter of leach solution was determined. The particles were then recounted to assure that all contamination had been removed. The true level of ^{233}U contamination of the particles and the apparent level of contamination (as determined by counting of the particles) can be used to determine the counting geometry of the particles. The counting geometry is given by a ratio of the counts of the contaminated particles to the total disintegrations found in the leach solution.

A difference in geometry was found between particles with low and high surface areas, as determined by krypton absorption. Fuel particles evaluated had surface areas ranging from 0.03 to 0.12 m^2/g. Particles with low surface area exhibited a counting geometry of approximately 0.25, and those with high surface area gave a counting geometry of approximately 0.20. There did not appear to be a linear relationship between surface area and counting geometry. The average counting geometry determined for the particles was 0.22, and the relative standard deviation of the mean was 13.6%.

Particles that exhibit a larger surface area have more irregular surfaces with open porosity. Activity located in the open pores of the particle surface is leachable but is not detected and counted when the particles are counted, resulting in a lower counting geometry. In addition, the absorbed activity below the horizontal midplane of the particles is not seen by the collecting electrode of the 2π gas-flow detector. As a result, the expected geometry for counting particles should be on the order of 0.25.

DETERMINATION OF ^{14}C IN PRIMARY BURNER OFF-GAS FROM HTGR FUEL

Liquid scintillation beta counting was evaluated for the determination of ^{14}C in carbon dioxide evolved during the burning of spent reactor fuel elements. A series of determinations was run on ^{14}C contained in CO_2 evolved from barium carbonate solution to determine the efficiency of collection of carbon dioxide. The carbon dioxide was absorbed in "hydroxide of hyamine," a quaternary chloride that has been converted to the hydroxide.

A barium carbonate solution containing a known amount of ^{14}C was acidified, and the evolved CO_2 was collected in a series of bubble columns containing hydroxide of hyamine. The beta activity of the hyamine solutions was determined by liquid scintillation counting to determine the efficiency of collection of carbon dioxide.

A series of two runs was made collecting CO_2 in the manner described above. In the first run 98.65% of the ^{14}C activity evolved in the CO_2 was found in the first bubble column, and in the second run 98.30% was found in the first bubble column. From the above results it appears that hydroxide of hyamine is an efficient absorber of CO_2. The yields from the barium carbonate solutions did not exceed 89%, but the hyamine solution in the first bubble column absorbed more than 98% of the CO_2 evolved.

CHARACTERIZATION OF THE SURFACE OF PYROCARBON-COATED PARTICLES[7]

During the process of bonding HTGR fuel particles into fuel rods, a carbonaceous bond is formed between the surface of the fuel particles and the rod matrix. During heat treatment and during irradiation, the matrix shrinks, and if the particle-matrix bond is too strong, the coating can be torn. Such torn coatings are very undesirable; thus, the strength of the particle-matrix bond is of great interest. The strength of this bond is thought to be related to the roughness and/or porosity of the outer layer of the pyrocarbon coating.

6. D. R. Johnson and F. L. Layton, *Effect of Glovebox Atmosphere on Oxygen Contamination of UC_2 Fuel Kernels*, Internal Memorandum CF 74-9-5 (September 1974).

7. Cooperative investigation with W. J. Lackey, Metals and Ceramics Division.

A method was developed for characterizing the surface of coated particles. Of particular interest was the depth to which the carbon coatings were permeable, since this seems likely to be important in determining the strength of the particle-matrix bond. In this method, the open pores of the particles are impregnated with nickel by removing all gases from the open pore under a vacuum (about 10 μm Hg), introducing nickel carbonyl vapor at a pressure of 1 atm, and decomposing the carbonyl at the surface of the particles heated to about 150°C; nickel subsequently deposits on the walls of the open pores. Upon examination of a metallographically polished cross section, it is possible to determine the depth to which the pores were interconnected with the surface, since all open pores contain metal deposits.

DECONSOLIDATION OF HTGR FUEL RODS

To determine burnup on individual particles in HTGR fuel rods, it is necessary first to deconsolidate the fuel rods and then to examine the separated particles by an appropriate method (optical microscopy, gamma spectrometry, or microradiography) to select intact particles for measurement. Deconsolidation of unirradiated HTGR fuel rods has been demonstrated with an electrochemical procedure and an apparatus fabricated to deconsolidate irradiated fuel compacts by remote operations.

The electrochemical deconsolidation is accomplished by placing the compact in a glass-tube anode compartment close to but not in contact with a platinum-flag anode. The glass tube, made to hold the compact in a vertical position, is slotted at the bottom to allow the coated particles and finely divided matrix graphite to drop into the cell during the electrolysis. A graphite electrode is used as the cathode and nitric acid as the electrolyte. The current is supplied by a regulated dc power supply. The electrolysis cell is provided with a reflux condenser and charcoal and/or caustic traps to prevent loss of acid or volatile fission products during electrolysis and/or refluxing.

Tests have shown for fuel rods with a matrix density of approximately 0.8 g/cm^3 that at a current of 2 A (current density about 100 μA/cm^2), the time required for deconsolidation is about 2 hr, and that the acid concentration can vary from 3 to 8 M with little difference in the time required for complete deconsolidation. Low acid concentration and low current density (<2 M HNO_3 and <2 A respectively) produce finer matrix graphite debris and require longer electrolysis times for complete deconsolidation. For any given acid concentration and current density, the time required for deconsolidation depends on the matrix density of the compact. With 8 M HNO_3 and a current of 2 A, a compact with a matrix density of 0.8 g/cm^3 requires about 2 hr for deconsolidation, compared with 6 to 8 hr for a compact with a matrix density of 1.7 g/cm^3. The coated particles are separated from the matrix graphite debris by flotation of the debris with water.

BURNUP MEASUREMENT OF PEACH BOTTOM REACTOR FUEL ELEMENTS

The General Atomic Company's destructive method of burnup analysis was evaluated and used to measure the burnup of fuel particles from Peach Bottom Reactor fuel elements.[8] The method employs stable fission-product zirconium as the burnup monitor, because the thermal fission yield of stable zirconium isotopes is nearly equal for ^{233}U and ^{235}U, the neutron absorption cross section for zirconium is low, the fission yield for stable zirconium is relatively high (about 0.31), and zirconium is amenable to chemical assay.

In this method, a sample consisting of one to three fuel particles, estimated to contain 0.5 to 3 μg of stable fission-product zirconium, is crushed and then dissolved in a perchloric acid–nitric acid mixture. The zirconium, uranium, and thorium are separated by anion exchange chromatography in a chloride medium, and each element is measured spectrophotometrically by the Arsenazo III method. The burnup, based on the total stable fission-product zirconium and the heavy-metal content, is given by

$$\text{FIMA} = \frac{N_{Zr}/Y_{Zr}}{N_U + N_{Th} + N_{Zr}/Y_{Zr}},$$

where FIMA = burnup (number of fissions per initial heavy metal atom), Y_{Zr} = total thermal fission yield of stable zirconium isotopes for ^{233}U and ^{235}U (0.31), N_{Zr} = number of atoms of zirconium found, N_U = number of atoms of uranium found, and N_{Th} = number of atoms of thorium found.

8. G. Buzzelli, *Spectrophotometric Determination of Fission Zirconium in Irradiated Nuclear Fuels,* General Atomic Company report GAMD-10072 (1972).

BURNUP ANALYSIS FOR HTGR FUEL TYPES BY MASS SPECTROMETRY[9]

Tandem mass spectrometers that have high abundance sensitivity and employ ion-counting detection are being used to develop techniques for obtaining highly accurate burnup analysis data on individual microspheres. The isotope dilution–mass spectrometry (IDMS) technique, when perfected, will have the advantage of determining the neutron flux at locations from which the fuel microsphere is removed. Besides the uranium isotopic values obtained, the total quantity of uranium and thorium and the quantity of a fission product will be measured by a triple-spike isotope dilution technique. To date, the IDMS technique for thorium and uranium has been essentially perfected for the Peach Bottom HTGR fuel; the technique for a suitable fission product from ^{233}U and ^{235}U is still under investigation.

The IDMS technique has been applied to a series of archive thorium-uranium microspheres for the Peach Bottom Reactor and to irradiated microspheres to determine the thorium-to-uranium ratio and the isotopic composition. In the IDMS method, after the microsphere is dissolved, an aliquot is first measured for isotopic composition and then a second aliquot is equilibrated with a double spike containing enriched ^{230}Th and ^{238}U; the newly established ratios are measured by mass spectrometry and then used to calculate the thorium-to-uranium ratio. From nine archive measurements, the average thorium-to-uranium ratio was found to be 5.57 ± 0.047, and for the "standard" irradiated solution the ratio was 6.40 ± 0.064.

We have initiated preliminary mass spectrometry studies with the aim of finding a suitable fission product that can be measured and used as a reliable burnup monitor for ^{233}U and ^{235}U. From a mass spectrometry standpoint, neodymium would be the element of choice, but the fission yields for ^{233}U and ^{235}U are dissimilar. Zirconium and cerium are possible monitors; however, special clean chemical separations will be required on microgram amounts of material.

GCMS AS A MONITORING SYSTEM FOR THE DEPOSITION OF CARBON ON FUEL PARTICLES[10]

The optimum deposition of carbon in a fuel-particle-pyrolysis fluidized reactor depends on several variables. When propylene is employed as the source of carbon, the variables include temperature, fuel load, and amount of propylene. An on-line method is needed to monitor the deposition process.

One approach to the problem is to monitor gas-phase components and correlate changes in component concentrations with "good" and "bad" carbon deposition. In the fluidized carbon reactor used as a model for deposition, propylene was the carbon source, argon was the carrier gas, and a cloth bag filter was used for soot removal before sampling. To test the applicability of an on-line mass spectrometer as a real-time monitor of the reactor, gas samples were collected as a function of time and then analyzed both qualitatively and quantitatively by GCMS. An Aerograph 1520 gas chromatograph with a gas sampling loop was interfaced directly to a GE 600 monopole mass spectrometer. A ⅛-in. Porapak R column was used to separate components. A thermal conductivity detector was used to quantify and the mass spectrometer to identify eluting components. Major components identified by GCMS were H_2, Ar, CH_4, C_2H_4, C_2H_2, CO_2, and C_3H_6. Carbon monoxide may have been present, but it was not detected due to the N_2 background in the mass spectrometer.

Experimental data indicate major differences in CH_4 concentration early in the deposition process. These differences may be related to the quality characteristics of "good" and "bad" carbon deposition. Also, minor differences in C_2H_2 and C_2H_4 were noted as a function of "good" and "bad" carbon deposition.

Secondary experiments were designed to sample gas-phase components without prior separation by gas chromatography. The mass spectrometer monitored CH_4 (m/e 16) and revealed quantitative data similar to those obtained by gas chromatography. Other components were noted in the gas phase by mass spectrometry. Two of these components are probably benzene and toluene.

DENSITY, pH, AND CONDUCTIVITY MEASUREMENTS OF ACID-DEFICIENT URANYL NITRATE SOLUTIONS

A study was initiated to determine the density, pH, and conductivity of acid-deficient uranyl nitrate solutions as a function of uranium concentration and temperature. The information gained from this study will be used in the process control of the preparation of uranium-loaded resin beads.

Six uranium concentrations at NO_3/U mole ratios of 1.5, 1.7, 1.9, 2.0, 2.1, and 2.3 were selected for study, and each concentration will be studied at six nitrate concentrations – 0.1, 0.3, 0.6, 1.0, 1.5, and 2.0 *N*. The

9. Cooperative investigation with the Mass and Emission Spectrometry Group.

10. Cooperative investigation with the Mass and Emission Spectrometry Group.

36 solutions have been prepared from a stock solution of uranyl nitrate and nitric acid. Measurements of pH, conductivity, and density are to be made at 25, 50, and 75°C. A set of experimentally derived curves will be made for each temperature, from which the uranium concentration of a given solution can be determined from its pH or conductivity.

COMBUSTION OF GRAPHITE BY LOW-TEMPERATURE ASHING

An LFE Corporation low-temperature asher, model 302, was purchased and evaluated to be used in the impurity analysis of GCR fuel materials. Large amounts of graphite associated with the fuel materials can be oxidized by an oxygen plasma slightly above room temperature. Low-temperature ashing prevents the loss of trace contaminants that are volatile at low temperatures.

A CONTINUOUS TRITIUM MONITOR FOR A REACTOR EXPERIMENT

A number of fuel rod irradiation tests have been done at ORNL in support of research on fuels for the gas-cooled fast reactor being developed at General Atomic Company. Currently, irradiation in the Oak Ridge Research Reactor (ORR) of a vented fuel rod, designated the GB-10 capsule, is in progress. This is one of two capsules designed to provide direct measurements of fission product release rates from an operating fast breeder reactor fuel rod.[11] A knowledge of the amount and the molecular species of tritium produced in a GCFR fuel rod is necessary to provide design engineers with flexibility in the choice of fuel cladding materials, coolant purification components, material for steam generator tubes, and the location, methods, and equipment for radioactive waste disposal.

A system for continuously analyzing tritium quantitatively in the helium sweep gas from the GB-10 capsule experiment has been designed. It is quite similar to the continuous tritium-monitoring system installed by General Atomic in the Peach Bottom Reactor. In brief, the sweep gas with fission gases present passes first through hot magnesium powder (about 500°C), where HTO is reduced to HT. After removal of radioactive species of argon, krypton, and xenon with liquid-nitrogen-cooled charcoal traps, the HT in helium passes through a heavily shielded ionization chamber, where its tritium content is measured with a 1-liter ionization chamber associated with a calibrated vibrating-reed electrometer connected to a strip chart recorder. As a periodic check on the electrometer results, a known volume of gas leaving the ionization chamber will be passed through hot CuO (about 500°C) to convert the HT to HTO, which will be trapped and subjected to liquid scintillation beta counting. This should give us a quantitative measure of the total tritium leaving the fuel capsule. If the sweep gas is allowed to bypass the hot magnesium powder, any HTO present will *not* be reduced but will be frozen in the liquid-nitrogen-cooled charcoal traps. Therefore, the subsequent analysis for HT will measure only tritium in the HT form that was originally generated in the fuel capsule. The concentration of HTO formed in the capsule can then be determined by the difference between the two analyses.

At present, individual components of the above system are being tested to determine the operating conditions needed to give reproducible quantitative results. Conversion of HT to HTO by hot CuO, trapping of the HTO by molecular sieve, and the exchange of trapped HTO by refluxing with distilled normal water have all been demonstrated to occur quantitatively.

ON-LINE MEASUREMENT OF FISSION GAS RELEASE[12]

Since August 1972, when the GB-10 fuel rod experiment was installed in the ORR, there have been periodic samplings of the fission gases. These samples (usually from 0.04 to 6 cm^3) are analyzed by Ge(Li) gamma-ray spectrometry with the PDP-15–Nuclear Data 50/50 data acquisition system at the ORR.

This year a Ge(Li) detector system was installed on line to the GB-10 experiment. The detector and its associated electronics are located in cell No. 1 on the second-floor balcony. The signal is transmitted over 200 ft by cable to the data acquisition system in the basement. The detector is used to monitor a helium-sweep gas line that carries the fission gases from the experiment. The system was calibrated with a mock-up of the sweep line and calibrated sources of ^{24}Na, ^{56}Co, ^{82}Br, and ^{160}Tb. There are five lead collimators, with widths of $1/16$, $1/8$, $3/16$, $1/2$, and $1\frac{1}{4}$ in. and lengths of 1 ft each. The system has been used to determine the quantity of fission gases as a function of flow rates and fuel power levels. It will also be used to determine the

11. J. A. Conlin et al., "GCFR Irradiation Experiments," *Gas-Cooled Reactor Programs Annu. Progr. Rep. Dec. 31, 1972,* ORNL-4911, pp. 212–33.

12. Cooperative program with the Nuclear and Physics Methods Group.

behavior of fission gases during simulated leaks, fuel breathing, and startup. This on-line system has the capability to monitor the individual fission gases continuously and to observe fission gases with half-lives of 10 sec or longer.

FISSION-PRODUCT SURVEILLANCE IN THE PEACH BOTTOM HTGR[13]

We have continued our assistance to the ORNL HTGR fission-product surveillance program. In this program we are studying the behavior of fission products in the Peach Bottom HTGR (a 115-MW thermal reactor owned and operated by the Philadelphia Electric Company). Components of the reactor in which fission products are measured include fuel elements, coolant during reactor operation, surfaces of the coolant circuit during reactor downtimes, and dust samples collected by the reactor's cyclone dust separators. As indicated before,[14] our objective in studying the Peach Bottom Reactor is to compare measured and predicted behavior of fission products in an operating HTGR. It is important to understand the behavior of fission products in the Peach Bottom Reactor, because it has operated over a fairly long period of time (since 1967) with a core consisting mainly of nearly identical power-producing (driver) fuel elements. The behavior of fission products and the chemical environment in the Peach Bottom Reactor might, therefore, be expected to differ significantly from those of test reactors, such as the Dragon Reactor in England, in which a large variety of experimental fuel elements are tested.

During this reporting period, we began an examination of a driver fuel element irradiated to 701 effective full-power days (EFPD) and continued analysis of a 384-EFPD element. We measured the contents of two coolant samplers that were operated between March 13 and May 28, 1974, and completed analysis of data for two coolant samplers operated in 1973. The design and operation of these coolant samplers have been described elsewhere.[15,16]

Measurements made in September 1973 (during reactor downtime) of fission products deposited on the reactor's coolant circuit were analyzed and evaluated. An additional measurement on the coolant circuit was made in June 1974. Measurements of fission gases in the reactor's coolant and core purge systems were also accomplished. A dust sample obtained from the reactor's dust collectors was subjected to chemical and radiochemical analysis.

During the past year the rate of release of ^{134}Cs and ^{137}Cs from the core into the primary circuit increased dramatically. Small amounts of ^{136}Cs can now also be found in the primary coolant circuit. The release of most other gamma-emitting fission products seems to have changed very little. We do not know yet how much the release of strontium isotopes has changed. The increased release rate of cesium isotopes has been confirmed in measurements on the 701-EFPD element, the coolant samplers, and the large ducts. The increased release began to be measurable early in 1973 and greatly accelerated after January 1974. Gamma dose rates adjacent to the coolant ducts downstream of the steam generator increased by a factor of 4 from September 1973 to June 1974. A gamma spectrum taken in June 1974 showed that this increase was due to deposition of ^{134}Cs and ^{137}Cs in the ducts. We estimate that as of June 1974 there was about 100 to 200 Ci of radiocesium in each of the steam generators. The increased release rate of cesium is thought to be due to diffusion through the fuel-element sleeves. The temperature of the core has increased significantly during the past year. It is not known, however, whether the release is occurring from most fuel elements or only a few elements operating atypically.

The concentration of ^{131}I in the coolant was measured with coolant samplers upstream and downstream of the steam generator in 1973 and 1974. Evaluation of the 1974 measurements is incomplete. Preliminary results indicate that the release rate of ^{131}I has increased during the past year, but we do not yet know exactly how much. We also have not derived the fractional amounts of iodine present as molecular species, components of dust particles, and organic iodides. Late in 1973, a leakage of oil into the coolant that had existed during the time we had studied the reactor was stopped. This has resulted in a dramatic reduction of dust in the coolant, and very little dust was found in the 1974 samplers. Because of the increased release rates and the absence of dust, the profiles of fission products (including ^{131}I) in diffusion tubes of the 1974 samplers correspond closely to

13. Cooperative program with the Chemical Technology Division.

14. W. S. Lyon et al., "Fission Product Behavior in HTGR Coolant Circuits," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 41.

15. H. J. deNordwall et al., "An Interim Report on Fission Product Release during Operation of the Second Peach Bottom Core," *Int. Conf. Nuclear Fuel Performance, Oct. 15–19,* British Nuclear Energy Society, 1973.

16. J. O. Kolb et al., "Fission Product Behavior in the Coolant Circuit of the Peach Bottom HTGR," *Gas-Cooled Reactor Programs Annu. Progr. Rep. Dec. 31, 1972,* ORNL-4911, p. 172.

profiles expected of molecular species. The interpretation of results from the 1974 samplers should thus be much more straightforward and should yield more information about fission products in the coolant than was possible from previously operated samplers.

Although incomplete, the postirradiation examination of the 701-EFPD fuel element has shown that the behavior of cesium isotopes is vastly different from that in the 384-EFPD element. Metallographic examination showed no significant increase in fuel-particle breakage in the fuel. Dimensional measurements on the fuel, sleeve, and spine clearly showed significant changes in the size of the element components. The principal result of these changes was to increase the size of the purge gap between the fuel and sleeve, thus reducing the rate of heat loss by the element, with a consequent temperature increase. Gamma scans of the fuel and measurements of sleeve sections revealed that nine fuel compacts in the highest fuel-temperature regions had lost about 45% of their radiocesium. Although the sleeve sections studied did not include the highest temperature regions, the concentration of cesium changed by a factor of nearly 3000 from the top of the fueled region to fuel compact 11. The sleeve adjacent to the hottest fuel (probably compact 18) could be still more radioactive.

These observations indicate that significant amounts of the cesium released from the fuel have been taken up by the sleeve. Additional work planned in this examination includes axial measurements of the fission product inventory in the sleeve and spine at positions adjacent to each fuel compact, determination of radial distribution profiles in both sleeve and spine at several selected positions, similar but limited analyses of other components of the element, and burnup determinations on the fuel. Results from these measurements are expected to provide a much better understanding of the behavior of cesium (and other fission products) in the element, as well as an estimate of the source term for calculation of release of fission products into the coolant.

The Peach Bottom Reactor is scheduled to be decommissioned early in the fall of 1974. This exercise probably will begin in October, at which time we will again measure the plate-out activities on the primary coolant ducts. Our plans also include participation in other studies subsequent to decommissioning. Although evaluation of many of the measurements made to date is incomplete, we now have a fairly quantitative picture of fission product behavior in the reactor. A comprehensive report describing our study procedures, results, and interpretations is in preparation.

GAMMA SPECTROSCOPY FOR HTGR PROGRAMS

During the past two years, gamma spectroscopy for the HTGR fission product surveillance program and for most of the programs concerned with postirradiation evaluation of HTGR fuels has been carried out mainly with a Nuclear Data 4410 pulse-height analyzer (PHA) system. This computer-based instrument, purchased in 1971 and previously described,[17] is relatively portable and has been taken several times to the Peach Bottom Reactor for measurements of fission products deposited in the primary coolant circuit and fission gases in the coolant and has been moved to the High Radiation Level Examination Laboratory for measurements on HTGR fuel. (The system is used for these specialized tasks and for other jobs requiring rapid analyses that cannot be met by other facilities of the Analytical Chemistry Division.) Early in 1974 we expanded the programs used to process gamma spectra, so that now we can identify radionuclides with results expressed as absolute activities (microcuries and disintegration rates) corrected for decay and normalized to unit sample weight.

We recognized in 1973 that, in spite of the extensive capabilities of the ND 4410 system, additional gamma spectroscopy equipment would be needed to meet an expanding need in HTGR measurements. Therefore, we purchased and recently installed a new and highly versatile spectroscopy system based on a PDP-11 computer. This system, a Tennecomp TP 5000, has a memory of 28,000 16-bit words and an industry-compatible magnetic tape unit on which both program and data files can be stored. Software to process gamma spectra, identify radionuclides, and compute absolute activities for radionuclides was also purchased. The system operates in a foreground-background mode with a foreground machine language program that accumulates spectra and a background FOCAL language program that does all computations. During the acquisition of a spectrum, other types of computations can be carried out, including the analysis of another spectrum. The system can easily be expanded at relatively low cost to permit simultaneous acquisition of up to eight spectra. Although still in the "checkout" stage, the system appears to operate as expected.

17. J. A. Conlin et al., "GCFR Irradiation Experiments," *Gas-Cooled Reactor Programs Annu. Progr. Rep. Dec. 31, 1972,* ORNL-4911, pp. 212-33.

AUTOMATIC SAMPLE CHANGER FOR THE ND 4410 PHA SYSTEM

An automatic sample changer has been fabricated to use with the ND 4410 computer-based PHA system. The changer, made to analyze HTGR fuel particles and other HTGR samples, consists of a turntable, a sample-counting chamber, and a Ge(Li) gamma spectrometer–detector. All three components are shielded with lead to reduce background and radiation hazards to personnel. The system is under direct control of the computer in the ND 4410 PHA system. Twenty samples placed in slots in the turntable can be sequentially moved into counting positions in the counting chamber for acquisition of gamma spectra. After a sample is counted, it is moved back to the turntable. Except when a sample is being moved between the turntable and counting chamber, a lead door isolates the two compartments to shield the detector from radiation from the turntable. The system has a very wide dynamic range in both counting times and source-to-detector distances for sample analysis. All mechanical and electronic units (including interfacing to the computer) have been fabricated. Some additional software development will be necessary before the computer will operate the changer.

5. Mass and Emission Spectrometry

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The addition of an ion microprobe mass analyzer (IMMA) during the past year has greatly enhanced the capability of the group, particularly for surface analysis. The IMMA is especially useful for trace-element determinations on grain boundaries and for depth profiling of metal surfaces. In the few months it has been in operation, the IMMA has been used to study the cause of failure of a Pt-Rh-W alloy used as a high-termperature thermocouple, as well as to investigate other alloys where it has been observed that inhomogeneities exist between crystals. The capabilities of the IMMA, combined with those already existing in spark-source mass spectrometry, provide a powerful laboratory for surface analysis and related studies.

A significant improvement in isotopic analysis of plutonium and uranium has been the development of Dowex 1 anion resin for the separation of both elements from dissolver solutions. A single resin bead containing both elements can be loaded onto a filament for isotopic analysis by surface ionization, using a tandem mass spectrometer equipped with pulse counting for ion detection. The technique should be especially useful in fuel burnup studies and safeguards applications.

To achieve more efficient and economical use of capital equipment within the Nuclear Division laboratories and plants, an Associated Electrical Industries MS-50 organic mass spectrometer with high sensitivity and high resolution (100,000) was purchased. This instrument will be used for samples, originating in all three plants, that are difficult to handle. It will be installed in this group in early 1975 and is partially committed to a special problems group in the Y-12 Plant, with the remaining time available for research and development studies of organic problems, such as those associated with coal and air-quality research. Many mutually beneficial exchanges of information on spark-source and thermal emission mass spectrometry have resulted from this interaction; for example, the Y-12 Plant laboratory has an electrical detection system that is of interest to our group's development of multielement isotope dilution methodology, and the Y-12 mass spectrometry group has a use and need for a computer-operated densitometer, which is under development in our group.

