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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

Period Ending September 30, 1972

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ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
For Period Ending September 30, 1972

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JANUARY 1973

OAK RIDGE NATIONAL LABORATORY
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Preface

The mission of the Division remained the same during this period – to provide overall analytical support to the projects and programs of the Laboratory in the form of research on new analytical techniques, development of methodology and instrumentation, and service analyses – but the cast changed noticeably. On May 1, 1972, J. C. White became director of the Division succeeding M. T. Kelley who had served as director since formation of the Division in 1948. Dr. Kelley continues to serve the Division as senior scientific advisor. It goes without saying that his contributions to the Division and to the Laboratory have been numerous and significant, and we are in his debt for his services over these many years. Fortunately, he continues in his exemplary fashion as is evidenced by his contributions in this report.

Additional changes in organization were made in June 1972, notably the appointment of W. D. Shults as assistant director. The new organization of the Division is shown in the Appendix of this report. C. Feldman, D. J. Fisher, and G. Goldstein constitute a technical staff with the primary responsibility for providing technical guidance in spectroscopy, instrumentation, and bio-organic analyses. Other changes reflect a consolidation of groups and some reorientation of research and development activities designed basically to take better advantage of individual talents and equipment and thereby increase efficiency of operation.

The past year has seen the Division expand its program on the characterization of cigarette tobacco smoke and condensate for the National Cancer Institute. The Division has also become increasingly involved with the Biology Division in the development of methodology for bioassay methods for carcinogeneity of cigarette smoke. The Division has in addition this year initiated its participation in the ORNL-NSF RANN program, an effort that epitomizes the ever-increasing involvement of the Division in environmental analyses, which spans the gamut from routine analyses through referee analyses to the development of new analytical techniques for environmental measurements.

Summary

1. INSTRUMENTATION AND ADVANCED METHODOLOGY

The research and development activities of this group continue to support the instrumentation needs of projects within the Analytical Chemistry Division as well as other divisions at ORNL and various government agencies. Among the new instrumentation developed during the past year is a radio-frequency furnace for the excitation of atomic emission and absorption spectra. A new photometer for emission/absorption has also been designed and fabricated. A unique monitor for chlorine and chloride in the atmosphere was developed for the Environmental Protection Agency; detection levels are in the 10- to 100-ppb range. A number of previous instrument designs have been updated for improved performance. Analytical research in support of the transuranium program is continuing. A new, high-precision, coulometric cell has been fabricated for general transuranium analysis. Also, the half-lives of several californium isotopes have been determined by an absolute specific-activity measurement. The polarographic and spectrophotometric behavior of several divalent actinides was investigated.

The preliminary work on the development of a specific-ion electrode for uranium is very encouraging. Many projects involving the programming of mini-computers have been completed. New achievements in this area include the evaluation of x-ray spectra from the scanning electron microscope, computer techniques for investigating plasma-excited spectra, the development of a computer interface for an atomic absorption spectrophotometer, and computer studies of electrochemical phenomena. A time-sharing service on the DEC 10 system was obtained this year. Initially the system was used to calculate air quality indices from Council on Environmental Quality data. The service was also used for gamma-ray spectrum resolution and in the ORNL tobacco smoke program. A project has been started to determine the unique areas of application of the GeMSAEC photometric analyzer to the analysis of trace elements. A project to develop phosphor screens for x-ray detection was completed for the U.S. Army.

2. BIO-ORGANIC ANALYSIS

The Bio-Organic Analysis Group has recently been formed by combining the Analytical Biochemistry Group and the Organic Analytical Section of the Methodology Group. Two programmatic areas, the tobacco smoke research program and bioanalytical research in support of Laboratory programs in human biochemistry, constitute the primary commitment of the new group. The broader objective is to establish the organic analytical and bioanalytical capabilities necessary to support Laboratory programs as interest expands to include organic chemical problems. Continued collaboration on existing bioanalytical problems and dedicated studies of tobacco smoke chemistry and inhalation bioassay methodologies have formed a broad base of organic analytical expertise.

Analytical assistance continues to be provided to the Molecular Anatomy Program and the Biochemical Separations Systems Development Group. Collaboration with the Biology of Human Variants Group of the Biology Division continued with studies of the thin-layer chromatography of important indoles, imidazoles, carbohydrates, and amino acids. Studies to make high-resolution gel electrophoresis a practical routine clinical tool have continued. Special electrophoretic techniques, including immunoelectrophoresis and isoelectric focusing, are receiving attention. The isolation and characterization of human placental antigens are being studied using electrophoretic methods. Work on prenatal diagnosis by chemical measurements on single isolated cells is continuing.