1. On leave of absence to IAEA, Vienna, Austria.
2. Instrumentation and Advanced Methodology Group.

We have continued design, development, and expansion of the interactive computer-operated data acquisition and processing system to read photographic plates produced by spark-source mass spectrometers (SSMS). For several elements we have successfully linked the data acquisition routine to 35 different isotope dilution (ID) programs. Mass spectrometric techniques for assessing and measuring environmental quality are being developed. The analytical system for simultaneously measuring total nitrogen and $^{15}N/^{14}N$ ratios has been improved by removing from the N_2 the H_2 formed during the thermal decomposition of NH_3. Incorporation of three reaction flasks into the analytical system makes it possible to analyze three samples per hour operating in a sequencing mode.

Under a two-year funding arrangement with the ORNL/NSF(RANN) project on Ecology and Analysis of Trace Contaminants, we are extending the IDSSMS technique to 20 or more elements by developing the necessary methodology for multielement isotope dilution. Additionally, in the second year the proposal will cover surface profiling and isotope dilution work with the IMMA. A mass balance for lead, cadmium, and zinc for the Allen Steam Plant was established by IDSSMS. We are continuing to develop methods and analyze fuel samples for EPA under an interagency agreement.

Most of the organic analyses done by both low- and high-resolution mass spectrometry during the past year have been for biologically oriented programs sponsored by EPA and NSF. Development work and instrument upgrading are under way which will give us the capability required for handling coal-derived liquids. Negotiations are also under way with General Electric for the use of the Mass Spectral Search System (MSSS), which is available on the GE Mark III computer network. Use of this system will be of great value in qualitative organic work.

During the past year a monopole mass spectrometer was installed in Building 4500S for bio-organic work in the ORNL Tobacco Smoke Research Program. A cooperative effort with the Metals and Ceramics Division in microsphere coating operations led to the purchase of a time-of-flight spectrometer to monitor characteristic by-product components that seem to indicate the quality of microsphere production runs. We have also continued assistance to other plants within the Nuclear Division in studying possible air pollution and exposure of workers to hazardous chemicals in line with OSHA regulations.

Service analyses, both mass and elemental impurity spectrometry, are conducted for some 18 ORNL divisions and projects. Over 70,000 analytical results were reported for this period. Isotopic abundance measurements were made on 53 different elements; the isotope dilution techniques developed were put into service laboratories rather quickly, as evidenced by their use for the measurement of samarium, thorium, and uranium in microsphere burnup analyses and for iron in the LWFBR $^{233}UO_2$ preparations.

MASS SPECTROMETRY DEVELOPMENT

Ion microprobe mass analyzer. For several years now it has been recognized that considerable applications exist within the Laboratory for a capability in ion microprobe mass analysis. Considerable effort and time were spent in formulating specifications for an instrument of this type. The end result of this effort was the purchase from Applied Research Laboratories of an ion microprobe mass analyzer (IMMA). The IMMA was delivered and the initial setup made early in 1974, and considerable debugging and modification were required before the instrument met our specifications. The IMMA was rendered serviceable in July 1974, when the gathering of operational experience commenced.

The investigation of a Pt-Rh-W alloy used in a high-temperature thermocouple was one of the first problems looked at with the IMMA. It had been observed that after this alloy was annealed at temperatures greater than 1000°C for approximately 1000 hr, its tensile strength dropped drastically. Since the alloy failed along grain boundaries, it was thought that perhaps some element or compound was segregating on these boundaries and thereby weakening the alloy and causing it to fail. A sample of the alloy was investigated by spark-source mass spectrometry to determine bulk

concentrations of trace elements. An attempt was also made to look at surface concentrations (to 1 μm depth) on the granular area where the sample had pulled apart in the tensile strength test.

The same specimen was then mounted in the IMMA to look at grain boundaries and other dendritic structures on the flat surface of the test piece. This sample was ideal for investigation because the individual grains had grown relatively large (on the order of 100 to 200 μm) and were clearly visible through the IMMA's optical microscope. Thus, if any particular element were concentrated on these boundaries, its presence could be easily correlated with observable locations on the sample surface. The sample as viewed through the IMMA's optical microscope is shown in Fig. 5.1.

A relatively intense primary beam of 20-keV positive molecular oxygen ions was used to etch an area of the sample and remove spurious surface contamination. After many monolayers had been removed, a mass scan of the clean region was made to determine what elements were present. Elements observed in this scan agreed with the results of the spark-source investigation. The primary beam was then focused down to about a 5-μm spot, and a search was made for elements localized on the grain boundaries. Of all the trace elements observed in the sample, silicon was the only one that exhibited localization on the grain boundaries. Figure 5.2 is an ion image of $^{28}Si^{+}$ made by rastering the primary beam over the area of interest. The ion image thus obtained was easily correlated with the optical image of the grain boundaries. Silicon was found in the bulk alloy only to the extent of 30 ppm. Another experiment was performed to determine whether the observed silicon was spurious surface contamination. A similar specimen was sawed at 90° to the surface exhibiting the silicon, and the edge was polished flat with diamond compound until no grain boundaries were visible through the optical microscope. The sample was loaded into the IMMA and pre-etched as the first sample was to remove surface contamination. The beam was then focused down to 5 μm diameter, and a search was begun for silicon localized on grain boundaries. Silicon was indeed found to be present on the inner grain boundaries. This experiment tends to confirm the idea that the silicon migrates to the boundaries during the annealing process. Other experiments are planned to determine the source of the silicon.

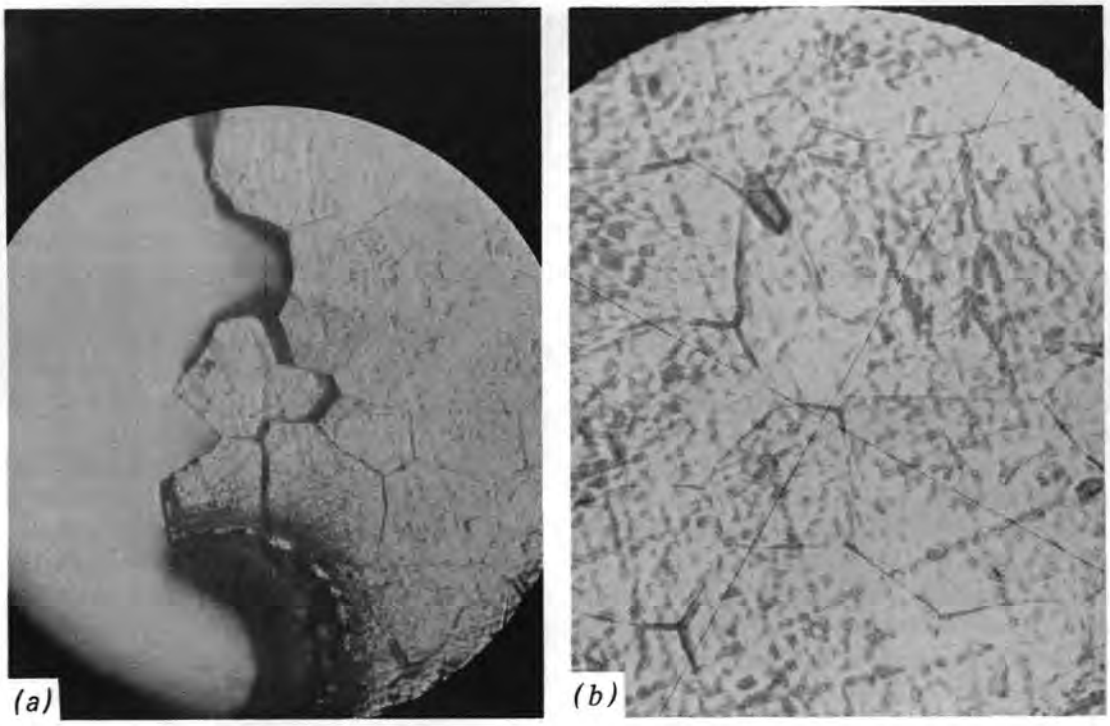

Fig. 5.1. Sample of a Pt-Rh-W alloy seen through the optical microscope of the ion microprobe mass analyzer. (*a*) General view, showing edge where fracture occurred. Individual grains are clearly visible. (*b*) View of the same surface, 200 to 300 μm back from the fracture edge. This is the area where silicon, localized on grain boundaries, was observed.

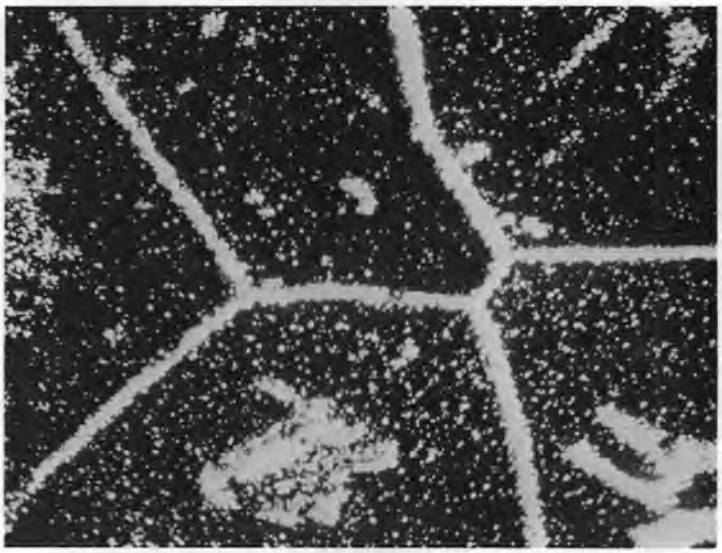

Fig. 5.2. Ion image made by rastering the primary beam while monitoring the $^{28}Si^+$ signal from the IMMA. Light areas indicate enhanced silicon concentration.

Our first adventure with the IMMA technique gives some idea of its power as an analytical tool. Ion imaging will prove to be invaluable to workers in metallurgy, ceramics, and other fields where a knowledge of the distribution of an element on a surface is required.

Our second endeavor with the microprobe proved to be a bit more troublesome. An attempt was made to explore some of the IMMA's quantitative aspects. A series of three known Nb-Mo-Zr ternary alloy metal standards were prepared and then polished and mounted in the microprobe. Preliminary results indicate that these so-called standards are not homogeneous on a microscale and are, therefore, useless as microprobe standards. Discussions with the people who prepared the materials indicate that microinhomogeneities were possible. Further work is planned to uncover the facts.

Another ternary Nb-Mo-Zr metal alloy, believed to be inhomogeneous by its manufacturer, was investigated to measure the extent of variation. The molybdenum content was thought to vary between 8.5 and 9.5%, but no measurable variation was detected with the IMMA technique. Independent electron microprobe analysis corroborated our findings for this sample.

Simultaneous plutonium and uranium isotopic analysis from a single resin bead. A method has been developed for the chemical separation of uranium and plutonium from dissolver solutions, using anion resin to adsorb both elements. A single resin bead containing both elements is loaded onto a mass spectrometer filament for measurement of the isotopic abundance of each element. This method permits analysis of plutonium free of isobaric interferences from americium and curium, which do not adsorb on anion resin from 7 to 8 M HNO_3 solutions. Plutonium and uranium have been analyzed in this laboratory for some time from a direct loading of a dissolver solution, but only the 239, 240, and 242 isotopes were clear of interferences in the plutonium analysis. Uranium analysis could usually be done from such a solution without serious problems. Direct loading also gave spectra that were difficult to "clean up" due to the high concentration of salts loaded with the elements of interest, thus giving rise to occasional erratic results. Frequently we were forced to make measurements on the PuO_2^+ ions because it was difficult to introduce enough reducing agent (in our system, benzene vapor) to obtain metal ion emission.

The chemical separation involves equilibrating the dissolver solution (7 to 8 M HNO_3) with several resin beads. In 7 to 8 M HNO_3, plutonium and uranium have distribution coefficients of 10^4 and 10 respectively. This favorable ratio, coupled with the fact that U/Pu ratios in dissolver solutions usually are on the order of 100/1, makes a desirable loading of plutonium and uranium for a simultaneous determination by enhancement of the plutonium concentration in relation to the uranium.

Analyses have been run which prove that reliable isotopic analysis of plutonium and uranium in spent reactor fuels can be done with minimal chemistry and sample handling. A dried aliquot of a typical dissolver solution containing approximately 10 μg uranium, 65 ng plutonium, and 10 μCi of fission products would be

a sufficient sample for making the determinations. The precision of an analysis expressed as relative standard deviation is <1% on major isotopes. The assay of ^{238}Pu, if in the range of 0.1 at. %, can be measured by the simplified resin bead technique. The ^{238}Pu assay can be improved with a correction scheme that eliminates the ^{238}U interference.

The main advantages of this simplified method are (1) decreased analytical laboratory separation costs, (2) reduction of radiation hazards in handling small samples in an unshielded laboratory, (3) reduction of sample transportation costs in the Safeguards program, and (4) a second technique for obtaining a reliable ^{238}Pu value. The third advantage, the lessening of radiation hazard in shipping and the resultant saving in transportation costs, may be the most important. This aspect of the method would be very important in Safeguards analyses, whether on a national or international basis. A paper describing this work has been accepted for publication.[3]

Nuclear Division related activities. A contract has been let for the purchase of an MS-50 mass spectrometer. This is a high-resolution (static resolving power of at least 100,000) organic instrument. The system will include a solids probe as well as a gas chromatograph sample inlet system. A batch sample inlet will be constructed at the laboratory to provide the capability of quantitative as well as qualitative analysis. The instrument is partially committed to providing rapid service to a special problems group in the Assembly Division of the Y-12 Plant, but part of the time it will be used for studies of organic samples such as coal-derived liquids and organic contaminants in the atmosphere.

This year our work with and for the Product Certification Division of the Y-12 Plant has been expanded. We are now providing some consultation and services to various groups concerned with gas sampling methods and analytical methods as well as actual analyses of samples. The Y-12 groups have been involved in both sample collection and analysis.

In addition to an exchange of gas analysis information and samples, we have been involved in an exchange of samples and information on spark-source mass spectrometer techniques. The group at the Y-12 Plant has an electrical detection system that is of interest to our group, and they are interested in our data collection system for the densitometer. Both groups have profited from this merging of ideas, since the capabilities of both have been improved.

During the past year, we isotopically certified assays of over 50 uranium metal samples for the Y-12 Plant. For this work, an instrument is required that has a high abundance sensitivity (10^6) capability for precise assay of minor isotopes at low parts-per-million levels. This unique capability is provided by our two-stage, 12-in.-radius surface ionization instruments, which are equipped with pulse counting for ion detection.

Surface analysis with the spark-source mass spectrometer. A method has been developed and is being used for certification of surface impurity levels in various alloy types. The method involves preparing a series of very short ion exposures (1×10^{-10} C or less) taken from various areas of the surface. The concentration of the impurity elements is then calculated in reference to a minor isotope of a component of the alloy. The calculations shown in Table 5.1 are representative of the surface volumes and crater sizes involved in the analyses. Studies are also being made of the concentrations of certain elements (B, Si, Al, Th, Ta, F, Fe, and Cr) on fracture surfaces of various alloy types. Figure 5.3 demonstrates one type of data being obtained. Further studies are under way in which the spark-source mass spectrometer and the IMMA are being used to study the same sample surfaces.

Table 5.1. Relationship of ion exposure to crater size

Exposure (C)	Volume (cm^3)	Crater radius (μm)
10^{-12}	8.6×10^{-11}	5.5
10^{-11}	8.6×10^{-10}	11.7
10^{-10}	8.6×10^{-9}	23.4
10^{-9}	8.6×10^{-8}	55
10^{-8}	8.6×10^{-7}	117

Monopole mass spectrometer. The General Electric model 600 monopole mass spectrometer was modified to allow gas chromatograph sample introduction, as well as direct atmospheric-pressure sampling capabilities. A new high-vacuum chamber was built for the spectrometer to provide a heated-inlet sampling system. Atmospheric-pressure sampling capabilities required the incorporation of a high-speed oil-diffusion pump (1200 liters/sec) for removal of large quantities of sample gas. The electronics of the ion current measuring circuit were altered to provide a high-speed oscillograph strip chart recorder. Five simultaneous tracings of the ion current are made at relative sensitivities of 0.1, 0.3, 1.0,

3. R. L. Walker, R. E. Eby, C. A. Pritchard, and J. A. Carter, "Simultaneous Plutonium and Uranium Isotopic Analysis for a Single Resin Bead – a Simplified Chemical Technique for Assaying Spent Reactor Fuels," *Anal. Lett.*, in press.

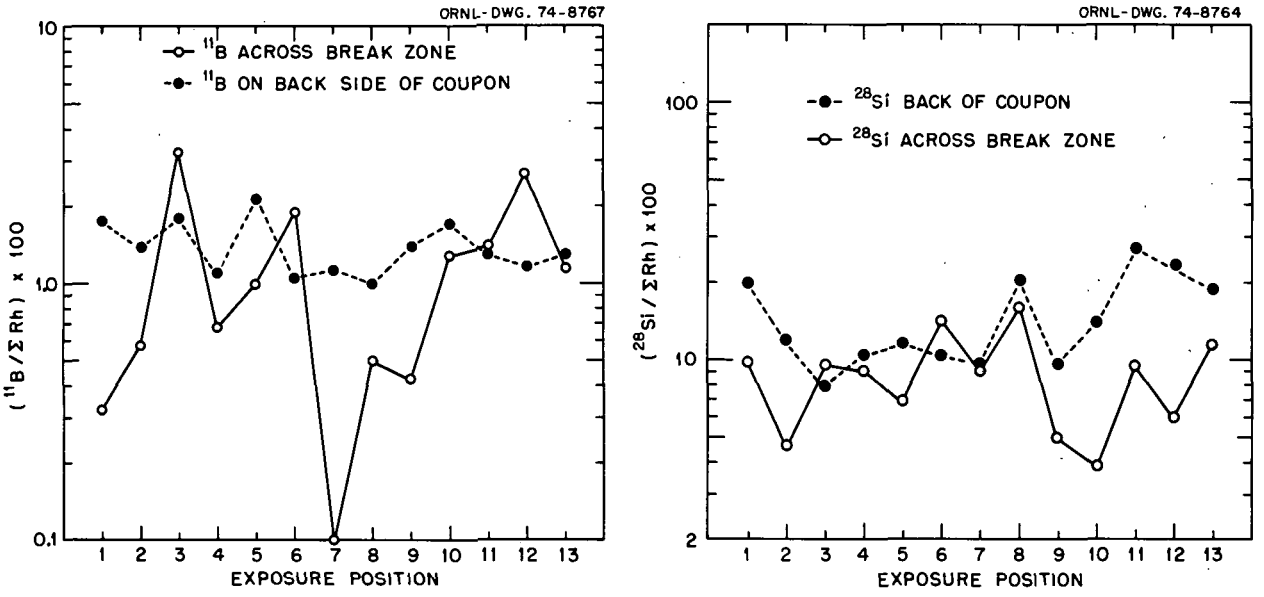

Fig. 5.3. Variation in boron and silicon concentrations at different positions across a fracture surface.

3.0, and 10.0. Mass spectra can be recorded from mass 2 to 300 *m/e* in a period of 3 sec. Continuous "real-time" spectra can be obtained visually on the cathode-ray oscilloscope.

After modification, this instrument was transferred from the Y-12 mass spectrometry area to Building 4500S for applications relating directly to the ORNL Tobacco Smoke Research Program. The monopole was used in a variety of modes in this program. It was used to monitor various components in the vapor phase of cigarette smoke at atmospheric pressure with no prior separation by gas chromatography. In this mode, it became an instantaneous (<2 sec) monitor of relative concentrations of various components in the vapor phase. Molecular ions of xylenes, furfural, toluene, methylfuran, benzene, CO_2, and H_2O were used as "unique" ions for monitoring purposes. The monopole was further used to monitor cigarette smoke effluents from gas chromatography for purity by ion-selective mass chromatography and in physiological studies. One such study monitored CO_2 levels (*m/e* 44) as a function of time in animal chambers containing mice and cigarette smoke. It was noted that the CO_2 levels in animal chambers containing cigarette smoke increased less rapidly than CO_2 levels in nonsmoked animal chambers.

Computer-operated densitometer. We have continued design, development, and expansion of the interactive computer-operated data acquisition and processing system to read photographic plates produced by spark-source mass spectrometers. A DUAL DECTAPE (magnetic tape) unit, model TD8-EM, was added to the system to provide bulk storage for the 8K PDP-8/E dedicated minicomputer. On unit 0 we have placed a DECTAPE MONITOR; on unit 1 we have set up our custom-designed 8K MODVF SSMSD interpreter. DECTAPE MONITOR is a machine-language executive program patterned after the Digital Equipment Corporation (DEC) DISK MONITOR. It uses the TD8-EM tape unit as the system device instead of a magnetic disk. The 8K MODVF SSMSD is a modified FOCAL operating system designed to acquire, process, and store programs and data under computer control. We have written a linking code that enables each of the monitors to access the other, thus providing a high degree of flexibility in the storage and recall of programs and data. The DUAL DECTAPE unit permits us to copy one tape reel onto another, providing a much-needed backup capability.

As first written, our emulsion calibration program implementing the Churchill two-line procedure was designed for manual entry of data on percent transmittance at the keyboard; we have now arranged for automatic computer entry of the same information, and we have increased the speed of calculation to the point where emulsion calibration on each individual photoplate is feasible.

We have successfully linked the data acquisition program (74) for reading the photoplates to the isotope dilution programs for the several elements of interest.

Data on peak height background for the sample and spike isotopes for up to 50 pairs of spectral lines are passed from program 74 to the desired isotope dilution programs. The 35 different programs are stored on magnetic tape in blocks of 2000 octal words and are called into core memory by our machine-language program, LPLG. This program has been designed to pass FOCAL pointers so that programs can be modified readily to accommodate different sample and spike volumes and concentrations. Both manual entry and automatic data acquisition computer programs can access the same isotope dilution program.

The development of our high-speed emulsion calibration procedure has forced us to change our isotope dilution programming philosophy. Originally, each program carried the emulsion calibration coefficients necessary for calculation of relative ion-beam intensities. When a photographic emulsion changed, a new set of coefficients had to be evaluated and entered into each program. The task of changing some 35 sets of coefficients seemed considerable. We have shortened the work by storing the coefficients in the data acquisition program rather than in the isotope dilution programs. Now when a program is called from magnetic tape into core memory, the coefficients are passed along to it automatically from the data acquisition program. It is necessary to change only one set of coefficients for recalibration – a much simpler process.

We have rewritten our FADC and FADZ function overlays for data gathering to operate with an AD8-EA analog-to-digital converter (ADC). This 10-bit ADC differs from the AD01-AP converter, for which the overlays had been written, in execution timing and instruction set. The new overlays acquire and average 512 decimal ADC measurements in $^1/_{60}$ sec, operating over the range of 0 to +2 V. A permanent interface based on a Philbrick model 1420 operational amplifier was installed on the densitometer to feed the multiplexed ADC, along with a panel meter, calibrated 0 to 100% transmittance, to assist the operator in visual checking of performance.

FOCAL programming to implement an internal standard technique was also written. Program 45 runs an interactive data acquisition procedure for producing relative ion-beam intensity values from single-line scans for up to 50 isotopes. The intensities are calculated and corrected for background with a linear interpolation scheme and a Churchill two-line calibration. We have succeeded in reducing calculation time from 4–7 sec to 1–2 sec by optimizing entry into the tabular data. The overall cycle time for entering a sample code, scanning the spectral line, and calculation is 10 to 15 sec.

A unique feature of program 45 is the use of a character-string function, FC. The command, S Z = FC(I,), allows a sample code (e.g., ER/166) to be entered at the keyboard to identify element and mass. S Z = FC(I), with no comma, returns the value, ER/166. By setting up two slightly different FC functions in two otherwise identical MODVF interpreters, we can now handle multiply charged ions. Both interpreters can access the same data acquisition programs.

After 50 isotopic lines have been scanned, or a flag set to –1, a paper tape containing relative ion-beam intensities and corresponding sample coding is punched by the PDP-8/E computer, in a format consistent with input requirements of the IBM 1130 computer. A new FOCAL H command was devised to create a Hollerith field in which information not requiring storage can be entered at the keyboard. The H command is used to punch plate numbers, exposures, and other sample information. The IBM 1130 computer is still required for the elemental analysis processing of relative intensity values from the densitometer operated by the PDP-8/E. The intensity information is transferred to the 1130 via paper tape. Stored on the disk of the 1130 is a file containing a table of the elements, the relative abundances of the isotopes, and the sensitivity factors of the MS7 to the various elements. Using the above information and a weight value of a known spike, the 1130 prints out the weight concentration of each element of interest in the original sample. If incorrect information should appear on the paper tape, a new, corrected paper tape can be created by execution of the symbolic editor, EDIT. New machine-language coding installed within EDIT directs a return to MODVF upon typing the command character, F. A utility program, PUNCH, was written in machine language to enable punching of sample identification codes on the paper tape input for the IBM 1130 computer.

As a step toward building a stand-alone data acquisition and reduction system based on the PDP-8/E, we are considering a FORTRAN compiler to generate SABR assembly-language coding. The FORTRAN object program should make it easier to store, sort, and return alphabetical information and to handle larger arrays of data. Our purchase and installation of an OS/8 ROM (read-only memory) should help in establishing FORTRAN on the PDP-8/E.

We have written a FOCAL-language program to handle overlapping spectra. The program evaluates the relative ion-beam intensity for a less dense spectral line located on the slope of a denser line.

We are continuing the development of programs and techniques for multielement spike procedures in isotope

dilution methodology. Automatic call and forced execution of one program by another is of vital concern, because of the small storage capacity of a minicomputer. We have written a library command with two execution modes: L G (45), G transfers a program from DECTAPE to core memory, starting execution at line 0; L G (45),G 12.6 transfers the same program similarly but starts execution at line 12.6. The number of programs that can be stored was increased from 64 to 89, and text storage was increased from 2000 to 2200 octal words. The search for stored programs should be faster, because of the elimination of DECTAPE storage of FOCAL pointers from page 0. The multielement spike programs will be applied at first to five isotopic pairs: PB 204-206, PB 204-208, CD 106-114, CU 65-63, and ZN 67-66.

The SERF MONITOR program, which is part of the computer package furnished by AEI Scientific Apparatus Limited for their MS7 mass spectrometer, does not allow execution of the high-level language, FOCAL, on the PDP-8/I. The reason is that SERF, like any good executive program, does not permit its own destruction. We have rewritten 4K FOCAL so that SERF can call and execute a FOCAL interpreter stored on the RF08 magnetic disk. SERF is destroyed by FOCAL operation, but it can be restored easily with execution of the system program, RAMNUC.

NSF(RANN) AND WORK FOR OTHERS PROGRAMS

We have continued to develop mass spectrometric techniques as part of the ORNL/NSF(RANN) project on Ecology and Analysis of Trace Contaminants. Further development and application of these techniques are being emphasized.

Measurement system for total nitrogen and $^{15}N/^{14}N$ ratios. The analytical system[4] designed for measuring total nitrogen and isotopic nitrogen ratios on small environmental samples has been improved. Earlier mass spectrometric measurements have shown a bias in the $^{15}N/^{14}N$ ratio of N_2 produced in the reaction

$$2NH_3 \xrightarrow[\text{Re}]{1050^\circ} N_2 + 3H_2 .$$

To determine whether the problem could be related to partial pressures of N_2 and H_2, a series of investigations was made of the effects of different sample pressures of N_2 and H_2 on the measured 28/29 ratios and the calculated ^{15}N abundance. At all sample pressures of tank nitrogen gas, up to the maximum that can be recorded on the mass spectrometer, the ^{15}N abundance remained constant. However, we have determined that, as the sample pressure of nitrogen plus hydrogen (N_2/H_2 = 1/3) from ammonia conversion increased, the 28/29 ratio decreased. Even at low sample pressures, the 28/29 ratio from nitrogen produced from ammonia conversion was found to be constant but different from that of tank nitrogen. Over this constant range a sample of tank nitrogen was analyzed, and a "discrimination factor" was calculated and applied to the converted-nitrogen ^{15}N determinations.

Samples of converted nitrogen and tank nitrogen were analyzed separately on a high-resolution mass spectrometer to identify any ion species that might be contributing to sample peaks. For the sample pressures investigated, there was little difference between the two samples. Three peaks appeared at the mass 28 and 29 positions, which were identified as N_2, CO, and hydrocarbons, possibly C_2H_4 and C_2H_5.

The bias in the 28/29 ratio of nitrogen converted from ammonia compared with tank nitrogen is not clearly understood; however, it was indicated that the impurities at the mass 28, 29, and 30 positions are related to the amount of hydrogen in the sample. To study this effect, the hydrogen-to-nitrogen ratio was increased in two converted nitrogen samples, and the results indicate that the 28/29 ratio decreases as the pressure of hydrogen in the sample increases. As a further test, nonreactive helium was added to converted nitrogen samples, with no detectable change in the 28/29 ratio. From this we conclude that an excess of hydrogen in the sample flask or in the mass spectrometer causes the production of interfering ions at mass 28, 29, and 30. An effort was made to reduce the amount of hydrogen in the samples by placing a heated Cu-CuO trap in the system. The hydrogen is removed at 500°C from the system by the following reaction: $CuO + H_2 \rightarrow Cu + H_2O$. By reducing the amount of hydrogen, we have eliminated this bias in the ^{15}N abundance measurements from NH_3 converted samples.

Three reaction flasks were incorporated into the manifold collection system, making it possible to accomplish three steps of collection by a sequencing mode. The analytical system can now turn out a complete isotopic and total nitrogen analysis on three samples per hour. With these final improvements to the system, the planned development work has been completed, and a final report is being prepared.

4. J. A. Carter et al., "Measurement of Nitrogen and Nitrogen Isotopic Ratios Using Reductive Pyrolysis Coupled with Mass Spectrometry," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 49.

Implications from our research are that investigators attempting to establish the movement of nitrogen fertilizers in groundwater by the shift in the $^{15}N/^{14}N$ ratio should make sure that the mass spectrometer used has a resolution ($M/\Delta M$) in excess of 2500, or that the nitrogen abundances are measured from purified N_2 samples.

Nitrogen and silicon isotopic measurements in silicon nitride. The Massachusetts Institute of Technology is studying the diffusion of Si_3N_4 into highly refractory materials. MIT was attempting to use Si_3N_4 enriched with the stable isotopes of ^{29}Si and ^{15}N but had difficulty finding a laboratory that could make the isotopic measurements. With the approval of the USAEC, our Mass Spectrometry Group at ORNL agreed to analyze several Si_3N_4 samples; the ^{15}N abundance will be measured on the developed nitrogen system,[4] and the ^{29}Si abundance measurements will be obtained by thermal emission mass spectrometry after silicon is converted to $BaSiF_6$.

To analyze the Si_3N_4 samples for ^{15}N abundance, a method was developed for releasing the nitrogen as N_2. Under normal conditions, silicon nitride is an amorphous, grayish-white powder and rather refractory (mp >1900°C). The nitrogen is difficult to release at temperatures normally available to the sample inlet system of the gas mass spectrometer; therefore, slurry samples of about 3 mg of Si_3N_4 were placed on V-shaped rhenium filaments. For each sample, the filament holder was sealed into a reaction flask of the total-nitrogen and ^{15}N system and evacuated. The flask was then tested for leaks, and if none were found the filament temperature was raised with the aid of a transformer and a Variac to approximately 500°C to drive off the water and surface-adsorbed atmospheric nitrogen.

Ion currents at mass 28 (N_2) were monitored as a function of the temperature of the sample. (Ion currents are proportional to the partial pressure of the gas being evolved.) The temperature was measured with an optical pyrometer. Evolved gases were collected for 3 min and then admitted into the sample system of the mass spectrometer. After the peaks were measured, the sample flask was evacuated and the next temperature level of the sample was attained. Evolution of N_2 starts at about 900°C and reaches a peak at 1550°C, and then the evolution of N_2 decreases as the temperature is increased to >1900°C. In these experiments, it was shown that sufficient N_2 was released for ^{15}N abundance measurements.

Multielement isotope dilution spark-source mass spectrometry development. We successfully proposed through the ORNL/NSF(RANN) program to build on our experience in analyzing for trace elements by isotope dilution spark-source mass spectrometry (IDSSMS).[5] In the first year, we are in the process of extending the technique to 20 or more elements by developing the necessary multielement enriched-isotope spike methodology. The second year of the proposal will cover additional isotope dilution and IMMA development techniques. The enriched stable isotopes have been selected and purchased from the Isotopes Division. Two major criteria, where possible, were used in the selection of the isotopes to be used. First, the isotope for the spike should occur in nature in low abundance, and second, it should have an odd mass. The odd mass becomes important when one is forced to work in a complex matrix. For example, $^{123}Te^{2+}$ ion produced in the mass spectrum at a mass position of $m/2e = 61.5$ would be free from any molecular species that might be formed. Doubly charged molecular species are rare. Other considerations prior to procurement were availability, purity, cost, and degree of enrichment. In most cases, the highest enrichment available was purchased. Stock solutions of each of the following isotopes have been prepared: ^{25}Mg, ^{43}Ca, ^{49}Ti, ^{53}Cr, ^{57}Fe, ^{61}Ni, ^{65}Cu, ^{67}Zn, ^{71}Ga, ^{73}Ge, ^{77}Se, ^{87}Sr, ^{91}Zr, ^{97}Mo, ^{106}Cd, ^{113}In, ^{125}Te, ^{135}Ba, ^{180}W, ^{203}Tl, and ^{204}Pb. Composite spike and initial equilibrium studies have been made. Graphite substrates show the most promise for use as conducting electrode material; surface film concentrations down to 10^{-10} g are measurable for many of the isotopes under consideration.

Allen Steam Plant mass balance for lead, cadmium, and zinc. We obtained from the Allen Steam Plant in Memphis, Tennessee, homogeneous representative samples, so we could establish the mass balance for lead, cadmium, and zinc by IDSSMS. Additional elements were measured by other techniques, and the results are reported elsewhere in detail.[6] In this study, the enriched spike for each element was added, so that the ratio between the spike isotope and the major isotope being measured was near unity. The imbalance measurements were Pb, −6%; Cd, +6%; and Zn, −2%. These results are within the experimental capabilities of the Q-2 emulsion used to detect the ions produced in the radio-frequency spark source.

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5. J. A. Carter et al., "Environmental Spectrometry," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973*, ORNL-4930, p. 51.

6. D. H. Klein et al., "Mass Balance for Thirty-three Elements at a Coal-Fired Power Plant," in preparation.

Spark-source mass spectrometry measurements of trace metals in gasoline for EPA. The analysis of gasoline for trace metals has continued this past year. The method of treatment with $CCl_4:Br_2$ followed by freeze-drying is still in use. The use of larger samples allows the detection limits to be set at lower values and the number of elements measured to be expanded.

Work is in progress to prepare standard solutions of organometallic compounds so that standard additions can be used to determine the recovery of individual elements. Work is also being done on extraction methods using these compounds dissolved in gasoline as indicators of recovery of the impurity elements. Recovery of an element added to gasoline has been found to depend strongly on the chemical nature of the element.

ORGANIC MASS SPECTROMETRY

Approximately 800 samples were analyzed by organic mass spectrometry during the past year. The major load was carried by the single-stage instrument, but high-resolution data were taken when they could be of value in qualitative analysis. The gas chromatographic inlet for the single-stage instrument has been invaluable in obtaining spectra of individual components of complex mixtures – a difficult, if not impossible, task when the direct-inlet probe is used.

We have received most of our samples from biologically oriented programs. A large part of the effort has been in assistance to the Chemical Technology Division, particularly the Body Fluids Analysis Program, and those programs sponsored by EPA, NSF, and AEC on identification of organic compounds in natural and polluted waters. Major support has been given to the Biology Division also, with emphasis on the programs of W. Lijinsky and G. M. Singer in their studies of naturally occurring amines and production of nitrosamines.[7] Preliminary data obtained with the monopole spectrometer from samples collected in the Metals and Ceramics Division microsphere-coating operation led to the purchase of a time-of-flight spectrometer, and further cooperative work will follow delivery of the instrument in November. This work is discussed in more detail in the section on Gas-Cooled Reactor Programs. We have also continued assistance to the Y-12 Plant in studying possible air pollution and exposure of workers to hazardous chemicals in line with OSHA regulations. Intradivisional cooperation has been primarily with the Bio-Organic Analysis Group in the Tobacco Smoke Research Program – for example, the monopole mass spectrometer analyses discussed in the section on Mass Spectrometry Development.

The Purchasing Division is negotiating a contract with the General Electric Company for our use of the Mass Spectral Search System (MSSS), which is available on the GE Mark III computer network. The MSSS is the best-known and most comprehensive mass spectral data base and search system in the world. It allows many options in library search modes and is expected to contain over 25,000 spectra by the end of this year. An ASR 33 teletypewriter and acoustic coupler have been purchased and will be available for use with the MSSS. We are sure that use of this system will be of great value in qualitative organic mass spectrometry.

We have improved the IBM 1130 computer program used for identifying peaks obtained in a mass scan of the single-stage mass spectrometer when interfaced to the computer. As stated in last year's report,[8] some data were lost when mass peaks were superimposed on a shifting baseline or a broad metastable peak. All peaks can now be located by use of signal averaging and slope detection rather than a threshold value.

We are presently constructing the ion source parts necessary for converting our instruments to field ionization and chemical ionization modes. These techniques employ very soft forms of ionization and are valuable in identifying molecular ions, especially with materials that fail to form molecular ions under electron bombardment. In addition, a 1200-liter/sec diffusion pump, water-cooled baffle, and gate valve have been received for installation on the research single-stage spectrometer. Replacement of the titanium sublimation pump with this high-speed system will allow us to use the spectrometer in developing field or chemical ionization and will generally improve the usefulness of the instrument.

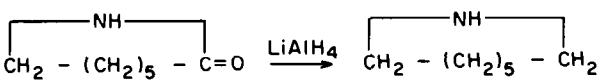
We are rebuilding the heated-inlet system used on the single-stage instrument before direct-inlet probes were available. This batch inlet will be necessary for quantitative analyses of coal-derived liquids. At the same time, we are studying the problems associated with the use of low-voltage electron bombardment in analysis of coal liquids. Both low-voltage–high-resolution and low-voltage–low-resolution mass spectrometric techniques are in use in industry for analysis of such mixtures. The

7. W. Lijinsky, W. H. Christie, and W. T. Rainey, *Mass Spectra of N-Nitroso Compounds,* ORNL-TM-4359 (October 1973).

8. J. A. Carter et al., "Organic Mass Spectrometry," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 54.

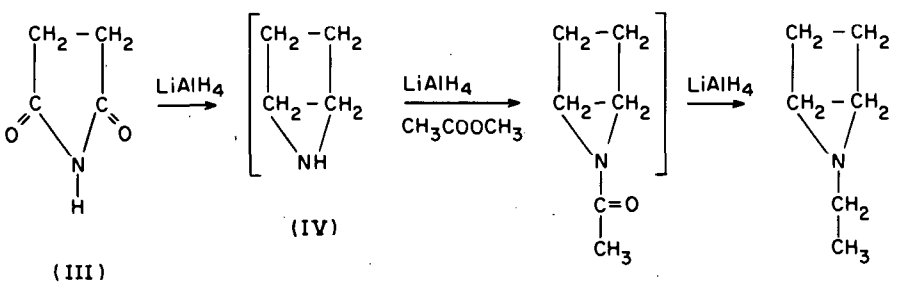
low-voltage techniques allow the study of spectra containing predominantly molecular ions (similar to field or chemical ionization) and result in much simpler calculations in quantitative analysis. We also expect to apply field and chemical ionization to the problem.

An interesting and unexpected reaction was detected in a series of samples analyzed for A. R. Jones of the Biology Division, who has been preparing a series of cyclic imines for use by W. Lijinsky in his nitrosamine research. The imines were prepared by reduction of the corresponding imides or lactams with lithium aluminum hydride, followed by destruction of excess hydride with ethyl acetate, as illustrated by the formation of heptamethyleneimine (II) from the lactam of 7-aminoheptanoic acid (I):



(I) (II)

Mass spectra of the products showed that heptamethyleneimine was formed as expected. However, no pyrrolidine (IV) was formed from succinimide (III), and only a small amount of hexamethyleneimine (from caprolactam) could be detected. Instead, in the latter cases a product was obtained that contained 28 mass units in excess of theoretical. Interpretation of the mass spectra led to the conclusion that these two imines had been ethylated during the reaction. Further study proved that the alkylation was taking place during excess hydride decomposition. When water was used to decompose the excess, no ethylation occurred; when ethyl butyrate was used, a butyl group was added to the imine. Therefore, it appears that an ester can undergo a reaction similar to ammonolysis, followed by reduction to a tertiary amine. Thus, in the following equation showing the reduction of succinimide (III) to pyrrolidine (IV), the pyrrolidine is acylated to *N*-acetylpyrrolidine (V), by reaction with methyl acetate, followed by reduction of the acyl derivative to the *N*-ethylpyrrolidine (VI) found by mass spectrometry:



(III) (IV) (V) (VI)

Satisfactory yields of the desired imines were obtained when water was used in the hydride decomposition.

During this study, we noted our first evidence that the heated stainless steel in our gas chromatograph inlet system might cause sample decomposition. Such problems are known to be important, especially in handling large polar molecules, but we have not experienced trouble before. During gas chromatograph–mass spectrometric analysis of the pyrrolidine product prepared by Jones, it was noted that large peaks were present at the $M^+ - 4$ mass position, indicating loss of four protons from the molecular ion. The occurrence of such losses, which are not expected in fragmentation of organic ions, led us to look for an explanation. Subsequent work showed that the loss of protons occurred in the inlet system, probably catalyzed by the large surface area of stainless steel in the helium separator, and did not occur in probe inlet samples. We have constructed a separator with a porous silver membrane of small area, which should cause less catalytic effect with thermally unstable compounds, and we hope to install it in the near future.

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 13,300 results were reported. Isotopic analyses were made on 53 different elements. Most of the isotopic analyses are for programs in the Isotopes and Chemical Technology Divisions. In the gas laboratory, gas compositions are determined on many inorganic and a few simple organic gases.

Actinides. Samples of the actinides uranium through californium are analyzed routinely. In addition, occasional requests for isotopic analyses of other radioactive or unusual samples are received. One unusual sample was a sample of einsteinum that had cooled for about ten months. It was found to be 99.986% ^{254}Es.

Another unusual sample was received from Neal Case of the Isotopes Division, who had irradiated approximately 2 mg of ^{244}Pu in an effort to produce ^{246}Pu. By isotope dilution using a spike of ^{242}Pu, we determined that the sample contained 48 ng of ^{246}Pu.

We were requested by J. H. Shaffer of the Chemical Technology Division to determine the amount of samarium in uranium microspheres. The samarium concentration ranges between 100 and 500 ppm. For the determination, the microspheres were weighed, calcined to remove resin, and finally dissolved. A known volume was spiked with enriched ^{148}Sm and ^{233}U. The samarium and uranium isotopic analyses were run on the same filament loading, and from the results the total quantities of the two elements were calculated. The samarium concentration value was good to about 2%.

Our work on the HTGR program has been directed toward developing methods for quantitative analysis for thorium and uranium and finding a good burnup monitor. We now have a double-spike standard containing ^{230}Th and natural uranium that can be used for the analyses. A more detailed description of this work is reported in the section of this report on Gas-Cooled Reactor Programs.

We again participated in the European "Safeguards" program, using the resin bead technique, which enables us to analyze for ^{238}Pu in the presence of ^{238}U, and ^{241}Pu in the presence of ^{241}Am, with no other separations. This is a promising technique and should find many uses in the laboratory.

Stable isotopes. Isotopic analyses were made on 40 different stable elements in the past year. The vast majority of this work is for the Isotopes Division in the Calutron Separations Program. During the past year, the emphasis has been on Cd, Os, Pd, Te, and Zr. These five elements have accounted for over half the work in this laboratory.

Gases. About half of the work in the gas laboratory is the certification of argon and helium cylinder gases. We have also made isotopic analyses on hydrogen, oxygen, carbon, sulfur, krypton, and xenon. We ran a series of samples for the Environmental Sciences Division to determine metabolism rates of small animals in their natural habitats. The animals were captured, injected with water containing deuterium and ^{18}O, then released. Later they were recaptured and blood samples were taken. The hydrogen and oxygen from the blood were sampled by W. R. Laing's group, and we analyzed the samples for their isotopic content, from which metabolism rates could be calculated.

We have given support to the HTGR program by analyzing various gas release samples. One series of samples were received in tubes sealed with rubber septa, which created a unique sampling problem. We solved the problem by fitting the gas manifold inlet system with a rubber septum to enable us to transfer the gas from the tubes to the mass spectrometer with a gas syringe. Little or no air inleakage was evident from the subsequent analyses.

We have recently installed a new vibrating-reed electrometer, which we hope will give us a larger dynamic range and better precision for gas analyses.

Elemental spectrometry. We provided emission spectrochemical and spark-source mass spectrometry analyses to 16 ORNL divisions and/or ORNL-related projects. A total of 57,273 results were reported during the past year, representing an increase of over 2000 results. Again, as in the previous year, Metals and Ceramics, Chemical Technology, Isotopes, and Health Divisions were the largest users of our elemental spectrometry service. Those four divisions account for about 70% of the reported results.

The direct-reading Paschen emission spectrometer has been used for quality assurance analyses on various alloy and metal samples submitted by the Inspection Engineering Department, particularly on aluminum alloys used in the HFIR; the latter samples are for quality assurance checks for the Operations Division. For the HTGR efforts, spark-source mass spectrometric procedures have been established for graphite and coated fuel microsphere samples so that boron-equivalent poison factors can be calculated.

Fuel analysis for LWFBR. In this program, 25 impurity elements are determined in $^{233}UO_2$ powders and various ^{233}U solutions by spark-source mass spectrometry (SSMS) and isotope dilution spark-source mass spectrometry (IDSSMS) techniques. The solid samples are separated into three aliquots for analysis because of the wide concentration ranges and variety of the elements of interest.

The first aliquot is used to determine the concentration of mercury by IDSSMS. It is dissolved and equilibrated with a spike of ^{196}Hg and allowed to amalgamate with a copper electrode. After a series of (1×10^{-9})-C exposures have been recorded on Q-2 photoplates, the densities of the ^{196}Hg and ^{202}Hg isotopes are measured, and the concentration of mercury in the sample is calculated with the PDP-8/E densitometer system.

The second aliquot is used to determine the concentrations of iron, phosphorus, and aluminum by the

internal standard method. The aliquot is dissolved and equilibrated with a spike of ^{57}Fe, and a portion of the solution is dried on graphite electrodes, from which a series of (1×10^{-9})-C exposures are made. The data are used to calculate relative sensitivity factors (RSF), which are then used to calculate the concentrations of the elements, corrected to an NBS uranium standard run with the sample.

The third aliquot is used to obtain concentration values for the remaining 21 elements. The concentration of iron measured in the second aliquot is used as the internal standard for this aliquot. A series of graded exposures (1×10^{-11} to 1×10^{-8} C) are recorded on the Q-2 photoplates. The PDP-8/E densitometer system is used to collect data from the photoplates and prepare punched paper tape containing relative intensity values for the different elements. The data on the punched paper tape are then processed on the IBM 1130 computer, which calculates the concentrations of the elements.

Elemental impurities in ^{233}U solutions are determined by any or all of the above procedures, depending on the analysis desired. Concentration ranges for the various elements are from 0.1 to 500 ppm, depending on the element and sample history. The precision of the method for the spiked element is generally in the 5% (relative standard deviation) range for a concentration of 100 ppm.

6. Bio-Organic Analysis

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T. W. Gilbert[5]	L. A. Littlejohn[7]	R. R. Reagan
C. C. Granger	A. H. Marshall	T. D. Roberts[8]

The Bio-Organic Analysis Group is presently committed to three separate but related projects. The first activity initiated at this Laboratory, the Tobacco Smoke Chemistry Project, is now a 10-man-year effort divided approximately 60:40 between routine analyses and analytical research and development. Experience in the chemical aspects of the smoking and health issue led to the initiation of a second project, Tobacco Smoke Inhalation Bioassay Research, which involves approximately 12 man-years equally divided between the Biology Division and this Division. At present, activities are directed at the development of viable approaches to dosing respiratory tract epithelium with whole tobacco smoke. Successes in inhalation bioassay research led to a third project, Smoke Exposure System Characterization. Unlike the first two projects, which are supported by the Smoking and Health Program of the National Cancer Institute, this new project is supported by the Council for Tobacco Research (CTR-USA). The extensive experience in smoke chemistry and analysis, coupled with a close relationship with the Biology Division, has provided an excellent base for participating in chemical, health, and environmental studies related to coal conversion processes. Work in this area is just beginning, but it is already apparent that an efficient transfer of capabilities is possible.

The three smoke-related projects are sufficiently interrelated to produce a synergistic effect, making the total program much more extensive than the sum of its parts. Chemical expertise greatly expedites bioassay and exposure chamber studies while also providing leads to biologically important constituents worthy of bioassay. Bioassay findings add immeasurable relevance and direction to chemical research. The thorough study of exposure systems ensures that viable systems are used in NCI-supported work. The net

1. Presently at Allied General Nuclear Services, Barnwell, South Carolina.
2. On loan to ORGDP.
3. Instrumentation and Controls Division.
4. GLCA participant from Earlham College, Richmond, Indiana.
5. On sabbatical leave from the University of Cincinnati, Cincinnati, Ohio.
6. ORAU summer research participant from Tennessee Wesleyan College, Athens, Tennessee.
7. Co-op participant from the University of Tennessee, Knoxville, Tennessee.
8. SCUU participant from Centenary College of Louisiana, Shreveport, Louisiana.

result is a program among the most comprehensive and best-known in the field. This is best illustrated by a very large number of visits from both novices and noted authorities to exchange information, and frequent requests for direct experimental support by other NCI and CTR-USA contractors. Support has been requested of biologists, chemists, and instrumentalists.

The principal activity in the Tobacco Smoke Chemistry Project is the chemical analysis of constituents of whole smoke, particulate matter, gas phase, and smoke condensate. Nonfiltered experimental cigarettes of carefully defined composition, approximately 25 types per series, are the principal samples. Cigarettes containing special filters, nontobacco cigarettes, and special-interest products such as a series of German cigarettes are also analyzed. Approximately 10,000 determinations are carried out per year. Approximately 50 constituents, ranging from gases such as CO and NO to compounds such as benzo[*a*] pyrene and indole, can be determined. The resulting data are compared with bioassay data obtained elsewhere in search of biologically significant constituents. Analytical research is aimed at improving the efficiency of routine operations and at allowing an increased chemical characterization of the smokes. Major accomplishments include (1) surveying sulfur-containing constituents as indicators of biological activity, (2) developing a multialiquot procedure for greatly increasing analytical efficiency while adding new constituents, and (3) establishing the "blind assay" as a means to increase greatly the chemical characterization and to provide leads to other biologically significant constituents.

Principal activities in the Inhalation Bioassay Research Project now center around four core tasks: (1) chronic exposure of rats to the inhalation of whole smoke, (2) dosimetry and tolerance studies, (3) tracheal transplant bioassay, and (4) chemistry of the exposure environment. The chronic exposure experiment is designed to test the possibility of producing lung cancers in rats. Serial killing and exposure modification studies are carried out in conjunction with the chronic exposure to provide information on pathogenesis and leads for protocols providing higher doses to the animal. Our contributions to this task include (1) the development, maintenance, and supply of exposure hardware, (2) monitoring the chemical nature of the exposure aerosol, and (3) monitoring biochemical changes in exposed animals. The major finding to date has been that rats can tolerate much higher doses than have previously been considered possible. This greatly increases promise for the successful induction of cancers and identification of pathological and biochemical states of predictive or interpretative value.

Dosimetry and tolerance studies are designed to test systematically the effects of smoke concentration and standing time, in a search for improved exposure protocols. This Division's contribution includes directing the study, monitoring the exposures, and analyzing resulting tissue samples. An important finding is that seemingly minor modifications in exposure sequence can have a major impact on the dose received by the animals.

Tracheal transplant studies are aimed at testing the feasibility of this model to test the carcinogenic potential of whole smokes on respiratory tract epithelium without involving the whole animal. Problems of toxicity, which severely limit inhalation exposure, are expected to be much diminished in this new model. Studies of smoke condensate implanted in the tracheas are now being de-emphasized in favor of studies of whole smoke. Our role in this area has been (1) the development of devices to prepare beeswax-condensate pellets for implantation, (2) the development of devices to dose transplants with whole smoke, (3) chemical analyses of carcinogen-containing pellets, and (4) study of the release rates of individual condensate constituents from beeswax pellets. Studies of the impact of transplant exposure on the host animal will soon supersede the chemistry of condensate-containing pellets. Principal findings to date are that the transplant model is viable for testing individual carcinogens and that beeswax is an

inappropriate vehicle for testing smoke condensate. Different constituents are released at dramatically different rates, so that only the slowly released constituents are responsible for the observed biological response.

Chamber chemistry studies are aimed at defining the quality of the smoke offered the animals, developing a nondestructive method for measuring dose, and monitoring the performance of machines used in exposure experiments. These activities are primarily the responsibility of this Division. Important findings to date include (1) that compositional changes during exposure are small for organic gas phase and for particulate matter constituents but large for gases (CO, CO_2, NO) involved in respiration, and (2) that the depletion of constituents during the exposure cycle provides a nondestructive measure of total dose and permits determination of the dose of any measurable smoke constituent. The aerosol offered the animal is thus quite "relevant" (not greatly affected by aging, only somewhat affected by differences between animals). Use of "dosimetry by depletion" will allow measurement of the doses received by individual animals throughout lifetime exposure.

The Smoke Exposure System Characterization Project is directed at evaluating exposure systems for reliability and relevance. A basic understanding of the chemistry of contained smoke aerosols is a long-range objective of this work. Results are used to select the preferred exposure system, to define exposures provided by any system of interest, and to interpret the biological responses resulting from routine bioassays. Significant results to date include (1) the finding that continuous smoke generators studied here are not operationally reliable at present, (2) the development of analytical techniques, including a continuous monitor for gas phase constituents, (3) a thorough evaluation of the standard Walton horizontal system, and (4) an initial assessment of the effects of animals, aging, and smoking conditions on the relevance of the aerosol.

The Tobacco Smoke Research Program as a whole is characterized by active collaboration with and support of other NCI and CTR-USA contractors. Activities have included the supply of specialty hardware, miscellaneous short-term studies, and direct experimental involvement in special dosimetry studies. We have been asked to direct a major dosimetry experiment in support of a CTR-USA contractor in the near future.

Work on coal-derived liquids has emphasized the evaluation of existing procedures for possible transfer to coal-derived samples. We find that phenol, the cresols, titrimetric acids, phenanthrene, benz[*a*]anthracene, benzo[*a*]pyrene, indole, and skatole are readily determined in at least one synthetic crude. Multicomponent profiling is readily carried out on coal-derived samples as well.

TOBACCO SMOKE CHEMISTRY

Control chemical analyses. Table 6.1 summarizes the constituents, parameters, and sample types now constituting the routine analytical capability. The routine determination of these constituents and parameters serves to monitor the quality of experimental products undergoing bioassay by other NCI contractors. The concentrations of the constituent determined here are also used in search of individual constituents responsible for or indicative of the tested biological impact. Identification of such constituents advances our understanding of chemical carcinogenesis in general and provides leads for process modifications that promise to produce a less hazardous cigarette.

The principal challenge of this activity results from the fact that a large number of samples must be analyzed for a large number of constituents. The matter is complicated further by the wide variety of analytical procedures required and by frequent requests to characterize smokes from unusual (nontobacco, special filtered, foreign, and modified) cigarettes. As research here and elsewhere identifies new chemicals of possible importance, methods must be developed to allow their routine determination. Major efforts in this project focus on achieving improved operating efficiency and on allowing maximum chemical characterization of each sample.

Approximately 1100 analyses of smokes (gas phase and particulate matter) and 1700 analyses of smoke

Table 6.1. Constituents and parameters of the control analyses capability[a]

Total particulate matter (pm*)	Gravimetric dry weight (cond*)
Water (pm*, cond)	Phenol (pm, cond*)
Nicotine alkaloids (pm*, cond)	*o*-Cresol (pm, cond*)
Tar (pm*)	*m*- + *p*-Cresol (pm, cond*)
Isoprene (gp*)	Colorimetric phenolics (pm, cond)
Acetaldhyde (gp*)	Catechol (pm, cond)
Acrolein (gp*)	Weak acids (pm, cond*)
Formaldehyde (gp*)	Very weak acids (pm, cond*)
Hydrogen cyanide (pm*, gp*)	Palmitic acid (pm, cond*)
Oxides of nitrogen (gp*)	Oleic, linoleic, linolenic acids (pm, cond*)
Carbon monoxide (gp*)	Stearic acid (pm, cond*)
Carbon dioxide (gp*)	pH (gp, pm, cond*)
Nitric oxide (gp)	Indole (cond*)
Hydrogen sulfide (gp)	Skatole (cond*)
Carbonyl sulfide (gp)	Phenanthrene (cond)
Sulfur dioxide (gp)	Benz[*a*]anthracene (cond*)
Carbon disulfide (gp)	Benzo[*a*]pyrene (cond*)
Thiophene (gp)	Glycerol (pm, cond)
Dimethyl sulfide (gp)	Cannabinoids (pm, cond)
Methyl disulfide (gp)	Nickel (cond)
Miscellaneous organosulfurs (gp)	Cadmium (cond)
Acetone (pm, cond)	Copper (cond)
Neophytadiene (pm, cond)	Zinc (cond)
Total particulate matter profile (pm, cond)	Mercury (cond)
Gas phase profile (gp)	Lead (cond)
Cigarette weight (*)	Tin (cond)
Cigarette resistance to draw	Titanium (cond)

[a]gp, gas phase; pm, particulate matter; cond, condensate; *, routine protocol determination.

condensates were completed since the last report period. As most analyses are carried out in quadruplicate, more than 10,000 determinations were completed. Approximately 80% of the analyses were carried out on primary experimental cigarettes (those undergoing bioassay elsewhere); the remainder were carried out on special products. The past report period marked the first extensive routine analysis of cigarettes containing tobacco substitutes. Reference standard blend cigarettes, cigarettes containing flue-cured and burley tobacco with different nitrate concentrations, and cigarettes containing mixtures of tobacco and tobacco substitutes received primary attention.

Several approaches have now been adopted to monitor the precision and accuracy of the routine analytical results. These approaches are (1) studies of precision, (2) comparisons of run-to-run agreement and agreement between results for similar parameters obtained by different methods, (3) repeated analyses of monitor cigarettes and samples from the standard experimental blend, (4) comparisons with literature values on a reference cigarette, and (5) collaborative studies with participating smoke chemistry laboratories. The precision we generally obtain is typical of that reported for comparable analyses in the literature.

We have made substantial progress in the past reporting period toward increasing efficiency and improving our ability to characterize samples. A matrix study was performed to evaluate sampling protocols. The study suggests that we need to analyze only half as many condensate samples to acquire equally reliable results. A consideration of analytical variability and lot-to-lot variability (resulting from variability in the generation and handling of subsequent condensate preparations) further suggests that, for certain samples, analyses can be carried out in duplicate rather than quadruplicate. If protocol modifications suggested by us are accepted by NCI, a reduction of 25 to 50% in the cost of condensate analyses may be possible. This is particularly important now, because the total number

of variables to be examined in the coming contract period has doubled. A further increase in efficiency may result from the incorporation of a newly developed "multialiquot" procedure for the determination of certain constituents.

New methods for the determination of free fatty acids,[9] carbon monoxide and carbon dioxide,[10] nitric oxide,[11] and sulfur-containing constituents[12] serve to increase efficiency, the number of constituents surveyed, or both. The method used for the determination of ciliatoxins[13] has recently been published. Multicomponent profiling and the "blind assay" concept developed here have been accepted as additional methods to characterize the samples more completely.

Data handling. The PDP-10 FORTRAN IV computer system has continued to be invaluable for handling the large amount of data generated in the program. We have continued to write new programs and modify old ones for handling the data in new ways, for preparing new table formats for in-house use and final reports, and for preparing bar graphs and correlation plots as visual summaries of data trends. Statistically treated data tables and summary tables have been completed, and correlation plots and bar graphs have been prepared for two series of cigarettes. A library is maintained of the final results of statistically treated data as binary files stored on magnetic tape and subject to recall at any time, allowing the earlier data to be treated or presented in new ways as ideas for more meaningful interpretations are generated.

A computerized data acquisition and analysis system has been developed for handling data from gas chromatographic analysis. The system takes data from the chromatograph, converts them to digital form, stores them on magnetic tape, and provides on-line integration and retention times of observed peaks. The operating program for the computer is written in a modified version of FOCAL. The data taking is controlled by interrupts generated by the computer's real-time clock, which avoids loss of data during transfers to magnetic tape or other operations and permits computation to be carried out during data taking without disturbing the time cycle. The raw data on the magnetic tape can be read into the PDP-10 computer and processed with a suitable FORTRAN program.

Multicomponent profiling and the blind assay. The traditional approach to defining the chemical composition of smokes and locating constituents indicative of or responsible for biological activity is through quantitative determination of selected constituents of known importance. The selected constituents may be biologically active, known to be indicative of the quality of the smoking product, or felt to be indicative of the composition of a certain subfraction of the smoke. A method is then developed specifically for the determination of the selected constituent and applied to large numbers of samples.

Multicomponent profiling – the chromatographic display of many individual constituents of a sample simultaneously – is an alternative method for characterizing the sample. Sample preparation and chromatographic conditions are simply optimized to allow visualization of a large number of constituents in a reproducible manner. When a large number of samples are available, the chromatographic response can be correlated directly with related data, for example, biological activity, on the same samples. Absolute calibration is not necessary, so all the peaks in the chromatogram can be tested for biological significance whether or not their identity is known. Since this approach allows testing of the significance of unknown constituents, it is called the "blind assay."

Applications of the blind assay method made to date have been limited to total particulate matter (TPM) and gas phase profiling. Studies were aimed at improvement in the discrimination of the TPM profiling methods[14] and extension of the blind assay to gas phase constituents of smoke.

Conditions were sought for TPM profiling that would allow improved separation of glycerol from nicotine, for better visualization of the component(s) eluting between the two peaks. One component of particular importance was found to be catechol. It was also of

9. M. R. Guerin, G. Olerich, and W. T. Rainey, "Gas Chromatographic Determination of Nonvolatile Fatty Acids in Cigarette Smoke," *Anal. Chem.* **46**, 761–63 (1974).

10. A. D. Horton and M. R. Guerin, "Gas-Solid Chromatographic Determination of Carbon Monoxide and Carbon Dioxide in Cigarette Smoke," *J. Ass. Offic. Anal. Chem.* **57**, 1–7 (1974).

11. A. D. Horton, J. R. Stokely, and M. R. Guerin, "Gas Chromatographic Determination of Nitric Oxide (NO) in Cigarette Smoke," *Anal. Lett.* **7**, 177–85 (1974).

12. A. D. Horton and M. R. Guerin, "Quantitative Determination of Sulfur Compounds in the Gas Phase of Cigarette Smoke," *J. Chromatogr.* **90**, 63–70 (1974).

13. A. D. Horton and M. R. Guerin, "Determination of Acetaldehydes and Acrolein in the Gas Phase of Cigarette Smoke Using Cryothermal Gas Chromatography," *Tobacco* **176**, 45 (1974).

14. M. R. Guerin, G. Olerich, and A. D. Horton, "Routine Gas Chromatographic Component Profiling of Cigarette Smoke for the Identification of Biologically Significant Constituents," *J. Chromatogr. Sci.* **12**, 385–91 (1974).

interest to design conditions such that all of the primary constituents, from phenol and the cresols to the free fatty acids, could be visualized. A number of column packings, types, and operating conditions have been investigated. The most promising of the columns tested is a 20-ft by ⅛-in.-OD glass column containing 4% OV-101 on Chromosorb G(HP). The sample is derivatized, a 5-μl aliquot is injected onto the column, and the temperature is programmed by being held constant at 90°C for 8 min, then raised to 210°C at 2°C/min. Phenol, the cresols, nicotine, catechol, glycerol, neophytadiene, palmitic acid, oleic-linoleic-linolenic acids, and stearic acid are visualized. The cresol and hydroquinone peaks are known to be contaminated with other constituents. Some question remains as to whether the fatty acids elute quantitatively. At least 20 additional constituents are visualized in the profile.

Studies have been directed at application of the blind assay technique to the gas phase of smoke for discovery of chemical indicators of carcinogenic activity. Present methods for measurement of the carcinogenic activity of tobacco products rely on painting of mouse skin with smoke condensate. Since constituents of the gas phase of smoke are not present in smoke condensate, the constituents are not causative agents in carcinogenesis as measured by skin painting bioassay. There is, however, evidence that constituents in the gas phase may be related to the biological activity of smoke condensate. Consequently, studies were initiated to assess the feasibility and value of the blind assay technique for gas phase constituents of smoke.

A high-resolution gas chromatographic profiling method was developed for blind assay of organic constituents in the gas phase. The method consists of the following steps: (1) smoke is generated under standard smoking conditions, (2) the gas phase of the smoke is separated and accumulated on the head of a capillary gas chromatographic column cooled with liquid nitrogen, (3) the column is temperature programmed to elute the gas phase constituents selectively, and (4) the areas of peaks in the chromatogram are measured and correlated with biological activity of the cigarettes. Figure 6.1 illustrates a chromatogram obtained by this method for smoke from the standard experimental blend. Approximately 150 peaks in the chromatogram are due to constituents of the gas phase with boiling points from about 20°C to 200°C, and only a few have been identified chemically.

An initial application of the method was made as a pilot study to nine cigarettes in NCI series I. High-resolution chromatographic profiles were obtained for the cigarettes, and the areas of 26 of the peaks in the chromatogram were correlated with biological activity. Peaks included in this study are designated in Fig. 6.1. Peak areas were correlated with T_{75} [time in days to 75% without tumor (Weibul fit)], assuming a linear relationship.

The biological activity of the experimental series is derived from skin painting results obtained by application of the smoke condensate at a constant dose level regardless of cigarette delivery. The skin painting results are, therefore, indicative of the intrinsic biological activity of the condensate and do not take into account variations in condensate delivery per cigarette, which are high. For this reason, chromatographic peak areas, normalized to cigarette delivery, were correlated with biological activity (T_{75}) for the 26 peaks numbered in Fig. 6.1. Using this approach, we find three peaks (19, 21, and 24) that correlate highly with skin painting results. The correlation plots indicate that the greater the magnitude of the normalized peak area, the more carcinogenic the smoke. A correlation plot for peak 21 is shown in Fig. 6.2.

This application of the blind assay technique indicates that the method shows considerable promise for revealing chemical indicators of biological activity in the gas phase of smoke. At least three and perhaps several more components of the gas phase are related to carcinogenic activity of tobacco smoke condensate. More detailed and comprehensive application of the method will be made in the future. Initial results of this study have been presented.

Multialiquot determination of protocol components. Phenol, *o*-cresol, *m*-cresol plus *p*-cresol, nicotine, palmitic acid, oleic plus linoleic plus linolenic acids, and stearic acid are "protocol" components, that is, components routinely determined on all primary experimental products. Glycerol is of increasing interest because smokes produced by tobacco substitutes contain abnormally high percentages of glycerol, which may adversely affect skin painting bioassay results. Catechol is of increased interest because it is known to be an active cocarcinogen and is present at relatively high concentrations in tobacco smoke.

Nicotine, the phenols, and the free fatty acids are determined by three separate procedures. The phenol procedure is laborious in that it requires steam distillation, extraction, gas chromatography, and scintillation spectrometry for reliable quantitation. A procedure for the routine determination of catechol has not been reported. Glycerol could be determined by one of

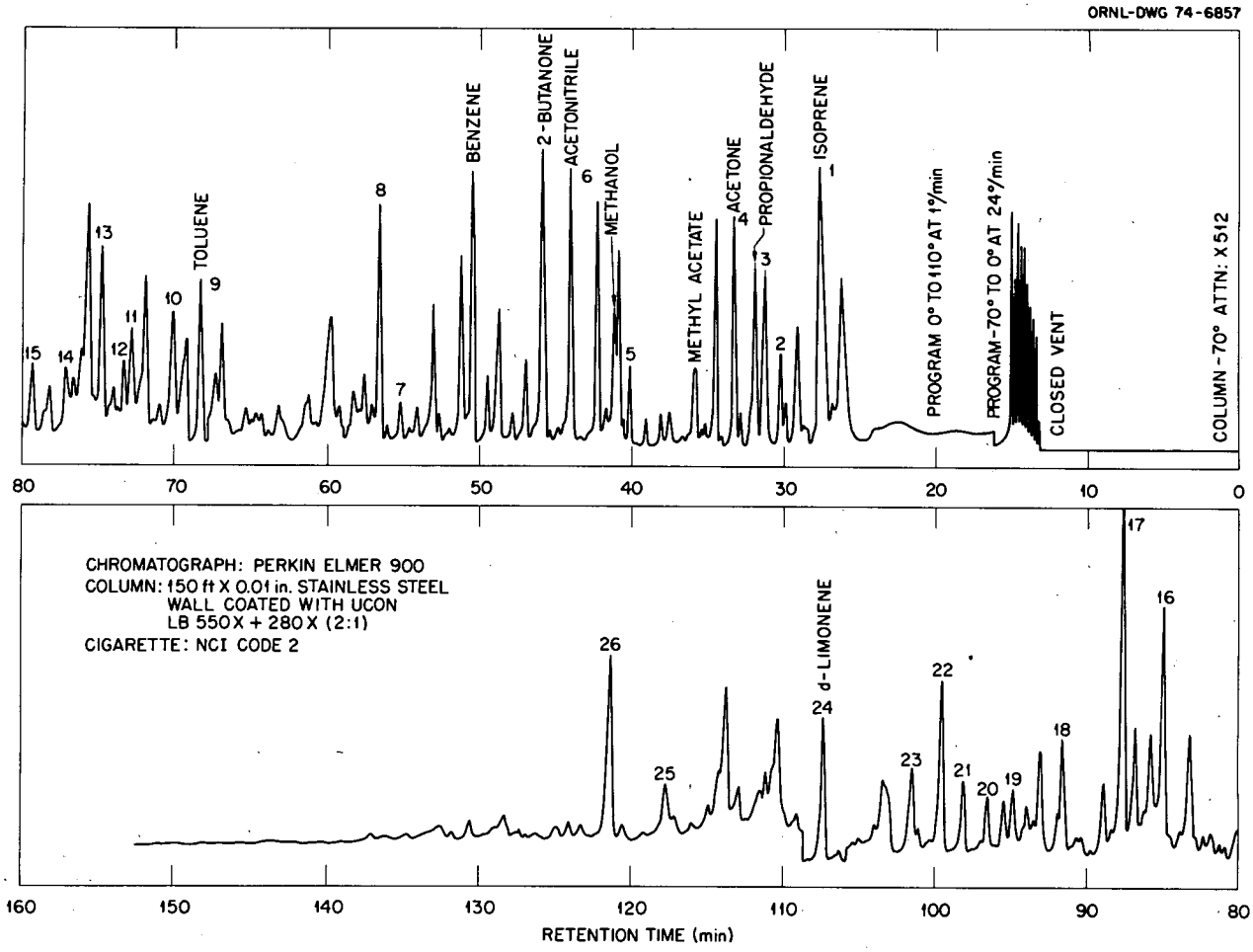

Fig. 6.1. Gas chromatogram of gas phase fraction of cigarette smoke.

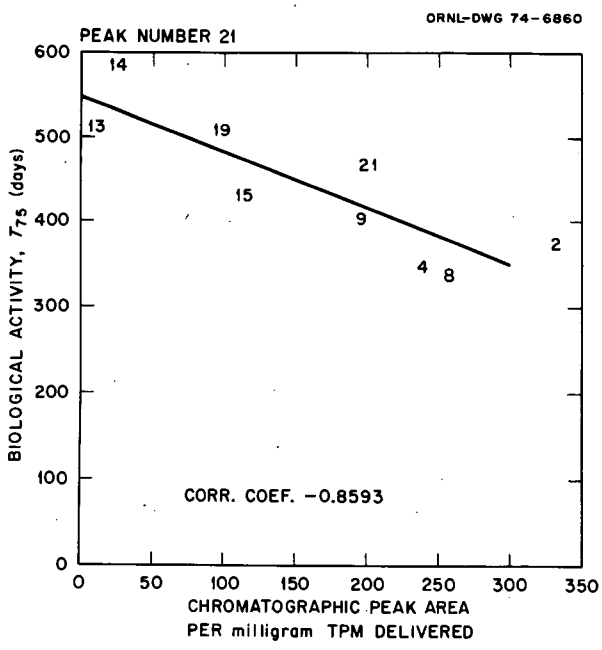

Fig. 6.2. Correlation plot of biological activity vs normalized peak area.

several modifications of a gas chromatographic method, but the method would require a separate sample from those used to determine nicotine, phenols, and acids.

We find that it may be possible to determine all the constituents mentioned in a single sample by injecting aliquots of that sample into separate chromatographs. Of particular importance is that the sample can be analyzed without prior separation steps. The sample, either total particulate matter or smoke condensate, is simply extracted or dissolved, respectively, in pyridine; trimethylsilylating reagent is added; and the solution is warmed for 30 min. A 5-μl aliquot is injected onto a methyl silicone column operated at 190°C to determine the free fatty acids.[9] A second 5-μl aliquot is injected onto a methylphenyl silicone (OV-17) column or onto a Dexsil column to determine glycerol, catechol, and nicotine simultaneously. A 5-μl aliquot is injected onto a 20-ft by $^1/_8$-in. Dexsil column at 110°C to determine the phenols. An added advantage of the procedure is that each cresol is determined separately rather than *m*-cresol plus *p*-cresol.

Standard addition experiments and comparisons of results obtained by the new procedure with those obtained by the standard procedures have been completed, and some preliminary conclusions are possible. Correlations between nicotine results obtained by the new and standard procedures over a series of experimental cigarettes agree very well. With the new method, nicotine peaks tend to "tail," suggesting that some nicotine may be irreversibly absorbed by the chromatographic system. This poses no problem for analysis of total cigarette deliveries but provides erroneous results when microsamples (such as those in inhalation chamber studies) are analyzed. The pyridine extract can be analyzed for nicotine prior to derivatization by direct injection onto Casterwax columns, for cases when the total quantity of nicotine is unusually small.

Results obtained for glycerol agree well with those obtained by established methods. Catechol results are not readily compared with results obtained by other procedures, because the reliability of published methods is suspect. Standard addition experiments suggest that the catechol results from the new method are reliable. The purity of the catechol peak has been confirmed by mass spectrometry.

The utility of this approach for the determination of phenol and the cresols is under intensive study. The greatly enhanced efficiency and added advantage of quantitating each individual cresol makes this an important contribution to the analytical chemistry of tobacco smoke. Because the phenolics are present at substantially lower levels than are glycerol, catechol, and nicotine, particular attention must be given to the possibility of interferences.

Neophytadiene, catechol, glycerol, and sulfur components – method and correlation with bioassay. We have been studying the possible relationship of neophytadiene, catechol, glycerol, and sulfur-containing compounds in smokes to biological activity. Interest in neophytadiene stems from the earlier reported finding that isoprene, principally resulting from pyrolysis of tobacco terpenes, correlates highly with mouse skin carcinogenesis. Measuring a major terpenoid directly in condensates or particulate matter is felt to be a better approach to assessing the role of these constituents than indirect assessment using isoprene deliveries. Catechol is of interest because recently reported data define it as a significant cocarcinogen, and it is the major phenolic constituent of smokes. Glycerol has become important with the addition of synthetic smoking materials (nontobacco) to the routine chemical and bioassay schedules. The effect of abnormally high glycerol concentrations on the bioassay method must be established. Sulfur-containing constituents are of interest because they have not been considered previously, and work at this Laboratory has provided the first reliable methods for their quantitative determination in smokes. Work has included development of new methods, analysis of smokes of known biological activity, and correlations of activity with constituent concentration.

We find that neophytadiene is readily determined in total particulate matter (TPM) by the direct injection of chloroform extracts onto a methyl silicone column operated isothermally. Standard addition experiments indicate complete recovery of neophytadiene with an overnight soak of filter pads containing the TPM. The identity and purity of the peak have been confirmed by mass spectrometry. Considering 31 different nonfiltered cigarettes from the first and second series of experimental products, we found concentrations ranging from 0 to 1.05 wt % TPM, 0 to 333 μg per cigarette.

Catechol and glycerol can be determined simultaneously with nicotine by the multialiquot technique described above. Considering a total of 31 different nonfiltered cigarettes from the first and second series of experimental products, we found catechol concentrations ranging from 0.2 to 0.8 wt % TPM, with most concentrations from 0.3 to 0.5 wt % TPM. Glycerol concentrations varied from 6 to 10 wt %, not including synthetic smoking materials. The two synthetics tested had glycerol concentrations of 34 and 52 wt % TPM.

Sulfur constituents are determined in the gas phase of smokes by direct gas chromatography with sulfur-selective photometric detection. Hydrogen sulfide,

carbonyl sulfide, and carbon disulfide require a commercial silica column for adequate separation. Organosulfurs, primarily dimethyl sulfide, diethyl sulfide, thiophene, and methyl disulfide, are determined on an FFAP column developed in house. Considering 11 filtered products and a total of 30 nonfiltered products from the first and second experimental series, we have found the following deliveries (per cigarette) to be typical: (1) 9 to 40 μg carbonyl sulfide, (2) 5 to 90 μg hydrogen sulfide, (3) 0.1 to 3 μg carbon disulfide, (4) 1 to 20 μg dimethyl sulfide, (5) 0.2 to 4 μg thiophene, and (6) 0.2 to 6 μg methyl disulfide. Little difference in the range of deliveries was found between filtered and nonfiltered products.

Correlation coefficients resulting from a comparison of biological activity with chemical concentration are presently under study. In the first series of experimental products, only neophytadiene correlates well ($r = -0.88$) with skin painting activity. Catechol, glycerol, and hydrogen sulfide may be related to biological activity ($r = 0.48$, 0.47, and -0.56 respectively). Data on organosulfurs and on the second experimental series are not yet fully evaluated.

Data on the sulfur delivery of cigarettes in the filter series have been correlated with whole-smoke bioassay tests. The bioassay tests include (1) inhibition of alveolar macrophage uptake of bacteria, (2) growth-inhibitory activity against cultured KB cells, and (3) in vitro ciliary activity. Hydrogen sulfide and carbon disulfide are highly correlated with one measure of ciliary activity. Dimethyl sulfide is highly correlated ($r = 0.79$) with the inhibition of macrophage uptake. Hydrogen sulfide and carbon disulfide are highly correlated ($r = 0.85$ and 0.86 respectively) with growth-inhibitory activity against KB cells. The results are to be studied in detail with the collaboration of personnel at Arthur D. Little, Incorporated, who provided the NCI with the whole-smoke bioassay data.

Polycyclic aromatic hydrocarbons (PAH). The analysis for the polycyclic aromatic hydrocarbons benz[*a*]anthracene (BaA) and benzo[*a*]pyrene (BaP) is the most laborious and time-consuming procedure we carry out. Several modifications introduced over the past year have considerably reduced the total analytical time and improved the recovery. The former practice of drying the acetone suspension before starting the extraction process has been discontinued, and the initial cyclohexane extraction is now being made on the acetone suspension diluted with water. The final cyclohexane extract is now passed through a Florisil column without a prior volume reduction, because it has been found possible to retain the polyaromatics on the column. The BaA and BaP are then eluted with a hexane-benzene solvent. The recovery with the new extraction and column procedures is increased by 10%, and time-consuming steps are eliminated.

The paper chromatographic separation of BaA from the other four-ring polyaromatics has been far from satisfactory because of the overlap of several fluorescent bands, which makes the isolation of the BaA band rather difficult. An acetylated cellulose column chromatographic separation has been developed to supplant the paper chromatographic separation. Radioactive counting of the eluting fractions is used to locate the eluting BaA peak precisely. At the same time, a small sacrifice in BaA recovery (discarding the shoulder fractions) gives a much cleaner product for the subsequent gas chromatographic analysis. Despite the partial sacrifice in BaA recovery on the acetylated cellulose column, the final BaA recoveries now average at least 10% better than in the past.

Analysis for PAH in cigarette condensate is difficult, due to the complexity of the condensate and the extremely low concentrations. The methodology developed here can be applied to PAH analysis in practically any matrix. For other matrices, it is likely that the analytical scheme for condensate analysis could be simplified considerably. Preliminary studies are under way to adapt our present smoke condensate methodology to PAH analysis of coal-derived liquids and biological samples.

Gas phase nitric oxide. One of the mechanisms for the formation of nitrosamines in cigarette smoke is the combination of NO and O_2 to form NO_2, and reaction of the latter with secondary amines to form nitrosamines. The adverse biological activity of the nitrosamines must be considered in inhalation experiments, and the determination of the nitric oxide precursor is important in discerning the chemical characteristics of smoke administered to animals in inhalation experiments.

A gas chromatographic method has been developed for determination of nitric oxide in cigarette smoke. A six-port, puff-averaging smoking machine[15] was used to inject a sample of smoke into the chromatograph. A Porapak P column was used to separate NO from all interferences. Nitric oxide elutes from the column, passes through a hydrogen-activated nickel catalyst at 500°C, and is converted to NH_3. The increase in electrolytic conductivity when the NH_3 dissolves in

15. M. R. Guerin and P. Nettesheim, "Sampling and Sample Preparation," *Tobacco Smoke Research Program Progress Report*, ORNL-4879 (April 1973), p. 4.

water in the Coulson detector is proportional to the NO content of the sample. We have applied this method to a number of selected experimental filter cigarettes. The relative standard deviation for the determination is 4.6% for samples containing 80 to 240 ng of NO and 8.5% for samples containing 20 to 80 ng of NO.

This method has the advantages of superior selectivity and of considerably less analysis time compared with the colorimetric method of Saltzman.[16] There is no advantage in time compared with the nondispersive infrared method of Williams and Belk,[17] but water, acetaldehyde, and ethylene interfere in their method. Nitric oxide analyses obtained on filter cigarettes by the infrared technique were correlated with those obtained by the new method, and a simple correlation coefficient of 0.94 was found. We have used the chromatographic method to determine NO in inhalation chamber experiments, to study the effect of aging on the NO content of the smoke, and to determine the uptake of NO by experimental animals.

INHALATION BIOASSAY RESEARCH

Inhalation bioassay research is a joint effort of the Biology and Analytical Chemistry Divisions. The primary responsibility for the development of bioassay methods suitable for the differentiation of experimental cigarettes must lie with the Biology Division; however, the scope of this study ranges from biology to chemistry and instrumentation. The portion delegated to the Analytical Chemistry Division includes (1) development of inhalation exposure hardware, (2) chemical characterization of the aerosol generated by the exposure system, (3) evaluation of the influence of animals on the aerosol, (4) determination of the dose actually received by the animals, and (5) chemical support for a novel bioassay system involving transplanted trachea.

Inhalation exposure hardware. The "double-puffer" system for smoke generation and exposure, described previously,[18] has become the system of choice for rat studies both here and at other NCI contractor laboratories. The current model (Fig. 6.3) has been improved in appearance and function by consolidation of all the components into a single cabinet, incorporation of a stirrer in the smoke chamber assembly to eliminate a smoke settling problem, and changing of the air supply to a fail-safe configuration. Normally open valves in the air supply now remove the possibility of suffocation as a result of power failure.

Efforts to improve and simplify the animal containers used for rats are continuing. We have adopted a cylindrical body tube with a simple conical headpiece, which provides for easy loading and fabrication. Further modifications may be required as the rats age and their body contours change.

We now have in use six double-puffer assemblies equipped with two full sets of side plates and body tubes and three single puffers. Enough additional body tubes have been fabricated to accommodate the control animals. We are building more of these systems for our own needs and for loan, at NCI's request, to Battelle Northwest Laboratory and to W. Dontenwill at the Research Institute of the German Cigarette Industry in Hamburg, West Germany.

Preliminary experiments to replace the Filamatic vial filler as a basic component of our inhalation smoker with a less cumbersome, readily available, and possibly less expensive device have been done. A puffing device that uses a controlled constant vacuum source was built from standard laboratory ware and suitable solenoid valves and coupled to one of our exposure units for comparison with the Filamatic puffing mechanism. The new scheme offers a capability not inherent in the assembly with the Filamatic – control of the puff pressure profile. For the Filamatic puffer, the peak in the profile occurred at approximately 1.15 sec with no hamsters and at approximately 1.75 sec with nine hamsters. In gaining improved control of the puff profile by using this new system, we have sacrificed the simplicity of adjustment that characterizes the Filamatic pump. A single adjustment of the Filamatic stroke length provides the necessary control of puff volume, but no control of the profile peak time. The line vacuum system as presently constituted requires manipulation of six interdependent variables, but it can control both volume and shape.

Chemical characterization of the Maddox-ORNL exposure system. A number of studies have been carried out to investigate the chemical composition and concentration of smoke in the Maddox-ORNL exposure system. General studies are reported in a later section (Smoke Exposure System Characterization). Specific studies in support of inhalation bioassay development are described here.

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

17. T. B. Williams and C. W. Belk II, "An Infrared Method for the Determination of Nitric Oxide in Cigarette Smoke," paper presented at 27th Tobacco Chemists Research Conference, Winston-Salem, N.C., October 3–5, 1973.

18. M. R. Guerin et al., "Inhalation Bioassay Methodology," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 17.

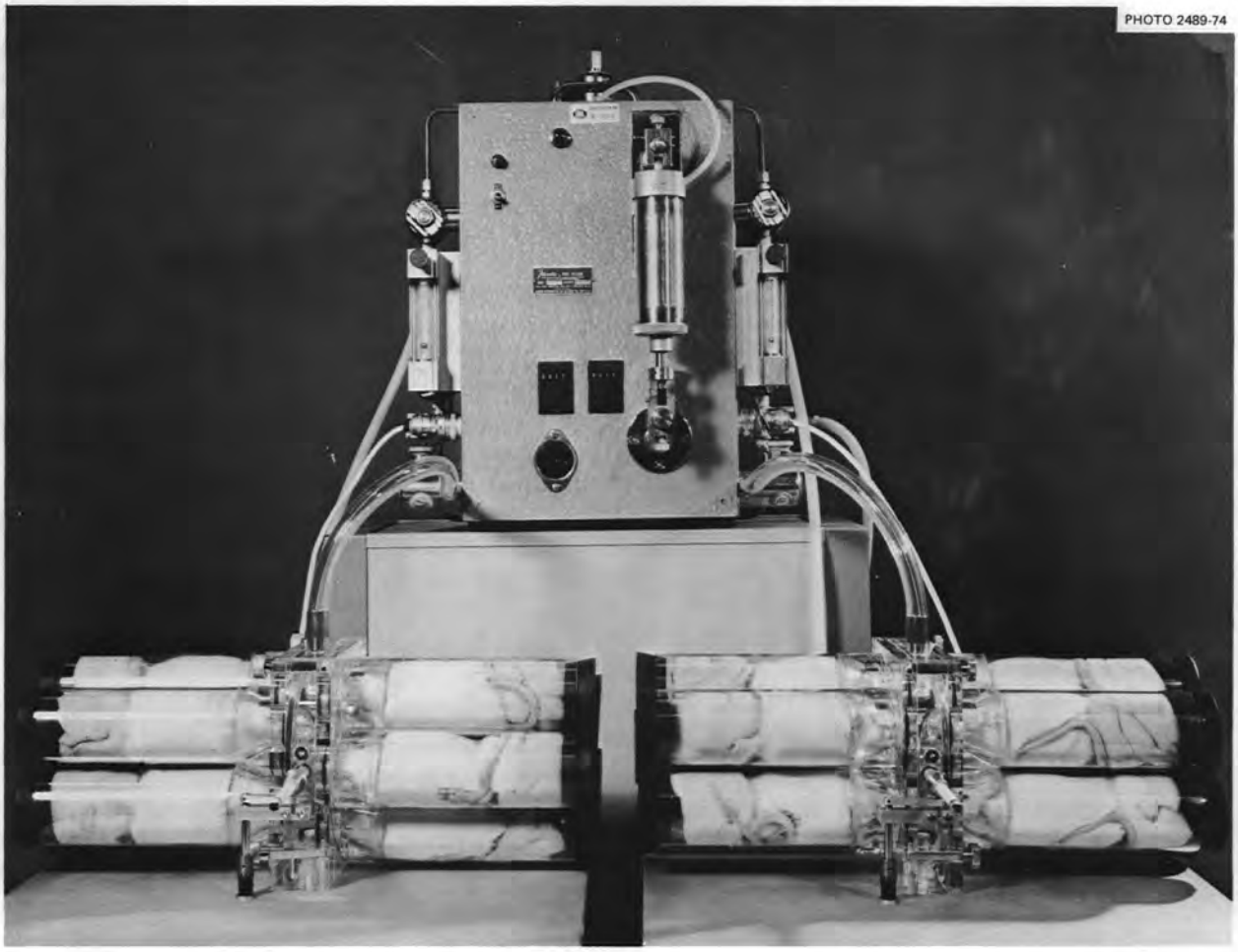

Fig. 6.3. Photograph of double-puffer exposure system with rats undergoing exposure.

Previously, we reported large concentration gradients in the exposure chamber of the Maddox-ORNL exposure system due to inadequate mixing and settling of smoke particulates.[19] Because of these concentration gradients, there was a possibility that animals were not uniformly exposed to the same concentration of smoke. A stirrer was placed in the exposure chamber to provide mixing. Smoke in the exposure chamber was sampled at selected positions, and nicotine was determined in the sampled smoke as an indicator of the smoke concentration. This work demonstrated that the stirrer effectively mixes the smoke, eliminating the possibility of nonuniform exposure. All Maddox-ORNL machines are now equipped with a stirrer as a standard component.

19. M. R. Guerin et al., "Smoke Generation – Biological Exposure Systems," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1973,* ORNL-4930, p. 20.

Modification of the Maddox-ORNL exposure system was made to provide variable smoke concentration. The machine was modified to smoke either one or two cigarettes into a chamber of either 350 or 700 ml volume, providing nominal smoke concentrations of 5, 10, or 20%. Data were collected which demonstrate that the modified system generates smoke properly. Losses of smoke to the vacuum pumping line were established for the various modified chambers. As expected, losses are greatest when two cigarettes are smoked into a 350-ml chamber (23%) and smallest when one cigarette is smoked into a 700-ml chamber (1%). Actual smoke concentrations in the exposure chamber were determined with these losses taken into account.

Dosimetry from chamber depletion. The most reliable method for establishing dose for inhalation exposures to tobacco smoke involves the use of smoke tracers.

Chemicals such as ^{14}C-labeled dotriacontane or decachlorobiphenyl are added to cigarettes. The tracer is carried with the particulate phase of smoke, impacts with the smoke particles in the respiratory tract, and is quantitatively determined in the tissues when the animals are killed. Relating the quantity of tracer found in the animal to the quantity offered allows a calculation of "dose."

The principal disadvantages of this method are that it is destructive (the animals must be killed) and that the relationship of tracer deposition to deposition of actual smoke constituents is not known. A common observation[20] in chamber chemistry studies on the Maddox-ORNL smoking machine is that measurable and often major decreases in concentration of smoke components accompany the presence of animals. In the absence of animals, little or no change in concentration is generally observed. If these concentration changes are due to irreversible removal of the constituents by the animals, chamber depletion could provide a direct measure of dose, and the dose of any measurable smoke constituent could be determined. More importantly, since this is a nondestructive method, animals could be examined throughout the course of chronic exposure experiments.

Comparative studies were performed to test chamber depletion methods for determining the dose of smoke deposited. Analysis of smoke in the exposure chamber early and late in the exposure period showed an appreciable depletion of the smoke particulate concentration during the exposure. For a 30-sec exposure, the smoke particulate concentration was depleted by 30%, and the depletion per animal was 3.0% (ten hamsters). Likewise, the depletion for a 40-sec exposure was 4.3% per animal. Use of tracer methods for direct measurement of the dose of smoke particulates received by the animals gave 2.1 and 3.3%, respectively, for 30- and 40-sec exposures. Assuming that depletion is due solely to uptake of particulates by the animals, and that tracer methods are reliable, the percent depletion per animal should be equal to the percentage of the tracer in the animal. Initial results indicated that the dose measured by depletion, although in reasonably good agreement for experiments of this type, is consistently higher than the dose measured by the tracer method. Additional studies have shown that the higher results from the depletion are partially due to loss of smoke particulates to the chamber walls. Adjustment for those losses gives closer agreement between the two methods.

Inhalation exposure dosimetry. We have continued studies for NCI on the deposition of smoke particulate matter in hamsters, and we have begun similar studies on rats. An experimental design matrix has been constructed that will allow a systematic evaluation of two variables, smoke time and smoke concentration. Emphasis so far has been on dosimetry during intermittent smoking and on development of suitable protocols for adapting the test animals to smoke. Some study of the differences between an inbred strain of hamsters and the conventional outbred strain in respiration and smoke deposition has been completed. We have also carried out some dosimetry studies on hamsters and on mice in support of work being done for CTR-USA.

In the past year we have completed 18 to 20 smoke deposition studies on hamsters and 11 studies on rats. Several of the studies were designed to compare smoke deposition in inbred hamsters (strain 87.20) and conventional Sprague-Dawley hamsters, because the former strain is reputed to be more resistant to the acute and chronic toxic effects of cigarette smoke. The combined results of the experiments in which all animals received the same treatment are shown in Table 6.2. It can be seen that decreased lung deposition for the 87.20 hamster corresponds well with their decreased respiration. The 87.20 strain also shows a corresponding

20. J. R. Stokely and M. R. Guerin, "Tobacco Smoke Inhalation Bioassay Exposure Chemistry. I. Intermittent Exposure to Standing Smoke," submitted to *Arch. Environ. Health.*

Table 6.2. Comparative dosimetry in 87.20 hamsters and Syrian golden hamsters[a]

Strain	Lung deposition		Carboxyhemoglobin level		Minute volume during smoke exposure	
	% of input	Ratio	%	Ratio	ml	Ratio
87.20	0.55	0.64	21.01	0.77	20.7	0.75
Syrian golden	0.86		27.31		27.5	

[a]Values given are averages derived from 20 hamsters per group.

decrease in carboxyhemoglobin content. These data suggest that the increased resistance of the 87.20 strain to smoke toxicity may be partly due to lower inhaled doses.

For most of our studies, ^{14}C-labeled dotriacontane (DTC) has been used as the tracer for dosimetry studies. Other groups have reported the use of ^{14}C-labeled hexadecane (HD)[21] and decachlorobiphenyl (DCBP).[22] We had previously done some work with HD,[23] and we recently repeated that work. The results indicated that deposition of HD was only about one-third that of DTC, and that the body distributions of the two compounds were substantially different. About 65% of the internal body activity of DTC was found in the lungs, but only 50% of the HD was found there. DCBP is desirable as a smoke tracer because it does not contaminate the equipment with radioactivity; however, its determination in tissue requires a tedious separation procedure followed by gas chromatography with an electron capture detector. We are proceeding with the development of an improved method for the determination of DCBP. Preliminary results indicate that the compound can be extracted into hexane homogenized with a dessicant, and the hexane extract can be cleared for gas chromatography by high-speed centrifugation.

We have measured the respiration of a group of hamsters after 12 cigarettes per day for a period of six months. An average minute volume of 30 ml was found during smoke exposure, compared with a value of 50 ml measured prior to smoke exposure on the test day. Initial respiratory volume of the animals was about 65 ml; however, the drop in normal volume cannot be ascribed to smoke effects, since the respiratory volume of the controls changed by nearly the same amount in the same time period. The 30-ml minute volume in smoke for the experienced smokers corresponds to a value of about 25 ml for animals that had not previously smoked.

Most of the dosimetry experiments with rats were done to help establish the most effective means of containment for rats. For the three types of rat containment tubes tested, there was no significant difference in the particulate matter deposition. It was also found that the amount of deposition, as well as its distribution, was essentially the same for rats as for hamsters. One of the rat studies was designed to measure the amount of accumulation of smoke particulate matter. Different sets of rats were given one, five, and ten labeled cigarettes. The results (Table 6.3) indicate that the accumulated particulate matter is proportional to the amount offered, the body distribution changing with time. The most recently completed dosimetry study on rats measured the distribution of smoke particulate matter within the respiratory tract. The distribution within the various lobes of the lung itself is relatively uniform on a weight basis.

Tracheal transplant support. Tracheal transplants were first exposed to undiluted whole smoke by forcing the smoke through a polyethylene tube temporarily joined to the trachea. A modified Filamatic pump was used to generate and deliver the smoke. It has now been found that smoke can be aspirated from a smoke chamber through a trachea either by a controlled vacuum or by a Harvard respirator. A satisfactory way to attach the trachea to tubes penetrating the skin and to attach these to the generating apparatus has yet to be developed. We have experimented with tubing of silicone rubber, polyethylene, Teflon, and Lycra. An NCI cannula material (spring-reinforced Lycra tube) is the best material tested to date. It accepts sutures, is

21. W. Dontenwill, H.-P. Harke, A. Baars, and C. Goertz, "Experimental Investigation of Inhalation and Deposition of Smoke Composition by Passive Smoking of Golden Hamsters with Cigarette Smoke," *Arzneim. Forsch.* **21**, 142 (1971).

22. C. I. Lewis, J. C. McGeady, H. S. Tong, F. J. Shults, and A. W. Spears, "Cigarette Smoke Tracer – Gas Chromatographic Analysis of Decachlorobiphenyl," *Amer. Rev. Resp. Dis.* **106**, 480 (1972).

23. M. R. Guerin and P. Nettesheim, "Hardware Development and Chemical Studies," *Tobacco Smoke Research Program Progress Report*, ORNL-4879 (April 1973), p. 61.

Table 6.3. Accumulation of smoke particulate matter in rats

No. of cigarettes	TPM (mg)						
	Lung	Larynx	Head	Jaw	Stomach	Intestines	Total
1	0.31	0.01	0.02	0.01	0.06	0.00	0.41
5	1.08	0.01	0.05	0.02	0.27	0.70	2.14
10	2.41	0.02	0.14	0.04	0.48	1.73	4.82

tough enough to withstand repeated connection to the external machinery, and has a fairly mild reaction with the tissues. Consideration is now being given to the design of suitable (probably molded plastic) fittings to be inserted into the skin to couple the cannulae with the smoke delivery system. Working models of a new smoking system that will draw and dilute the smoke and push it through the tracheas, and of an aspiration system, are being designed. They will be compared for ease of handling and for amounts of smoke deposited in the tracheas.

Measurement of uptake and impact. The establishment of dose received is very important, but of equal importance is the evaluation of the impact of that dose. Thus, it is important to develop sensitive and, eventually, nondestructive methods that will be indicative of changes taking place in the animal as a result of smoke insult. The constraint introduced by a nondestructive method requires that samples from the animal be restricted to available physiological fluids such as urine and blood. The presence of nicotine and/or its major metabolite, cotinine, may serve as a good indicator of dose. However, analysis for those compounds in real physiological samples is not simple, because of the low level at which they occur and because any real sample is complicated by the presence of many other physiological substances.

Development of an assay for nicotine and cotinine has been approached in two ways: (1) development of a radioimmunoassay similar to the procedure of Langone, Gjika, and Van Vunakis,[24] and (2) development of a conventional assay involving either gas chromatography or liquid chromatography after extraction from the physiological sample. The radioimmunoassay technique requires little sample cleanup because it employs the specificity of antibodies and thus meets with almost no interference. A suitable antiserum has not yet been obtained, but the procedure for the assay has been fairly well defined. A 2-ml DEAE-cellulose anion exchange column at pH 8 readily separates nicotine from antibodies, and the antigen-antibody complexes are held on the resin until the complex is disassociated and eluted by a different solvent system.

The possibility of using high-pressure aqueous liquid chromatography to screen urine for changes resulting from smoke exposure is being evaluated. Samples of urine from smoked and unsmoked hamsters and mice have been chromatographed, and about 20 differences have been noted in the chromatograms for the two groups.

A differential method for carboxyhemoglobin has been adapted from the literature.[25] It appears to be quite sensitive and will be used to complement chamber depletion methods for carbon monoxide; however, several problems are evident. Total blood volume of the animal must be known, so techniques employing tracers to determine blood volume must be perfected. Other problems arise from sampling: How quickly must or can a blood sample be taken after smoke exposure? and Does all the carbon monoxide depleted from the chamber appear as carboxyhemoglobin?

SMOKE EXPOSURE SYSTEM CHARACTERIZATION

Smoking devices have been used here and at other laboratories for some time to expose experimental animals to tobacco smoke for development and application of inhalation bioassay techniques. Little information has been available on the chemical composition, concentration, or aerosol properties of smoke offered to animals in these devices. Such information is needed (1) to assess the relevance of smoke generated by different devices to smoke generated by humans, (2) to define the concentration of smoke offered to animals during exposures, and (3) to identify the interaction of smoke components with smoke itself, machine components, or experimental animals. During the past year, studies have been made for the CTR-USA to provide information on smoke offered to animals by three exposure devices that are being considered for use in large-scale exposure experiments. One of these devices, the Walton horizontal smoking machine, is a highly developed static exposure system that provides exposure to a small number of animals ($\leqslant 20$). The other two devices, the Lorillard LACS-II and Process and Instruments SEM-I, are dynamic exposure systems capable of exposing large groups of animals (>100) to cigarette smoke. Both the LACS-II and SEM-I systems were developed only recently, and currently only one prototype model of each system is available. Extensive studies on smoke concentration, smoke distribution, operational characteristics, and smoke composition have been made on the Walton horizontal exposure system. The LACS-II and SEM-I systems have not yet been fully evaluated; only their operational character-

24. J. J. Langone, H. B. Gjika, and H. Van Vunakis, "Nicotine and Its Metabolites. Radioimmunoassays for Nicotine and Cotinine," *Biochemistry* **12**, 5025 (1973).

25. B. T. Commins and P. J. Lawther, "A Sensitive Method for the Determination of Carboxyhemoglobin in a Finger Prick Sample of Blood," *Brit. J. Industr. Med.* **22**, 139 (1965).

istics have been studied, and preliminary measurements of smoke concentration and composition have been made.

Development of sampling and analysis methodologies. Three methods have been investigated for sampling smoke in the exposure systems: (1) pulse sampling, in which a known volume of smoke is removed from the exposure system over a short time (<2 sec); (2) continuous sampling, in which a sample is withdrawn continuously; and (3) in situ sampling, in which a physical property of the smoke is monitored continuously without sample removal. Pulse sampling has been used extensively for studies on the exposure systems, mainly because existing techniques for analysis of smoke can be readily used with this sampling method. Two variations of the pulse sampling method were considered for application to the systems. One consisted of individual puff sampling, in which a sample is removed from the exposure chamber on a selected puff of the cigarette and immediately transferred to on-line instrumentation for analysis. The other consisted of sampling of the exposure chamber on all puffs from the cigarette and collection of a composite sample from all puffs. Due to poor reproducibility caused by high puff-to-puff variability, sampling on all puffs was the preferred method except in cases where reactive constituents (NO) were under study. Smoke particulate samples were trapped on a filter pad, and gas phase samples were collected in a holding container or by cryothermal trapping. A special device was built for pulse sampling, equipped with timers that were synchronized with timers on the exposure systems, so that repetitive sample removal could be made at any time during the smoke exposure cycle.

Using pulse sampling, we have devised a method for measurement of smoke concentration in the exposure systems. It relies on determination of nicotine and carbon monoxide as particulate and gas phase indicators of smoke concentration. Because of small quantities of nicotine in samples from the exposure systems, standard methods for collection of particulates and analysis of nicotine were modified. A special low-dead-volume filter holder and small filter pad were utilized for collection of particulate samples. The particulates were dissolved in the minimum volume of solvent, and gas chromatographic conditions were optimized for high sensitivity. Carbon monoxide in smoke from the exposure systems was determined by a modified version of the standard gas chromatographic method. The major modifications were the use of a finer column packing and doubling the length of the column to improve its resolution.

One of the major limitations of the analysis of smoke in exposure systems is small sample size. We have demonstrated, however, that a number of analytical methods for normal samples can be readily adapted to exposure system samples. In addition to nicotine and carbon monoxide, the following constituents have been successfully determined in exposure system samples: phenol, catechol, glycerol, free fatty acids, neophytadiene, carbon dioxide, nitric oxide, hydrogen, acetaldehyde, acrolein, and isoprene.

Measurement of smoke concentration and uniformity. Factors such as initial mixing of smoke when it enters the Walton exposure chamber and smoke uniformity during the exposure period were studied to assure that all animals exposed on the machine are offered the same concentration of smoke. We have demonstrated that mixing of smoke is nearly instantaneous as it enters the Walton exposure chamber, and that there are no animal exposure sites where the smoke concentration is high during puffing. During the exposure period, the smoke is distributed uniformly in the chamber. On initiation of a smoke purge cycle (fresh air admitted to chamber), the smoke concentration drops rapidly in a uniform manner at all exposure sites, and smoke is undetectable when the next puff is taken on the cigarette.

With nicotine and carbon monoxide as indicators of smoke concentration, we have determined the smoke concentration in the Walton system under typical exposure conditions. Nicotine measurement in the exposure system gives a calculated smoke concentration of 8.1% under typical exposure conditions. Carbon monoxide measurement gives an 8.6% smoke concentration. These concentrations, determined by direct measurements, agree well with the theoretical concentration (8.6%) based on the puff volume, chamber volume, and correction for losses of smoke through vent lines.

Measurement of smoke composition. The composition of smoke offered to animals in the exposure system is of considerable importance in inhalation studies. The relationship of animal studies to human experience requires that animals receive smoke that duplicates "human smoke" as closely as possible. The overall objective in this work is to provide information on the composition and particle size characteristics of smoke offered to animals by any machine, and to determine whether and how the smoke differs from smoke generated under standard smoking conditions. Alterations in composition and/or particle size due to positive puffing, smoke aging, or smoke interaction with animals or machine components are being investi-

gated. Investigation of smoke composition in the exposure systems is being pursued in three different ways. First, techniques are being developed for analysis of specific smoke components in the exposure devices: carbon dioxide, carbon monoxide, water, nitric oxide, nicotine, hydrogen, acetaldehyde, acrolein, isoprene, and oxygen can now be determined in the exposure systems. Second, high-resolution gas chromatographic profiling techniques are being studied to provide multicomponent analysis of several hundred components of smoke; methodology for gas phase organics in smoke is now complete, and studies have begun on particulate phase components. Third, apparatus has been designed and built for studying particle size characteristics of smoke in exposure systems, and final testing of the apparatus is now under way.

Initial application of the multicomponent profiling of gas phase organics was made to the Walton machine. Comparison of profiles obtained early and late in the exposure period permitted conclusions with regard to smoke aging. It was found that the profiles were nearly identical in terms of the presence and magnitude of peaks, indicating little or no change in organic gas phase composition due to aging of the smoke. Comparisons of the profiles were also made to ascertain the effect of a full load of mice on composition. Significant differences were observed, which suggested interaction between animals and smoke. First, the magnitude of all peaks was significantly lower with animals, suggesting that the animals depleted the overall concentration of the gas phase organics. Second, there was evidence of significant compositional changes, since peaks disappeared or appeared. These observations indicate possible compositional changes in the smoke that would adversely affect the relevance of the smoke offered to animals with the Walton machine. More detailed studies are under way to provide additional data on the gas phase organics in the machine.

Because the Walton machine is a limited-volume (384 ml) intermittent smoking machine, the effect of animals' breathing on the composition of smoke and other gases in the exposure chamber must be considered. The respiratory gases carbon dioxide and oxygen are of particular importance because of their possible effects on the animals' breathing and on the relevance of exposure with the device. Oxygen was determined in the chamber by puff-by-puff pulse sampling and gas chromatography with a molecular sieve (5 Å) column. For a 30-sec exposure period, the animals deplete the oxygen concentration from 21 to 16.5%. The purge is effective in replenishing the chamber with oxygen. If the exposure is extended to periods longer than 30 sec, the oxygen level continues to decrease to about 11% at about 100 sec. For normal exposures of 30 sec duration, the oxygen depletion is not serious in terms of animal survival, but it is possible that animal respiration is affected.

Continuous monitors of smoke in exposure systems. Pilot studies were made on the following methods of monitoring: (1) simultaneous withdrawal and monitoring of hydrogen by thermal conductivity detection, (2) simultaneous withdrawal and measurement of total thermal conductivity, flame ionization response, and flame emission of metals in smoke, (3) continuous monitoring of CO and CO_2 by dispersive infrared spectrophotometry, and (4) in situ measurement of light scattering without sample withdrawal. From these, methods for monitoring hydrogen and thermal conductivity were developed to the application stage, and they have been used for studies on the Walton and Lorillard systems.

In the hydrogen monitoring device, smoke is withdrawn continuously from the exposure system at a low flow rate (1 cc/sec) through a filter and gas scrubber, which removes particulates, water, carbon dioxide, and most organic compounds. The filtered and scrubbed smoke passes through one channel of a low-volume thermal conductivity detector. Smoke reaching the detector consists of N_2 (80%), O_2 (19%), CO (0.5%), H_2 (0.2%), methane (0.03%), and organic gases at very low levels. The other side of the detector samples ambient air. The net response is due to CO, methane, and H_2; but since the thermal conductivities of CO and methane are near the thermal conductivity of air, the response is due primarily to H_2 in the gas phase.

The selectivity of the device to hydrogen in smoke was tested in two ways. First, gas mixtures were made containing smoke components at approximately the concentration levels that would be found in 10% smoke. The gas mixture was sampled with the device, and the response was compared with the response due to hydrogen at the concentration expected for smoke. No significant interference by other components in the smoke was noted. The selectivity of the device was also tested by a comparison of the analysis of hydrogen in smoke by a gas chromatographic method that separates hydrogen from other smoke components with the analysis obtained on the prototype device. Agreement between the two methods was good.

Initial application of the hydrogen monitoring device was made to the Walton smoking machine. The smoke concentration in the exposure chamber increases rapidly at the inception of the puff, remains essentially constant for the duration of the exposure period, and

then drops to zero during the purge period. Mixing time, smoke uniformity, and purging rate were determined from the response curves. The filtering and scrubbing processes allow mixing of the smoke and prevent instantaneous response. From studies to date, we estimate the response time to be less than 5 sec and probably on the order of 1 to 3 sec.

Although the hydrogen monitoring device provides data that can be related to the absolute smoke concentration in an exposure system, the response time is not adequate for assessment of rapid fluctuations in smoke concentration. The basic device was modified to provide faster response by removing the scrubber tube and reducing dead volumes, so that the device responds to the total thermal conductivity of all gas phase components. Even without the scrubber, we estimate that the system response is still due mainly to hydrogen; other components in the smoke contribute only about 15% to the total thermal conductivity response. Without the scrubber, the response time of the device is decreased to about 1 sec (90% response). Applications of total thermal conductivity detection have been made to the Walton and Lorillard exposure systems.

Preliminary experimentation has been carried out toward the development of an optical monitor for smoke chamber particulate concentration on the Walton smoking machine. A low-powered helium-neon laser that emits light at 633 nm has been acquired, and a photometer has been assembled that utilizes a 9558 photomultiplier tube with an appropriate high-voltage supply and an operational amplifier circuit to measure the anode current. Full-scale current ranges of 10^{-7} through 5×10^{-5} A are available for presentation on a fast strip chart recorder. This system is easily capable of displaying irregularities in the rise and fall of smoke concentration attending each puff in the Walton exposure chamber.

Although the beam from the laser will penetrate the smoke across the full diameter of the chamber and still produce a substantial amount of scattered light, the resultant intensity of that light is a composite of scattering and absorption along its path and not a simple function of smoke concentration. The recorded signal may drop off as a more-or-less exponential function of time when the purge begins, or it may rise to a maximum and then drop off, depending on the relative contributions of scattering immediately in front of the detector and along the light path to it. We have seen a distinct and progressive decrease in the signal as time passes during each puff when the laser beam is passed through the chamber perpendicularly to its flat walls and the detector is immediately above. We have repeated these observations, showing virtually the same results with an incandescent light source. Transmitted light at the same point in the chamber (incandescent source) shows first a decrease and then an increase in transmission before the purge begins. An interpretation of these observations would be premature at this time, except to say that a possibility for a simple monitoring photometer is real. Further work is planned with both the scattering and transmission techniques.

Operational characteristics. The Walton, Lorillard, and Process and Instruments exposure systems have been surveyed for operational reliability. Operational studies of the systems have revealed some difficulties and have suggested means of correcting the difficulties.

Calibration of puff volumes with the Walton system is difficult and time consuming, but once the calibration is made, only occasional checks are needed for verification. The puff volumes are relatively unaffected by cigarette weight and pressure drop and appear to remain stable for long periods. A particular problem is the inapplicability of the present design to smoking of three cigarettes simultaneously. Static burn rates increase to the point where the number of puffs required to consume a cigarette falls well below that found for analytical smoking.

Operational difficulties encountered with the Lorillard system include improper operation of the collets, which causes loading and lighting problems, and difficulty with the puff chamber return mechanism. Particular difficulty has been encountered with the four-way smoke distribution valve – sluggish operation or complete failure. It was also found that no provision was made to supply air to the animals in the event of a power failure.

Operational characteristics of the Process and Instruments system are now under study. Serious problems have been encountered, due to a temperature rise to about 90°C in the vicinity of the cigarettes during smoking, which causes nonstandard puff volumes and possibly affects deliveries of smoke components from the cigarettes. We are collaborating with the designer of the system to eliminate this problem. Improvements in design of electronic components in the system have also been suggested.

SPECIAL STUDIES AND SERVICES

Special studies not directly related to our major research and development activities have been carried out to support other NCI and CTR-USA contractors and Laboratory programs. These studies utilize special

equipment, methods, or expertise developed in the Tobacco Smoke Research Program and usually are short term with limited objectives.

Dog dosimetry. The VAH exposure method (used at the Veterans Administration Hospital, East Orange, N.J.) for chronic exposure of tracheotomized dogs to whole smoke involves direct coupling to the cigarette. On inhalation, smoke is drawn directly from the cigarette into the trachea. On exhalation, a check valve prevents the expired air from exiting through the cigarette, ensuring solely oral and nasal exhalation. The technique presumably allows high doses of fresh smoke but is difficult to control precisely, because both smoke generation and inhalation depend on the animal. The ADL (Arthur D. Little, Cambridge, Mass.) exposure system, developed principally by Dr. S.P. Battista, offers an alternate method for dosing tracheotomized dogs. Smoke is generated mechanically and rapidly expelled into a holding tube fitted with a flap valve at one end and attached to the tracheotomy tube at the other end. Since the smoke is generated by carefully controlled puff parameters and animals are not involved in smoke generation, the composition of the smoke and the dosimetry should remain relatively constant throughout chronic experiments.

An important question was whether a dose could be provided to the animals by the ADL system comparable with that provided by direct smoking. At the request of NCI, a collaborative study involving ORNL, ADL, and the VAH was initiated to determine the dose of smoke received by the animals with each system. The ADL system was tested at three and six puffs per minute, with 35-cc puff volumes and 2-sec durations. Existing tracer methods for determining dose were used.

Our role in the study included (1) acquiring the animals, (2) developing a modified organ analysis method to allow examination of larger samples, (3) evaluating a dosimetry method based on electron capture determination of decachlorobiphenyl in the event that ^{14}C could not be used at the VAH, (4) visiting sites to inspect facilities, adjust machines, and set up equipment, (5) assisting in exposing the animals to labeled smoke, and (6) analyzing filter pads and organs resulting from the actual exposures. The final experiment consisted of exposing five dogs, one at a time, to labeled cigarettes under the three exposure conditions. Lung, trachea, larynx, esophagus, and stomach were taken for ^{14}C determinations. The quantity of ^{14}C found in the animal was converted to "equivalent" quantities of tar and nicotine by comparison with the total quantity offered to the animal and the "specific activity" of the smoke.

Descriptions of the limitations of the methodology and the detailed examination of each deposition site are beyond the scope of this summary, but certain general conclusions can be stated. The percentage deposition and the equivalent quantities of nicotine and tar for the VAH exposure are similar to those for the ADL three-puff exposure, although a slightly greater (unlikely to be statistically significant) dose may be provided by the VAH exposure. The dose provided by the ADL six-puff exposure is greater (likely to be statistically significant) than that provided by the VAH system. Body distribution varies slightly (statistical significance not yet known).

The principal goal of this work, to establish the approximate dosimetric performances of the two systems, has been reached. The ADL system can be used in future dog exposure studies without concern that dramatically lower doses accompany its use.

Smoke deposition in mice on the Walton exposure system. Smoke deposition experiments were carried out to provide initial data to CTR-USA on the dose of smoke received by mice under one set of exposure conditions on the Walton exposure system. Our existing smoke deposition methodology using [^{14}C] dotriacontane was applied to this investigation. Twenty mice were exposed to smoke labeled with [^{14}C] dotriacontane under a typical exposure condition with the Walton system. Immediately after exposure, the animals were killed, and four organs (lungs, larynx, head, and stomach) were taken for ^{14}C analysis. Animal-to-animal variability in this experiment was much lower than that observed previously for rats and hamsters on the Maddox-ORNL exposure system. The relative standard deviation for lung deposition on the Walton system, for example, was about half that observed with rats or hamsters on the Maddox-ORNL system. Depositions in the various organs analyzed, expressed as percentages of total smoke offered, were as follows: lungs, 0.43 ± 0.08; larynx, <0.01; head, 0.08 ± 0.08; stomach, 0.31 ± 0.14; whole body, 0.82 ± 0.22. Deposition of smoke in mice exposed on the Walton system was about half that found for rats and hamsters smoked on the Maddox-ORNL system under similar conditions. The lower dose is probably due to the smaller animal size.

Miscellaneous analyses. Miscellaneous gas chromatographic analyses were performed in support of Laboratory programs. A gasoline vapor–ozone mixture was chromatographed for personnel of the Biology Division to determine whether ozone oxidation significantly affects the composition of the gasoline vapors. A high-resolution (capillary column) chromatographic method was developed for these investigations.

Norbornyl alcohols were determined in a reaction product mixture for members of the Chemistry Division. Components in a cleaning solvent were identified by cochromatography for the Instrumentation and Controls Division. Butylated hydroxytoluene was determined in animal feeds for personnel of the Biology Division.

COAL-DERIVED PRODUCTS

Survey of existing analytical methodologies. It is likely that ORNL will become increasingly involved in research and development related to processes that produce fuels and petrochemical feedstocks from coal. Engineering aspects of these processes and, particularly, biological and environmental aspects of the technology will require attention. Although processes can be designed without sophisticated chemical support at present, a detailed chemical characterization of products, process streams, and waste streams is imperative for biological and environmental studies. Bioassays, whether to test biological hazard or environmental impact, can be selected or developed only after the nature of the chemicals present has been established. Knowledge of the presence and quantities of individual chemical species will also provide the engineer with data necessary to identify promising process modifications.

Our initial interest is to survey existing analytical capabilities generated from studies of tobacco smoke analysis to determine their applicability to coal-derived samples. An assessment of existing Analytical Chemistry Division capabilities to lead and support future bioassay and engineering efforts at ORNL and an assessment of future analytical needs are emerging from this survey. Our effort to date has focused on one coal-derived sample, the liquid product from the Synthoil process. This approach was chosen to allow consideration of a maximum number of analytical methodologies on a liquid sample representative of those produced by all conversion processes.

We find that remarkable similarities exist between the analysis of smokes, particularly smoke condensates, and the analysis of the coal liquid. Many smoke-related procedures are directly applicable to analysis of the coal-derived sample, and other procedures require only minor modifications. Modifications suggested by our initial work generally simplify the procedures, and procedures found to be directly transferable work better for the coal-derived sample than for smoke samples. The physical and chemical characteristics of the coal-derived sample (a "crude" to be subjected to further refining) are very similar to those of condensed smoke. Sampling, sample handling, and storage problems are thus almost identical. It is apparent that the only viable approach to chemical characterization of the coal-derived sample is to rely on sophisticated prefractionation methods and employ every analytical technique at our disposal. Complete reliance on direct gas or liquid chromatography can serve only to visualize the major (infrequently the most important) constituents.

Table 6.4 illustrates the quantitative results obtained to date on the coal-derived liquid and compares them with the concentrations found in the condensate from the Kentucky reference cigarette (1R1). The direct titrimetric determination of "acids" provides an easily determined measure of acid content and can serve as a routine screening method. The coal-derived liquid is seen to contain essentially no "weak acid" (predominantly carboxylic acid) component, but a high "very weak acid" (predominantly phenol function) component. No strong acid is visualized. The phenol and cresol concentrations are found to total approximately 1.6 wt % of the coal-derived liquid (a high content) when determined by the new direct derivatization–gas chromatography method discussed under the section on tobacco smoke chemistry. The larger quantity of phenols in the coal-derived liquid make this analytical procedure more easily applied to coal than to smoke samples.

Phenanthrene, benz[*a*]anthracene, benzo[*a*]pyrene, indole, and skatole were also determined by existing methods, to evaluate our ability to determine isomeric

Table 6.4. Comparison of constituent levels in tobacco smoke condensate and a coal-derived liquid

Constituent	Kentucky reference cigarette smoke condensate	Coal-derived liquid
Weak acids (meq/g)	1.35	0
Very weak acids (meq/g)	0.85	1.10
Phenol (mg/g)	4.2	4.90
o-Cresol (mg/g)	0.7	2.36
m-Cresol (mg/g)	0.7	5.48
p-Cresol (mg/g)	1.5	2.96
Phenanthrene (ppm)	22	413
Benz[*a*]anthracene (ppm)	1.15	18
Benzo[*a*]pyrene (ppm)	0.78	41
Indole (ppm)	630	210
Skatole (ppm)	390	128

polynuclear aromatic hydrocarbons and nitrogen heterocyclics. The procedures were found to be directly applicable, and indications are that considerable simplification may be possible. The data (Table 6.4) reveal very high concentrations of phenanthrene and benzo[*a*] pyrene, significant levels of indole and skatole, and a surprisingly low concentration of benz[*a*] anthracene.

Direct gas chromatographic analysis was surveyed briefly to establish its value for gross characterization of the major constituents and for further evaluation of our existing capabilities. We find that the whole sample can be gas chromatographed using our standard TPM profiling conditions. Approximately 60 major constituents are thus visualized. Figure 6.4 illustrates a high-resolution profile of the "50°C volatiles" of the coal-derived liquid. The method used to obtain this chromatogram is essentially identical to that developed for gas phase cigarette smoke profiling. Such techniques are useful at present only to visualize and eventually to establish gross composition. Combined with element-selective detectors and the blind assay concept, the resulting methods may prove of significant value for rapid surveys of composition and identification of biologically important species.

The sample used to acquire the reported data and to test our methods is not necessarily representative of the true final product – only a small quantity was taken, and the composition of the product is likely to change with time. This, coupled with the facts that a limited amount of work has been done and that our interest has been to survey methods, makes us hesitate to consider the data in Table 6.4 completely accurate. The unusual distribution of three-, four-, and five-membered ring PAH compounds raises a further question. There is no doubt, however, that the coal-derived liquid tested contains high concentrations of both carcinogens and cocarcinogens. By comparison with the condensate from the Kentucky reference cigarette – a significant carcinogen in the mouse skin model – we would predict a substantially greater skin carcinogenicity associated with the coal-derived liquid. The material should be handled accordingly.

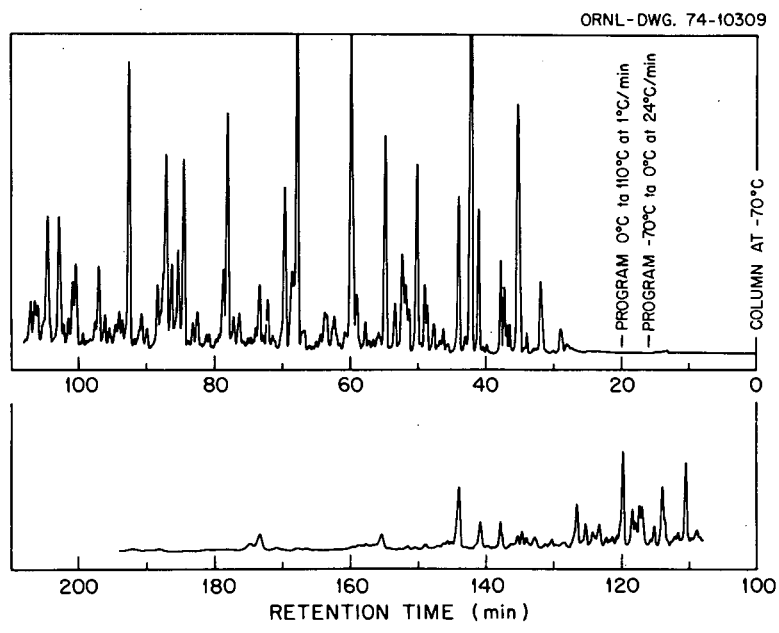

Fig. 6.4. High-resolution gas chromatogram of "50°C volatiles" from a coal-derived liquid.

Part B. Service Analyses

The past year has been brighter and more successful monetarily for the service groups in the Division. The number of personnel has increased by 2 chemists and 11 technicians since January 1, 1974. The Chemical Technology Division continues to be the main supporter of analytical work, which comes primarily from the LWBR and TRU programs.

Support work for the HTGR and MSRE reactor programs is continuing to increase. The main analyses are coating densities, chlorine leach for faulty particles, uranium, oxygen, and carbon, and isotopic and corrosion products.

The Environmental Laboratory continues to perform a variety of special work and to function as a liaison group between our Division and the Environmental Sciences Division. At present, one special project is the determination of plutonium in samples of water and vegetation at background levels.

Housekeeping and safety were improved during the past year, primarily in storage of chemicals and glassware, as well as in general neatness of all laboratories.

The Quality Control Program has increased primarily in the field of atomic absorption and Technicon colorimetric determinations.

Table B.1 gives a summary of the service analyses made by the laboratories of the Analytical Chemistry Division.

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]	General Hot Analyses Laboratory[d]	Environmental Analyses Laboratory[e]	
ORNL divisions						
Analytical Chemistry	262	713	377	58	127	1,537
Chemistry	565	50	46	2	224	887
Chemical Technology	11,449	2,140	2,983	23,398	818	40,788
Director's				206		206
Environmental Sciences	1,128	198	1,199	2,366	49,037	53,928
Health	5,217				179	5,396
Health Physics	39	40	20	1,685	2	1,786
Inspection Engineering	1,236					1,236
Isotopes	12,329	5,105	27	2,020		19,481
Metals and Ceramics	15,519	702	4,750	726	174	21,871
Neutron Physics	451		100	117	8	676
Operations	415		1,002	9,098	434	10,949
Physics	668	26	28	819		1,541
Plant and Equipment				4		4
Reactor	1,333	298	346	4,356		6,333
Solid State	2,945	40	190	6		3,181

Table B.1 (continued)

Organization	Number of results reported by					Total
	Elemental Spectrometry[a]	Mass Spectrometry Service Laboratory[b]	General Analyses Laboratory[c]	General Hot Analyses Laboratory[d]	Environmental Analyses Laboratory[e]	
Thermonuclear	185					185
Miscellaneous		2,427	350	240	104	3,121
Others						
K-25				18		18
Los Alamos Scientific Laboratory		153		23		176
Safeguards		884				884
Y-12	1,027	480	123	20		1,650
Miscellaneous	2,505	72				2,577
Total	57,273	13,328	11,541	45,162	51,107	178,411

[a]Average number in group, 4 scientists and 3 technicians.
[b]Average number in group, 1 scientist and 4 technicians.
[c]Average number in group, 4 scientists and 13 technicians.
[d]Average number in group, 15 scientists and 15 technicians.
[e]Average number in group, 4 scientists and 4 technicians.

7. General Hot Analyses Laboratory

J. H. Cooper, Head

C. E. Lamb[1]	H. A. Parker	J. M. Peele
L. C. Bate	J. C. Price	T. G. Scott
G. Goldberg	M. E. Pruitt	C. C. Foust
C. R. Johnson	J. M. Shaboskie	R. E. Jones
E. C. Lynn	J. S. Wike	J. D. Pendleton
C. P. Baker	N. J. Ford	E. C. Fearnow
L. D. Bible	L. R. Hall	R. A. Jones
R. Burns	J. R. Moore	W. H. Akers
W. M. Caldwell	S. H. Prestwood	P. W. Pair
J. H. Davidson	N. A. Teasley, Jr.	

About half of the 45,000 analyses done by the General Hot Analyses Laboratory were for the Chemical Technology Division in support of the Transuranium Processing Plant and the LWBR fuel production program. The LWBR Pilot Plant requested assistance in measuring the oxidation rate of U(IV) in nitric acid. For measurement of the trace amounts of U(IV), Fe(III) was reduced with the U(IV), and the Fe(II) formed by reacting it with potassium ferricyanide was measured. The blue color of the ferrocyanide so formed was measured spectrophotometrically. The Transuranium Processing Plant requested the measurement of ^{126}Sn in their process. The high levels of fission product activities made the detection of ^{126}Sn virtually impossible without separation. The tin was extracted from 6 *M* HCl into hexone and stripped into 1 *M* tartaric acid. A second hexone extraction and strip into oxalic acid gave decontamination factors of about 70. The decontaminated aliquots were scanned for radioactive tin on the gamma spectrometer.

Samples from the Peach Bottom Reactor were analyzed for tritium and strontium. Tritium was measured in pieces of graphite by burning the graphite in oxygen and trapping the water in an ice bath. Aliquots of the water were counted for tritium. The residue from the burned graphite and sections of metallic diffusion tubes were leached or dissolved and analyzed for strontium.

Samples of environmental waters and vegetation have been analyzed for plutonium. As much as 5 liters of water is evaporated, and the plutonium is separated by carrying on a PrF_3 precipitate. Wet oxidation of vegetation and dissolution in nitric acid gives a sample amenable to plutonium measurement by TTA extraction. Planchets with 1 or 2 dis/min of alpha activity have been counted (for over 24 hr) on our alpha pulse-height analyzer to measure the various isotopes of plutonium present.

The Neutron Activation Analysis Laboratory at the HFIR has been used to determine trace elements in a number of samples from the Environmental Sciences Division. These nondestructive analyses have been made using the Nuclear Data–PDP-15 analyzer, a Ge(Li) detector, and program MONSTR. Two special problems were handled for K-25: preparation and calibration of some radioactive standards of ^{198}Au, and determination of chlorine in aluminum wire. The latter required chemical separation and apparently represents the only reliable way to make this determination that K-25 has found.

1. On loan to the Personnel Division.

8. General Analyses Laboratory

W. R. Laing, Head

L. J. Brady
H. G. Davis
G. R. Wilson

M. R. Childs
D. E. Coffey
C. J. Coley
P. S. Gouge
J. H. Hackney
A. H. Matthews
B. Philpot
H. Simmons, Jr.
L. J. Suneson
C. L. Watson
K. I. Webb
V. L. White
M. W. Williams

Several new procedures were established in support of HTGR programs. A series of pyrolytic carbon-coated microspheres were calibrated for density and used in tetrabromoethane–methylene iodide density gradient columns. These standards, whose density ranged from 2.80 to 3.21 g/cm^3, were used in the measurement of the density of SiC fragments. Pyrolytic carbon fragments were also measured with a benzene-tetrabromoethane column. Forty samples analyzed during one month showed a relative standard deviation of 0.4%.

A visual inspection followed by a chlorine leach procedure was set up to determine the number of bare or cracked fuel particles in a 10,000-particle batch. Correlation has been good between the two techniques, although occasionally a cracked particle will show up in the Cl_2 leach that has not been seen under the microscope.

Uranium oxycarbide microspheres prepared from loaded ion-exchange beads were analyzed for uranium, carbon, oxygen, density, and surface area. The reactive nature of this material required the use of an inert-atmosphere glove box for all sampling operations.

Ion-exchange resin beads loaded from acid-deficient $UO_2(NO_3)_2$ and from UO_2F_2 solutions were checked for loss on drying and for uranium, fluorine, and isotopic content and subjected to thermogravimetric analysis.

Several methods were studied for the measurement of low acidity and acid deficiency of concentrated (100 to 300 mg/ml) $UO_2(NO_3)_2$ solutions. The previously used complexing agent, potassium oxalate, did not give a definitive break at low acid and high uranium concentrations. Sodium sulfate and sodium fluoride were tried as complexing agents. The best end points were obtained with NaF in 85% acetone solution. A number of samples have been analyzed by this method.

In support work for the Molten Salt Reactor Program, samples of fuel salt, $LiF \cdot BeF_2$, and $NaBF_4$ coolant salt were analyzed for major components and corrosion products. Salt from reductive extraction experiments was checked for uranium content. Lithium-bismuth alloy from these tests was analyzed for uranium, lithium, and carbon.

Three new methods have been established for Environmental Sciences Division work. Metabolism rates for small animals in their natural habitats were measured by monitoring the change in $^2H/^{18}O$ in their blood. Animals were captured, injected with labeled H_2O, released, recaptured, and sampled. The ^2H was separated as $^2H_2$ and the ^{18}O as $C^{18}O_2$ for measurement by mass spectrometry.

A dichromate oxidation procedure, similar to a chemical oxygen demand test, was set up to measure organic carbon in snails. The snail (1 to 5 mg total weight) was crushed between two glass plates and digested in a dichromate–sulfuric acid mixture, and the amount of reduced chromium was determined spectrophotometrically. A total of 175 snails were analyzed by this method.

Nitrate can be reduced in methyl alcohol solutions by bacterial action. The progress of the reaction was followed by measuring the methyl alcohol consumption. Methanol was determined by gas chromatography on a water-saturated 15% Carbowax 20M on Chroma-

sorb P column with a flame ionization detector. Alcohol levels from 5000 ppm down to 20 ppm were found.

A major project during the year was the recovery of about 25 g of ^{62}Ni isotope from a large single crystal (about 270 g) of a ferrite of the approximate formulation $^{7}Li_{0.75}$-$^{62}Ni_{0.25}$-Fe_2O_4 and from various ceramic matrices in which ^{62}Ni had become dispersed in an accident in a prior attempt at growing the crystal. The ^{62}Ni was separated from the iron by passage of a 10 *M* HCl solution of the elements through a large column of Dowex anion-exchange resin and from the ^{7}Li by precipitation as NiS. In another recovery, 2 kg of Eu_2O_3 was purified by precipitation as the oxalate from HNO_3 solution after preliminary passage through a column of activated carbon to remove organic matter. Preparations made during the year included TmN, EuS, and $^{158}GdF_3$. Several alloys of Ni_3Ga doped with iron were made, and numerous other alloys were annealed under various conditions. An attempt was made to prepare single crystals of $NbSe_2$ from the commercial powder by the halogen vapor transport method using bromine. Small crystals were obtained, but another attempt using iodine will be made.

In other programs, low levels (25 ppb) of cyanide were determined by the pyrazolone spectrophotometric method, and higher levels (100 ppm) were titrated with $AgNO_3$ solution. Boron was measured in EuB_6. Amines at the 10-ppb level were determined spectrophotometrically. Sulfur and fluoride were measured in fly ash and coal. Uranium mine tailings were analyzed for uranium, barium, and calcium. An apparatus was constructed to monitor sodium and potassium levels in cigarette smoke by flame emission. The aluminon method was used to determine the aluminum content of $^{233}UO_2$. Europium was titrated with EDTA in the analysis of EuC, Eu_2O_3, EuS, and EuB_6.

9. Environmental Analyses Laboratory

R. R. Rickard, Head

N. M. Ferguson
T. G. Harmon
C. A. Clark
J. D. Hill
P. K. Long
J. R. Lund
C. K. Talbott
J. H. Oxendine
M. E. Peters, Jr.

The Environmental Analyses Laboratory reported approximately 51,000 analytical results last year. Most of this analytical service was in support of Environmental Sciences Division programs. In addition to this analytical service, an effort was made for the laboratory to function as a liaison group between various analytical specialists within our Division and staff members of the Environmental Sciences Division. During the year, special sample-preparation service was provided to facilitate the use of neutron activation analysis, spark-source mass spectrometry, emission spectroscopy, and atomic absorption spectrometry. The Environmental Analyses Laboratory is located in Buildings 2026 and 2024.

SAMPLE PREPARATION AND MERCURY ANALYSIS (BUILDING 2026)

A special sample-preparation laboratory was used to prepare and process a variety of aquatic and terrestrial samples for trace element analysis. This laboratory is equipped with a HEPA prefiltered air inlet system and operates under a slightly positive pressure to preclude outside air entry. Some "clean room" operating controls are imposed upon the laboratory's operation to reduce the level of airborne contaminants. Samples prepared for cadmium, lead, and zinc analyses were sent to the Mass and Emission Spectrometry Laboratory, and samples requiring the use of neutron activation were transferred to the Nuclear and Physics Methods group. Samples submitted for chromium analyses were processed and then analyzed in our atomic absorption spectrometry laboratory. We have also prepared numerous samples for the determination of mercury. These determinations were made in a laboratory adjoining the sample-preparation laboratory. A cold-vapor atomic absorption instrument was used to measure mercury in processed samples, and a gas chromatograph–microwave emission system was used for the measurement of methylmercury in sample extracts. Both of these instruments were developed by members of the Instrumentation and Advanced Methodology Group.

GENERAL ENVIRONMENTAL ANALYSES (BUILDING 2024)

Most of the 51,000 analyses performed last year reflect the productivity of our group members working in the laboratories located in Building 2024. Their effort was in support of the Environmental Sciences Division's Walker Branch Watershed Program and other special projects. Atomic absorption spectrometry and autoanalyses accounted for most of the analytical service. Atomic absorption spectroscopy was employed for a host of elemental analyses, whereas autoanalysis was dedicated solely to measuring phosphate, nitrate-nitrite, ammonia, and sulfate levels in water samples. The interest in organic and inorganic carbon in water and particulate samples required full-time operation of an Oceanographic carbon analyzer, but only a token effort was expended during the year on the carbon, nitrogen, and sulfur analyzer.

In the near future we will have the capability (previously nonexistent) of analyzing slightly radioactive samples by atomic absorption; several research programs are awaiting this service. During the coming year we expect to increase our productivity in atomic absorption and autoanalysis by the addition of new instrumentation.

10. Industrial and Radiation Safety

G. R. Wilson

Only two of the six medical treatment cases we had in the past fiscal year were involved with normal laboratory operations, handling glass and chemicals. The other four cases involved falls, strains, and bumps, which can and do occur at home as well as at work. Three safety and housekeeping inspections were held during the year, and it was noted that the housekeeping seems to improve with each inspection; gradually the safety hazards are being found and corrected. Three new members have been appointed to the inspection team: H. W. Dunn, monthly employee; J. H. Hackney, weekly employee; and N. Marion Ferguson, supervisor. This will enable us to split into groups and cover the Division more rapidly. The four emergency cabinets for which the Division is responsible have been stocked and sealed.

Eleven radiation work permits have been issued for hazardous work areas. All work was done without incident or overexposure to ionizing radiation. There have been no unusual occurrences during the fiscal year

11. Quality Control Program

G. R. Wilson

The number of control programs has increased from 36 to 45, even though some programs were dropped because of infrequent use. In October 1973, the Environmental Analyses Laboratory began the Technicon colorimetric determination of nitrate nitrogen and the determination of ammonia nitrogen on a control that also contains phosphate and sulfate, all at very low levels. Control programs for the atomic absorption determinations of cadmium, lead, and zinc were begun in January 1974. Since the General Analyses Laboratory is now receiving molten-salt-type samples, control programs have been initiated for the colorimetric determination of beryllium and low levels of iron, chromium, and nickel in the presence of lithium, uranium, and thorium, which are also determined. The NBS steels, which have been used as controls in the Leco carbon determination, are now also being used as sulfur controls.

In January 1974, a weighted limit of error was calculated from the data accumulated over a two-year period. From these calculations, some changes were made in the expected limits of error:

Method	Former fixed limit of error (%)	New fixed limit of error (%)
Leco carbon	7	6
Organic carbon infrared absorption	15	10
All atomic absorption methods	5	4
Technicon colorimetric phosphorus	20	10
Colorimetric thorium (low level)	2	5

The fixed limits of error for the newly established programs will be reevaluated as more data become available.

The overall quality level remained the same as last year at 93.4%, and the number of control results increased from 1952 to 2000. 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 1973–June 1974

Laboratory	Number of control results		Quality level[a] (%)	
	Total	Outside fixed limits	1973	1974
Environmental Analyses	823	50		93.92
General Hot Analyses	726	24	91.7	96.69
General Analyses	451	58	95.0	87.14
Total	2000	132		
Average			93.4	93.40

[a]Control results within 2S limits.

Table 11.2. Distribution by method of control results for July 1973–June 1974

Type of method	Constituent	No. of programs	No. of results	Total for method
Atomic absorption	Calcium	1	63	
	Cadmium	1	7	
	Cobalt	1	23	
	Chromium	1	25	
	Iron	1	3	
	Lead	1	11	
	Magnesium	1	60	
	Nickel	1	19	
	Potassium	1	40	
	Sodium	1	49	
	Zinc	1	9	
				309
Colorimetric	Beryllium	1	4	
	Chromium	2	9	
	Iron	2	29	
	Molybdenum	1	8	
	Nickel	2	32	
	Nitrogen	3	213	
	Sulfate	1	2	
	Phosphorus	1	142	
	Thorium	2	134	
	Uranium	1	50	
				623
Coulometric	Uranium	3	463	
				463
Flame photometric	Lithium	2	16	
	Sodium	1	12	
				28
Fluorometric	Uranium	2	88	
				88
Gravimetric	Carbon	2	111	
				111
Infrared absorption	Carbon	2	183	
				183
Volumetric	Fluoride	1	7	
	Nitrate	1	48	
	Sulfur	1	14	
	Uranium	1	51	
	Thorium	2	75	
				195
Total		45		2000

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 Divisional Advisory Committee was composed of:

V. A. Fassel, Deputy Director, Ames Laboratory, USAEC,

L. B. Rogers, Professor of Chemistry, Purdue University (until Sept. 1, 1974; currently at University of Georgia),

S. Siggia, Professor of Chemistry, University of Massachusetts,

E. C. Dunlop, Central Research Department, E. I. duPont de Nemours and Co., Wilmington, Delaware (effective 1975).

CONSULTANTS

Our special relationship with the Department of Chemistry of the University of Tennessee continues through the participation of professors and co-advisors to graduate students who are carrying out their research as part of the Division's program.

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

J. A. Dean, University of Tennessee, advises and works with the Division as a whole.

M. T. Kelley (Adjunct Research Participant) advises and works with computer programs, in particular.

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

GRADUATE THESIS RESEARCH PROGRAM

J. L. Bowling. Dr. Bowling was awarded the Ph.D. degree from the University of Tennessee. His research under the direction of G. Goldstein, W. D. Shults, and J. A. Dean involved the investigation of the utility of kinetically controlled and catalytic reactions to perform environmental determinations by parallel spectrophotometric analysis.

R. V. Crosmun. A graduate student from the University of Tennessee, Mr. Crosmun has continued research on the application of the radiofrequency 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. Mrs. Crosmun has continued research on pulsed anodic stripping voltammetry with a wax-impregnated graphite electrode and has initiated a program on coulometry under the direction of J. R. Stokely, T. R. Mueller, and J. A. Dean. She is a graduate student from the University of Tennessee.

SHORT COURSE IN TECHNIQUES OF GAS CHROMATOGRAPHY

A. D. Horton of this Division organized and taught a short course in techniques of gas chromatography (GC). Twenty-one persons attended the sessions, which consisted of nine one-hour lectures and one six-hour laboratory. Components of GC equipment, their functions and proper selection, detectors, operation of the equipment in various modes, troubleshooting, and gas sampling (taught by A. S. Meyer) were the main subjects discussed. Upon completion of the course, participants answered a questionnaire concerning usefulness of the course, suggested improvements, etc. The results indicated that all participants felt the course was very helpful and educational, and that additional courses on this or other subjects would be welcome. Most participants felt more time should be devoted to laboratory material. All concerned feel the experience was worthwhile, and the possibility of other short courses is presently under study.

GREAT LAKES COLLEGES ASSOCIATION EDUCATIONAL PROGRAM

This cooperative program is now in its fifth 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, under the direction of A. S. Meyer, assisting with voltammetric studies in fluoroborate media, primarily, some work in fuel-type media; 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 the Tobacco Smoke Research Program under the direction of M. R. Guerin.

SOUTHERN COLLEGE UNIVERSITY UNION EDUCATIONAL PROGRAM

T. D. Roberts, Centenary College of Louisiana, Shreveport, Louisiana, spent the spring semester in the Division under the SCUU-ORNL program. He was assigned to J. R. Stokely to assist in the Tobacco Smoke Research Program.

IAEA FELLOWSHIP PROGRAM

Dr. Susan Danali, IAEA Fellow from the Greek Atomic Energy Commission, spent five months in the Division working with J. S. Eldridge in the Lunar Analysis Group on techniques of computer resolution of NaI gamma-ray spectra, calibration of a low-level gamma-ray spectrometer, and methods of germanium crystal spectroscopy with a new system. Dr. Danali was with the Division from December 1973 to May 1974.

G. G. Thern, IAEA Fellow, CNEA, Buenos Aires, Argentina, was assigned to the Division in October 1973 for a one-year period to work on burnup analysis and postirradiation examination of nuclear fuel, under direction of W. S. Lyon.

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 promising high school graduates. G. Goldstein serves as "Dean" for these guests during their visit.

Co-op Student

L. A. Littlejohn, University of Tennessee, Knoxville, Tennessee.

ORAU Summer Research Participant

Dr. C. B. Honaker, Tennessee Wesleyan College, Athens, Tennessee, spent the summer working with A. D. Horton on Tobacco Chemistry.

ORAU Summer Undergraduate Research Trainees

B. A. Effron, Cornell University, Ithaca, New York, worked with J. F. Emery.

B. R. Irvin, St. Andrews College, Laurinburg, North Carolina, worked with H. H. Ross and briefly with L. D. Hulett.

E. R. Malone, Alcorn A&M College, Lorman, Mississippi, worked with D. L. Manning.

ORNL Summer Employees

V. E. Norvell, recent graduate of the University of Tennessee, Knoxville, Tennessee, worked with Y. Talmi in gas chromatograph–microwave-excited spectrometry.

Dr. G. A. Nyssen, Associate Professor of Chemistry, Trevecca Nazarene College, Nashville, Tennessee, spent the summer training and applying x-ray photoelectron spectroscopy techniques with L. D. Hulett.

ORNL Sabbatical Employees

T. W. Gilbert of the University of Cincinnati, Ohio, arrived in the Division in August to spend a nine-month sabbatical period working with M. R. Guerin in the tobacco smoke and coal conversion programs.

L. A. Knecht of Marietta College, Marietta, Ohio, started a nine-month sabbatical appointment in the Division in September to work on trace-metal studies of environmental and biological materials, under the direction of H. H. Ross.

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

J. E. Caton

Consultant:	Smoking and Health Program, National Cancer Institute

L. T. Corbin

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

J. S. Eldridge

Secretary:	Subcommittee on the Use of Radioactive Standards, Committee on Nuclear Sciences, NAS-NRC

Cyrus Feldman

Member:	Committee E-2, Emission Spectrochemical Analysis, ASTM Subcommittee on Photographic Photometry Subcommittee on Atomic Absorption Analysis Publications Committee, Society for Applied Spectroscopy
Scientific Editor:	*Optics and Spectroscopy* (English translation of Russian journal *Optika i Spektroskopiya*)

G. Goldberg

Member:	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 Labelled 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
Member:	Filtration Subgroup, Tobacco Working Group, National Cancer Institute ORNL Ph.D. Recruiting Committee

A. D. Horton

Member:	Committee E-19, Chromatography, ASTM Subcommittee 3, Research

L. D. Hulett

Treasurer:	Sigma Xi–RESA, Oak Ridge Chapter
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 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 Scientific Committee 25 on Radiation Protection in the Use of Small Neutron Generators, NCRP 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*

W. T. Rainey, Jr.

Treasurer:	Sigma Xi–RESA, Oak Ridge Chapter

S. A. Reynolds

Member:	Committee D-19, Water, ASTM Subcommittee 4, Methods of Radiochemical Analysis Committee E-10, Nuclear Applications and Measurement of Radiation Effects, ASTM Standards Committee, ANS Standards Subcommittee ANS-16, Isotopes and Radiation Division, ANS Environmental Sciences Division, ANS Committee on Environmental Analytical Methodology, ACS

E. Ricci

Chairman:	Committee on Analytical Applications of Radiation and Isotopes, ANS

H. H. Ross

Member:	ORNL Graduate Student Selection Panel, ORNL

W. D. Shults

Councilor:	Analytical Chemistry Group, East Tennessee Section, ACS
Chairman:	ORNL Graduate Student Selection Panel, ORNL
Coordinator:	ORNL/NSF(RANN) Ecology and Analysis of Trace Contaminants Program
Secretary-Elect:	Fellowship Committee, ACS
Member:	Industrial Cooperation Committee, ORNL Panel on Chlorine and Vapor Phase Hydrogen Chloride, NAS Panel on Environmental Quality Indicators, NAS Environmental Quality Advisory Board, City of Oak Ridge Site Review Teams, NSF(RANN) 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
Titular Member and Secretary:	Commission V.7, Analytical Radiochemistry and Nuclear Materials, IUPAC
Chairman:	Federation of Analytical Chemistry and Spectroscopy Societies
Member:	Analytical Specialists Group, Union Carbide Corporation Technology Subcommittee

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
Bondietti, E. A.,* F. H. Sweeton,* T. Tamura,* R. M. Perhac,* L. D. Hulett, T. J. Kneip	"Characterization of Cadmium and Nickel Contaminated Sediments from Foundry Cove, New York," pp. 211–24 in *Proc. First Annu. NSF Trace Contaminants Conf. Held at Oak Ridge National Laboratory, August 8–10, 1973,* compiled by W. Fulkerson, W. D. Shults, and R. I. Van Hook	TIC, OIS, USAEC, Oak Ridge, Tenn., 1974
Dyer, F. F., L. C. Bate	"A Compilation of Modern Nuclear-Decay Data for High-Resolution Gamma Spectroscopy (IAEA-SM-170/44)," pp. 379–89 in *Nuclear Data in Science and Technology,* vol. 2.	IAEA, Vienna, 1973
Ross, H. H., G. T. Rasmussen*	"Modern Techniques and Applications in Cerenkov Counting," p. 363 in *Liquid Scintillation Counting: Recent Developments,* ed. by P. E. Stanley and B. A. Scoggins	Academic Press, New York and London, 1974
White, J. C. W. S. Lyon, J. A. Carter, C. Feldman, N. E. Bolton,* W. Fulkerson,* W. D. Shults	"Analytical Techniques for Determining Levels and Fates of Trace Elements in a Fossil-Fueled Steam Plant (IAEA-SM-175/23)," pp. 455–70 in *Comparative Studies of Food and Environmental Contamination,* ed. by E. R. A. Beck	IAEA, Vienna, 1974

Articles

Bamberger, C. E.,* J. P. Young, R. G. Ross*	"The Chemistry of Tellurium in Molten Li_2BeF_4"	*J. Inorg. Nucl. Chem.* **36,** 1158–60 (1974)
Bate, L. C.	"Determination of Minor Elements in Soil Profiles by Neutron Activation Analysis"	*J. Radioanal. Chem.* **15,** 193–202 (1973)
Bate, L. C., W. S. Lyon, E. H. Wollerman*	"Gold Tagging of Elm Bark Beetles and Identification by Neutron Activation Analysis"	*Radiochem. Radioanal. Lett.* **17,** 77–85 (1974)
	(See Dyer, F. F.)	
	(See Lyon, W. S.)	

AUTHOR(s)	TITLE	PUBLISHER
Battista, S. P.,* M. R. Guerin, G. B. Gori*	"A New System for Quantitatively Exposing Laboratory Animals by Direct Inhalation"	*Arch. Environ. Health* **27**, 376–82 (1973)
Bell, J. T.,* D. A. Costanzo, R. E. Biggers	"Plutonium Polymerization – II. Kinetics of the Plutonium Polymerization"	*J. Inorg. Nucl. Chem.* **35**, 623–28 (1973)
Bowling, J. L.,* J. A. Dean,* G. Goldstein	"Determination of Selenium in Natural Waters Using the Centrifugal Photometric Analyzer"	*Anal. Lett.* **7**, 205–13 (1974)
Bowling, J. L.,* J. A. Dean,* W. D. Shults	"Determination of Atmospheric Ozone Using the Centrifugal Photometric Analyzer"	*Anal. Lett.* **6**, 933–41 (1973)
Carlson, T. A.,* L. D. Hulett	"The History and Promise of ESCA at ORNL"	*ORNL Review*, Fall 1973
Carter, J. A., D. R. Matthews,* R. L. Walker, J. R. Walton	"Measurements of Nitrogen and Nitrogen Isotopic Ratios Using Reduction Pyrolysis Coupled with Mass Spectrometry"	*Anal. Lett.* **6**, 951–60 (1973)
	(See Goering, J. J.)	
	(See Thompson, G. M.)	
	(See White, J. C.)	
Christie, W. H., D. H. Smith, H. S. McKown	"Data Acquisition and Processing for High-Resolution Mass Spectrometry Using a Small Non-Dedicated Computer"	*Chem. Instrum.* **5**, 43–58 (1973–1974)
	(See Mrochek, J. E.)	
Clayton, F. R.,* G. Mamantov,* D. L. Manning	"Use of Lanthanum Trifluoride Membrane Reference Electrode in Molten Fluorides"	*High Temp. Sci.* **5**, 358–64 (1973)
	"Electrochemical Studies of Uranium and Thorium in Molten LiF-NaF-KF at 500°C"	*J. Electrochem. Soc.* **121**, 86–90 (1974)
Costanzo, D. A.	(See Bell, J. T.)	
Dyer, F. F., L. C. Bate	"Determination of ^{131}I in Reactor Dust Particles Collected on Silver Filters"	*Radiochem. Radioanal. Lett.* **16**, 59–64 (1974)
	(See Lyon, W. S.)	
	(See Raman, S.)	
	(See Ricci, E.)	
Eldridge, J. S., G. D. O'Kelley,* K. J. Northcutt, E. Schonfeld*	"Nondestructive Determination of Radionuclides in Lunar Samples Using a Large Low-Background Gamma-Ray Spectrometer and a Novel Application of Least-Squares Fitting"	*Nucl. Instrum. Methods* **112**, 319–22 (1973)
Eldridge, J. S., G. D. O'Kelley,* K. J. Northcutt	"Radionuclide Concentrations in Apollo 16 Lunar Samples Determined by Nondestructive Gamma-Ray Spectrometry"	*Proc. Fourth Lunar Sci. Conf.* **2**, 2115–22 (1973)
Feldman, C.	"Perchloric Acid Procedure for Wet-Ashing Organics for the Determination of Mercury (and Other Metals)"	*Anal. Chem.* **46**, 1606 (1974)
	"Preservation of Dilute Mercury Solutions"	*Anal. Chem.* **46**, 99–102 (1974)
	(See Huckabee, J. W.)	
	(See White, J. C.)	

AUTHOR(s)	TITLE	PUBLISHER
Goering, J. J.,* D. M. Nelson,* J. A. Carter	"Silicic Acid Uptake by Natural Populations of Marine Phytoplankton"	*Deep-Sea Res.* **20,** 777–89 (1973)
Goldstein, G., W. L. Maddox, M. T. Kelley*	"Spectrophotometric Analysis with the GeMSAEC Fast Analyzer. Determination of Zinc Using (4-2-Pyridylazo)resorcinol (PAR)"	*Anal. Chem.* **46,** 485–89 (1974)
Goldstein, G., W. T. Rainey	"Development of Specifications for Labeled Nucleotides and Related Compounds. Specific Activity Measurements by Mass Spectrometry"	*J. Label. Compounds* **9,** 805–15 (1973)
Guerin, M. R., G. Olerich, A. D. Horton	"Routine Gas Chromatographic Component Profiling of Cigarette Smoke for the Identification of Biologically Significant Constituents"	*J. Chromatogr. Sci.* **12,** 385–91 (1974)
Guerin, M. R., G. Olerich, W. T. Rainey	"Gas Chromatographic Determination of Non-Volatile Fatty Acids in Cigarette Smoke"	*Anal. Chem.* **46,** 761–63 (1974)
	(See Battista, S. P.)	
	(See Horton, A. D.)	
Hewette, D. M., II,* W. R. Laing	"Detection of Defective SiC Layers in Coated Nuclear Fuel Particles"	*Nucl. Technol.* **21,** 149–50 (1974)
Horton, A. D., M. R. Guerin	"Determination of Acetaldehydes and Acrolein in the Gas Phase of Cigarette Smoke Using Cryothermal Gas Chromatography"	*Tobacco Sci.* **176,** 19–22 (1974)
	"Gas-Solid Chromatographic Determination of Carbon Monoxide and Carbon Dioxide in Cigarette Smoke"	*J. Ass. Offic. Anal. Chem.* **57,** 1–7 (1974)
	"Quantitative Determination of Sulfur Compounds in the Gas Phase of Cigarette Smoke"	*J. Chromatogr.* **90,** 63–70 (1974)
Horton, A. D., J. R. Stokely, M. R. Guerin	"Gas Chromatographic Determination of Nitric Oxide (NO) in Cigarette Smoke"	*Anal. Lett.* **7,** 177–85 (1974)
	(See Guerin, M. R.)	
Huckabee, J. W.,* C. Feldman, Y. Talmi	"Mercury Concentrations in Fish from the Great Smoky Mountains National Park"	*Anal. Chim. Acta* **70,** 41–47 (1974)
Hulett, L. D.	(See Carlson, T. A.)	
Jones, Lois M.,* R. L. Walker, J. C. Stormer, Jr.*	"Isotope Composition of Strontium and Origin of Volcanic Rocks of the Raton-Clayton District, Northeastern New Mexico"	*Geol. Soc. Amer. Bull.* **85,** 33–36 (1974)
Laing, W. R.	(See Hewette, D. M., II)	
Lyon, W. S.	"A Reviewer's Life is Not a Happy One"	*Radiochem. Radioanal. Lett.* **16,** 163–66 (1974)
	"Californium, Here You Come"	*Radiochem. Radioanal. Lett.* **17,** 229-32 (1974)
	"High and Low Flux Experiments at the High Flux Isotope Reactor"	*Radiochem. Radioanal. Lett.* **17,** 135–37 (1974)
	"Pollution: Inorganics Are In Again"	*Radiochem. Radioanal. Lett.* **16,** 227–30 (1974)
	"Putting the Meet Back in Meetings"	*Radiochem. Radioanal. Lett.* **17,** 1–5 (1974)

AUTHOR(s)	TITLE	PUBLISHER
Lyon, W. S.	"Radiochemical Activities at the Oak Ridge National Laboratory–Analytical Chemistry Division"	*J. Radioanal. Chem.* **20,** 779–89 (1974)
	"The Nuclear Chemist as Dermatologist"	*Radiochem. Radioanal. Lett.* **15,** 135–38 (1973)
	"The Past Perfect Versus Future Shock"	*Radiochem. Radioanal. Lett.* **15,** 247–50 (1973)
	"The Perils of Pu, I"	*Radiochem. Radioanal. Lett.* **18,** 117–21 (1974)
	"The Perils of Pu, II"	*Radiochem. Radioanal. Lett.* **18,** 159–63 (1974)
	"X-Raying the X-Ray Fluorescence Technique"	*Radiochem. Radioanal. Lett.* **16,** 1–4 (1973)
Lyon, W. S., E. Ricci, L. C. Bate, F. F. Dyer	"Reliability in Scientific Evidence Based on Multi-Trace Forensic NAA"	*J. Radioanal. Chem.* **15,** 399–404 (1973)
Lyon, W. S., E. Ricci, H. H. Ross	"Nucleonics"	*Anal. Chem.* 46, 431R–36R (1974)
	(See Bate, L. C.)	
	(See White, J. C.)	
Maddox, W. L.	(See Goldstein, G.)	
Manning, D. L., G. Mamantov*	"Studies of the Electroreduction of Uranium(IV) in Molten $LiF\text{-}BeF_2\text{-}ZrF_4$ by Square Wave Voltammetry"	*Electrochim. Acta* **19,** 177–79 (1974)
Manning, D. L., J. R. Stokely, D. W. Magouyrk*	"Studies on Several Uranyl Organophosphorus Compounds in a Poly(vinyl chloride) (PVC) Matrix as Ion Sensors for Uranium"	*Anal. Chem.* **46,** 1116–19 (1974)
	(See Clayton, F. R.)	
	(See Stokely, J. R.)	
Matthews, D. R., W. D. Shults, J. A. Dean*	"Gas Chromatographic Determination of Aqueous Halides"	*Anal. Lett.* **6,** 513–22 (1973)
McKown, H. S.	(See Christie, W. H.)	
Mrochek, J. E.,* S. Katz,* W. H. Christie, S. R. Dinsmore*	"Acetaminophen Metabolism in Man as Determined by High-Resolution Liquid Chromatography"	*Clin. Chem.* **20,** 1086 (1974)
Mrochek, J. E.,* W. T. Rainey, Jr.	"Gas Chromatography and Mass Spectrometry of Some Trimethylsilyl Derivatives of Urinary Glucuronides"	*Anal. Biochem.* **57,** 173–89 (1974)
Mueller, T. R.	(See Ross, H. H.)	
Northcutt, K. J.	(See Eldridge, J. S.)	
Olerich, G.	(See Guerin, M. R.)	
Rainey, W. T., Jr.	(See Goldstein, G.)	
	(See Guerin, M. R.)	
	(See Mrocheck, J. E.)	

AUTHOR(s)	TITLE	PUBLISHER
Raman, S.,* R. L. Auble,* F. F. Dyer	"Weak Gamma Transitions in 129-Day $^{123}Sn^{g}$ Decay"	*Phys. Rev. C* **9**, 426 (1974)
Ricci, E.	"New System for Activation Analysis with Thick-Target, 110-MeV Electron Bremsstrahlung"	*Nucl. Instrum. Methods* **114**, 477–81 (1974)
	"Sensitivities for Photon-Activation Analysis with Thick-Target, 110-MeV Electron Bremsstrahlung"	*Anal. Chem.* **46**, 615–18 (1974)
	"Sensitivities in ^{252}Cf Neutron Activation Analysis"	*Trans. Amer. Nucl. Soc.* **18**, 92 (1974)
Ricci, E., T. H. Handley, F. F. Dyer	"Analysis of Traces at ORNL's New High-Flux Neutron Activation Laboratory"	*J. Radioanal. Chem.* **19**, 141 (1974)
	(See Lyon, W. S.)	
Ross, H. H., T. R. Mueller	"Low-Cost Logic Probe with Memory"	*Electronic Experimenter's Handbook*, Spring Edition, 77–80 (1974)
	(See Lyon, W. S.)	
Shults, W. D.	(See Bowling, J. L.)	
	(See Matthews, D. R.)	
	(See White, J. C.)	
Smith, D. H.	(See Christie, W. H.)	
Stokely, J. R.	(See Horton, A. D.)	
	(See Manning, D. L.)	
Talmi, Y.	"Determination of Zinc and Cadmium in Environmentally Based Samples by the Radiofrequency Spectrometric Source"	*Anal. Chem.* **46**, 1005–10 (1974)
	(See Huckabee, J. W.)	
Thompson, G. M.,* R. L. Walker, J. A. Carter, D. N. Lumsden*	"Procedures for Thorium and Uranium Extraction from Calcite"	*Radiochem. Radioanal. Lett.* **16**, 53–56 (1973)
Walker, R. L.	(See Carter, J. A.)	
	(See Jones, Lois M.)	
	(See Thompson, G. M.)	
	(See Walton, J. R.)	
Walton, J. R., A. E. Cameron,* R. L. Walker, T. L. Hebble*	"Determination of the Abundance of Krypton in the Earth's Atmosphere by Isotope Dilution Mass Spectrometry"	*Int. J. Mass Spectrom. Ion Phys.* **12**, 439–53 (1973)
	(See Carter, J. A.)	
Young, J. P.	(See Bamberger, C. E.)	
Zittel, H. E.	"The Effect of Gamma Radiation on Some Organic pH Indicators"	*Radioanal. Chem.* **14**, 19–28 (1973)

Theses

Bowling, James Lawrence	*An Investigation of the Utility of Kinetically Controlled and Catalytic Reactions to Perform Environmental Determinations by Parallel Spectrophotometric Analysis*	University of Tennessee, Knoxville, March 1974
Canada, D. C.	*Isotopic Ratios as a Selective Requirement for Mass Fragmentography*	Purdue University, December 1973

Reports

AUTHOR(s)	TITLE	REPORT NO. AND DATE
Bolton, N. E.,* W. Fulkerson,* R. I. Van Hook,* W. S. Lyon, A. W. Andren* J. A. Carter, J. F. Emery, C. Feldman, L. D. Hulett, H. W. Dunn, C. J. Sparks, Jr.,* J. C. Ogle,* M. T. Mills*	*Trace Element Measurements at the Coal-Fired Allen Steam Plant – Progress Report, February 1973–July 1973*	ORNL-NSF-EP-62 (June 1974)
Carter, J. A.	*Report of Foreign Travel to Karlsruhe, Germany, and Vienna, Austria, February 10–21, 1974*	ORNL-CF-74-3-24 (Mar. 15, 1974)
Corbin, L. T.	*Statistical Quality Control Report, Analytical Chemistry Division, July through September 1973*	ORNL-CF-73-10-33 (Oct. 15, 1973)
	October through December 1973	ORNL-CF-74-1-17 (Jan. 14, 1974)
	January through March 1974	ORNL-CF-74-4-41 (Apr. 18, 1974)
	April through June 1974	ORNL-CF-74-7-30 (July 24, 1974)
	July through September 1974	ORNL-CF-74-10
Fulkerson, W.,* W. D. Shults, R. I. Van Hook*	*Ecology and Analysis of Trace Contaminants Progress Report, January 1973–September 1973*	ORNL-NSF-EATC-6 (Jan. 1974)
Larson, N. M.,* R. Crosmun, Y. Talmi	*Theoretical Comparison of Singly-Multiplexed Hadamard Transform Spectrometers to Scanning Spectrometers*	ORNL-TM-4603 (July 1974)
Reed, R. E.,* E. D. Bolling,* J. F. Emery	*Effects of Neutron Irradiation upon Metallographic Materials*	ORNL-TM-4604 (Aug. 1974)
Shults, W. D., L. T. Corbin	*Analytical Chemistry Division Research and Development Summary – September and October 1973*	ORNL-CF-73-11-8 (Nov. 1, 1973)
	November 1973	ORNL-CF-73-12-7 (Dec. 3, 1973)
	December 1973 through January 1974	ORNL-CF-74-2-4 (Feb. 1, 1974)
	February 1974	ORNL-CF-74-3-11 (Mar. 1, 1974)
	March 1974	ORNL-CF-74-4-31 (Apr. 1, 1974)
	April 1974	ORNL-CF-74-5-6 (May 1, 1974)
	May 1974	ORNL-CF-74-6-34 (June 1, 1974)
	June 1974	ORNL-CF-74-7-12 (July 1, 1974)
	July 1974	ORNL-CF-74-8-6 (Aug. 1, 1974)
	August 1974	ORNL-CF-74-9-4 (Sept. 1, 1974)

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 variety of subjects, reflecting the Division's broad spectrum of activities.

Eighteenth Conference on Analytical Chemistry in Nuclear Technology

The theme of this conference, which was held at the Riverside Motor Lodge in Gatlinburg on October 22–24, was "Analytical Chemistry in Energy Programs." In addition to 47 papers, the conference included a panel discussion on "Multielement Analysis," and a workshop on "The Application of Multielement Detectors to Applied Spectroscopy." Eight other sessions were titled: Actinides in Environmental Samples, Principles and Applications of Method for Multielement Analysis, Applicability of Multielement Detectors to Spectroscopy – Present Status, Analysis of Nuclear Fuels and Waste, Role of Analytical Measurements in Nuclear Safeguards, Thermonuclear Reactors – Some Analytical Aspects, Chromatographic Techniques in Fossil Fuel Systems, and General Analysis.

Members of the Conference Committee were L. J. Brady, Chairman; H. R. Beatty, Treasurer and Exhibits Coordinator; W. H. Christie, Technical Program Chairman; and J. A. Carter, W. S. Lyon, Jr., W. T. Rainey, Jr., R. R. Rickard, J. R. Stokely, Y. Talmi, and J. C. White.

Alexander Zucker, Associate Director of Physical Sciences, ORNL, was the speaker at the dinner on October 22.

In addition to attendees from AEC laboratories, universities, other government-sponsored laboratories, and industrial laboratories, representatives from Canada, West Germany, and Austria participated in the program.

At Meetings of Professional Societies, Conferences, and the Like

AUTHOR(s)	TITLE	PRESENTED AT
Carter, J. A., W. H. Christie, J. C. Franklin	"Spark Source and Ion Microprobe Mass Spectrometric Studies"	Sixth Annual Conference on Surface Studies (Y-12), Oak Ridge, Sept. 10–12, 1974
Carter, J. A., J. R. Walton, D. R. Matthews, R. L. Walker	"Rapid Measurement of Total Nitrogen and ^{15}N in Soil Groundwater and Plant Tissues Using Reductive Pyrolysis Coupled with Mass Spectroscopy"	Second Annual NSF-RANN Trace Contaminants Conference, Asilomar Conference Grounds, Pacific Grove, Ca., Aug. 29–31, 1974
Christie, W. H.	"Ion Microprobe Mass Analysis – A New Concept in the Microanalysis of Solids"	Mass Spectrometry, Y-12, Jan. 8, 1974
		ORAU Traveling Lecture, University of Georgia, Geology Dept., Jan. 9, 1974
		ORAU Traveling Lecture, Florida Atlantic University, Chemistry Dept., Jan. 11, 1974
	"The Ion Microprobe Mass Analyzer – A New Analytical Technique for the Analysis of Surfaces"	Chemical Technology Division Luncheon Seminar, ORNL, Mar. 5, 1974
Christie, W. H., J. A. Carter, J. C. Franklin, H. S. McKown, W. T. Rainey, Jr., R. L. Walker, D. C. Canada	"New Capabilities in Mass Spectrometry"	Analytical Chemistry Division Annual Information Meeting, ORNL, Feb. 4–5, 1974
Corbin, L. T.	"Control of Costs in Analytical Chemistry Laboratories"	Panel Discussion, 17th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 23–25, 1973
Costanzo, D. A.	"Analytical Coordination of HTGR"	ORNL Program Committee, ORNL, Sept. 26, 1973
	"Sample Inspection System, HTGR Fuel Refabrication Pilot Plant"	Task Force Review of the HTGR Fuel Refabrication Pilot Plant, ORNL, Aug. 19–21, 1974

AUTHOR(s)	TITLE	PRESENTED AT
Eldridge, J. S.	"Apollo Expeditions – Five and One-Half Years Among the Rocks"	Analytical Group, East Tennessee Section, American Chemical Society, Oak Ridge, Nov. 29, 1973
Emery, J. F.	"Instrumental Neutron Activation Analysis"	ORAU Course on Trace Analysis for Environmental Pollutants, Oak Ridge, July 23, 1974
Emery, J. F., F. F. Dyer	"Multielement Determination in Environmental NAA Using MONSTR"	Second International Conference on Nuclear Methods in Environmental Research, Columbia, Mo., July 29–31, 1974
Franklin, J. C.	"Special Gas Analysis Methods"	Gas Analytical Conference, Mound Laboratory, Miamisburg, Ohio, June 11–12, 1974
Franklin, J. C., J. A. Carter, W. H. Christie	"Spark-Source and Ion Microprobe Mass Spectrometric Studies"	Sixth Annual Conference on Surface Studies (Y-12), Oak Ridge, Sept. 10–12, 1974
Goldstein, G.	"Labeled Compounds"	Chemical Technology Division Luncheon Seminar, Aug. 6, 1974
Guerin, M. R.	"Cigarette Smoke, Smoking, and Smokers"	ORNL Bimonthly Information Colloquium, Oak Ridge, July 30, 1974
	"Tobacco Smoke Characterization: A Model for Coal Liquefaction – Analytical Research"	Workshop on Analytical Needs of the Future as Applied to Coal Liquefaction, Greenbo Lake, Ky., Aug. 21–23, 1974
Horton, A. D., M. R. Guerin, J. R. Stokely, A. S. Meyer	"Determination of Nitrogen-Containing Components in the Gas Phase of Cigarette Smoke by Use of the Coulson Electrolytic Conductivity Detector"	27th Tobacco Chemists' Research Conference Winston-Salem, N. C., Oct. 3–5, 1973
Hulett, L. D.	"Electron Spectroscopy for Chemical Analysis"	ORAU Traveling Lecture, Memphis State University, Mar. 8, 1974
	"Electron Spectroscopy for Chemical Analysis"	ORAU Traveling Lecture, West Virginia University, Feb. 27, 1974
	"Scanning Electron Microscopy"	ORAU Traveling Lecture, University of Louisville, Feb. 26, 1974
	"Scanning Electron Microscopy and Photoelectron Spectroscopy"	University of Tennessee Medical Units, Memphis, Tenn., Apr. 19, 1974
Hulett, L. D., G. A. Nyssen	"Catalyst and Corrosion Studies by Photoelectron Spectroscopy"	Sixth Annual Conference on Surface Studies, ORNL, Sept. 12, 1974
Hulett, L. D., T. Tamura*	"Scanning Electron Microscope Applications in Environmental Pollution Problems"	65th Annual Meeting of American Society of Agronomy–Crop Science Society of America–Soil Science Society of America, Las Vegas, Nev., Nov. 11–16, 1973
Hulett, L. D., T. Tamura,* L. R. Wilson,* C. S. Helling*	"Studies of the Adsorption of Toxic Materials on the Surfaces of Clays by Photoelectron Spectroscopy"	Fifth Northeast Regional Meeting of the American Chemical Society, Rochester, N.Y., Oct. 17, 1973
Jones, Lois M.,* R. L. Walker, S. E. Kesler,* J. M. Barton, Jr.*	"Eocene Porphyry Copper Province Greater Antilles"	The Geological Society of America Meeting, Dallas, Texas, Nov. 12–14, 1973
Kelley, M. T., R. W. Stelzner, J. M. Dale, N. Marion Ferguson	"Operation of a PE-403 Atomic Absorption Spectrophotometer with a PDP-8/E Computer"	17th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 23–25, 1973
Laing, W. R., L. T. Corbin	"ASTM Methods for Nuclear Materials"	17th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 23–25, 1973

AUTHOR(s)	TITLE	PRESENTED AT
Lyon, W. S., N. E. Bolton,* J. F. Emery, D. H. Klein*	"Instrumental Neutron Activation Analysis of Effluents from Coal Fired Steam Plants"	Second International Conference on Nuclear Methods in Environmental Research, Columbia, Mo., July 29–31, 1974
Moore, F. L.	"Progress in Pollution Abatement of Toxic Materials"	Analytical Chemistry Division Annual Information Meeting, ORNL, Feb. 5, 1974
	"Pollution Abatement of Toxic Materials"	NSF Site Review, ORNL, Mar. 11, 1974
Mrochek, J. E.,* S. Katz,* W. H. Christie, S. R. Dinsmore*	"The Metabolism of Acetaminophen in Man as Determined by High-Resolution Liquid Chromatography"	Sixth Annual Symposium on Advanced Analytical Concepts for the Clinical Laboratory, ORNL, Mar. 15, 1974
Rainey, W. T.	"Mass Spectrometry"	Chemical Technology Division Biotechnology Luncheon Seminar, June 4, 1974
Rainey, W. T., W. H. Christie, W. Lijinsky*	"Mass Spectrometric Studies of *N*-Nitroso Compounds"	Reg. ACS Meeting, Charleston, S.C., Nov. 7–9, 1973
Reynolds, S. A.	"Analysis for Plutonium in Environmental Materials"	Analytical Chemistry Division Annual Information Meeting, ORNL, Feb. 4, 1974
Ricci, E.	"New Facility for Activation Analysis with Thick-Target, 110-MeV Electron Bremsstrahlung"	American Nuclear Society Winter Meeting, San Francisco, Calif., Nov. 11–16, 1973
	"Sensitivities in ^{252}Cf Neutron Activation Analysis"	American Nuclear Society Annual Meeting, Philadelphia, Pa., June 23–27, 1974
Ricci, E., W. F. Harris,* D. E. Reichle*	"Environmental Baselines by NAA of Tree-Core Samples"	Second International Conference on Nuclear Methods in Environmental Research, Columbia, Mo., July 29–31, 1974
Ross, H. H.	"Flameless Atomic Absorption and Emission Analysis"	Analytical Specialists Meeting, Union Carbide Corp., Parma, Ohio, Oct. 15–16, 1973
Stokely, J. R., M. R. Guerin	"Chemical Characterization of Tobacco Smoke in an Intermittent Animal Exposure Device"	27th Tobacco Chemists' Research Conference, Winston-Salem, N.C., Oct. 3–5, 1973
Talmi, Y., C. Feldman	"The Determination of Traces of Arsenic: A Review"	American Chemical Society National Meeting, Atlantic City, N.J., Sept. 1974
White, J. C.	"Challenges in Quantifying Energy Measurements"	ORNL Summer Seminar Series, Oak Ridge, July 29, 1974
	"Forecasting Analytical Needs for Energy Research"	Centenary Celebrations of The Society for Analytical Chemistry, London, England, July 16–19, 1974
	"Standard Reference Materials and Meaningful Measurements"	Panel Discussion on "Industrial Chemicals," Symposium on Standard Reference Materials and Meaningful Measurements, National Bureau of Standards, Gaithersburg, Md., Oct. 29–Nov. 2, 1973
Zittel, H. E.	"Chemical Discharges and Sanitary Effluents Sections in Environmental Impact Statements for Nuclear Power Plants"	Georgia Institute of Technology Short Course on Environmental Impact Statements for Nuclear Power Plants, Atlanta, Ga., Nov. 26–30, 1973

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)	SUBJECT	DATE
Biscar, J. P., Univ. of Wyoming	"Laser-Produced Electromagnetic Molecular Electronic Resonance Scattering in Biological Molecules and in DNA's"	Oct. 26, 1973
Canada, D. C., ORNL	"Isotopic Ratios As a Selective Requirement for Mass Fragmentography"	Apr. 23, 1974
Colchin, R. J., ORNL	"Status of Thermonuclear Project and Possible Analytical Chemistry Involvement"	May 14, 1974
Dean, J. A., Univ. of Tenn.	"Application of Analytical Techniques to Minor Constituents in Inorganic Materials"	Dec. 13, 1973
	"Ion Selective Electrodes"	Apr. 11, 1974
	"Liquid Chromatography"	Nov. 20, 1973
	"Methods for Surface Analysis"	Feb. 14, 1974
	"Surface Analysis Methods – Continued"	Mar. 14, 1974
	"Thermal Analysis"	Jan. 17, 1974
Goff, Robert F. 3-M Company, Minneapolis, Minn.	"Ion Scattering Spectroscopy"	Nov. 12, 1973
Hulett, L. D., ORNL	"Rebirth of X-Ray Fluorescence"	Mar. 21, 1974
Hurt, H. B., ORNL	"Attitude – The Subjective Element"	June 18, 1974
Lenihan, J. M. A., Western Regional Hospital Board, Glasgow, Scotland	"Mercury in Medicine"	July 22, 1974
Mamantov, G., Univ. of Tenn.	"Impressions of the Soviet Union – Scientific and Otherwise"	Aug. 13, 1974
Schulten, H. R., Institut für Physikalische Chemie, der Universität Bonn, Bonn, Germany	"Field Desorption Mass Spectrometry"	May 31, 1974
Singer, G. M., ORNL	"Nitrosamines in the Environment"	Oct. 16, 1973
Ulrikson, G. U., ORNL	"Description of the Environmental Information Systems Office"	Mar. 5, 1974
Wasserburg, G. J., D. Papanastassiou, California Inst. of Technology	"Isotopic Evidence for a Lunar Cataclysm"	Dec. 13, 1973

PATENTS

AUTHOR(s)	TITLE	PATENT NO.	DATE ISSUED
Moore, F. L.	"Extraction of Mercury from Alkaline Brines"	3,785,803	Jan. 15, 1974
Mueller, T. R., D. J. Fisher	"Automatic Controlled-Current Coulometric Environmental Monitor"	3,835,008	Sept. 10, 1974

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

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	Anal. Biol. Chem.	*Anal. Chem.*	*Anal. Lett.*	*ANSI Methods*	*ASTM Methods*	*Chem. Instrum.*	*Clin. Chem.*	*Environ. Sci.*	*ESD Report*	*J. Amer. Chem. Soc.*	*J. Environ. Quality*	*J. Phys. Chem.*	*Nucl. Data*	*Nucl. Sci. Eng.*	*Nucl. Technol.*	*Radiochem. Radioanal. Lett.*	*Talanta*	Books & Theses	Proposals	Total
Caton, J. E.			1																	1
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Feldman, C.		1								1				1						3
Goldstein, G.	2						5													7
Kubota, H.		1																		1
Lyon, W. S.		3			3	1									1	2				10
Manning, D. L.		4						1												5
Moore, F. L.		4																	1	5
Mueller, T. R.		5				1														6
Rainey, W. T.																			2	2
Reynolds, S. A.		1		1	5				1		1		1	1	1		1			13
Ricci, E.		1																		1
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