The tobacco smoke chemistry project has expanded in both scope and depth. The staff is now providing general chemical support facilities for NCI tobacco-related projects. The analytical facility has been improved, special-interest cigarettes have been accepted for chemical study, studies to characterize a special smoke generation system have been ini-

tiated, and the number of determinations to be carried out on standard experimental cigarettes has increased. Research activities have produced procedures allowing the routine determination of isoprene and free fatty acids in smokes. The use of several techniques for the characterization of metals in smokes is being studied. The procedure developed here for the analysis of polynuclear aromatic hydrocarbons has been greatly improved. A new technique has been developed for the study of sulfur compounds in smokes and has been applied to confirm our earlier contention that popularly held concepts of sulfur composition are in error. Evidence for the presence of organosulfur compounds in condensates has been obtained. Research activities are expanding to support new responsibilities.

The tobacco smoke inhalation methodology project, a collaborative effort with the Biology Division, has expanded in scope and depth. The goal is now the development of a viable inhalation bioassay, with intratracheal cannulation being only one approach. Several smoke generation–exposure machines have been designed and fabricated. The previous design has been modified to allow the use of improved animal containment tubes and to expose a greater number of animals per pump. Several new mouthpiece–cannula assemblies have been constructed and studied with regard to the effect of various cannula materials on smoke absorption. Methodologies have been established for the use of radiolabeled paraffins in studies of lung dosimetry. Studies have been initiated on the composition of smokes after passage through the nasal turbinates of hamsters.

Special problems have continued to receive attention where possible. The system for the analysis of carbon, nitrogen, sulfur, and phosphorus in solid ecological samples is now in routine use. A pilot study of various trap systems for the collection and subsequent gas chromatographic analysis of human breath volatiles has been completed. A study of the purity of important biochemicals has been published.

3. ENERGY PROGRAMS

The automated in-line measurement of U(III) concentration in a thermal convection loop was continued. These analyses continued to show excellent reproducibility and clearly demonstrate the adventitious oxidation of U(III) by contaminants introduced during the insertion of corrosion specimens and the recovery of U(III) by oxidation of the chromium from the structural metal and specimens. A comparison of the experimental voltammetric and derivative waves with those computed from theoretical considerations has shown that, while the reduction of chromium makes a significant contribution to the early part of the wave, an excellent match between theoretical and experimental data is obtained in the region of the peak reduction current. Moreover, the presence of chromium does not introduce any significant error in the potential at which the maximum in the derivative wave occurs. The location of the derivative maximum is used to compute the U(III) concentration. Under the reducing conditions at which the loop has been operated chromium is the only corrosion product that is present in significant concentrations. The voltammetric determination of chromium is complicated by its proximity to the larger uranium wave. With a proposed stripping technique it is possible to extract a measurable chromium wave from the reoxidation curves. Calibrations of this method are in progress. A system of voltammetric electrodes is being installed on a large engineering test loop to measure corrosion products and active protons in coolant-salt streams.

The role of hydrogen in the coolant salt has been shown to be more complex than originally thought. It now appears that both melts and salts contain $NaBF_3OH$ as a relatively stable species. In the melts, however, studies indicate that a small fraction of the hydrogen is present as an electroactive species (possibly HF, HBF_4, HBF_3OH), which is in relatively rapid equilibrium with a vapor species. In addition, the frozen salt may contain adsorbed water which is partially converted to $NaBF_3OH$ on melting.

A newly developed LaF_3-windowed cell has made possible the measurement of the fundamental BF_3OH^- absorption in $NaBF_4$ melts at 3640 cm^{-1}. No evidence for the isotopic exchange was seen when hydrogen isotopes were diffused into $NaBF_4$ melts in a silica cell, but chemical reactions which formed BF_3OH^- (or BF_3OD^-) did occur. The original infrared pellet calibration data for proton determination (as BF_3OH^-) seems confirmed through standard additions of $NaBF_3OH$ to $NaBF_4$ salts, which were then melted under isothermal conditions. A liquid condensate collected from the vapor above $NaBF_4$ melts was found by NMR to contain about equal quantities of nonionic hydrogen and fluorine.

A chromium reduction wave [Cr(III) → Cr(0)] is observed at about −1.0 V vs a Pt QRE in molten $NaBF_4$-NaF (92-8 mole %). The voltammogram is reasonably well defined and appears to be analytically useful (at 500°C) but occurs close to the potential limit

of the melt. In view of an apparent anodic shift in the potential limit with increasing temperature, it may prove to be difficult to resolve the chromium voltammogram at temperatures approaching 600°C.

The electrochemical reduction of Ti(IV) in molten LiF-NaF-KF at 500°C was studied by means of voltammetry, chronopotentiometry, and chronoamperometry. The reduction of Ti(IV) to Ti(III) was found to proceed reversibly at both platinum and pyrolytic graphite electrodes; further reduction of Ti(III) to the metal was shown to be a reversible process that involves alloying with the platinum electrode. Standard electrode potentials for these two processes, Ti(IV) + $e \rightleftharpoons$ Ti(III) and Ti(III) + $3e \rightleftharpoons$ Ti(0), are −0.058 V and −1.798 V, respectively (both with respect to a unit mole fraction Ni(II)/Ni electrode).

The electrochemical oxidation of Ti(III) at unsheathed platinum and sheathed glassy carbon electrodes was studied in molten LiF-BeF_2-ZrF_4 at 500°C. Well-defined voltammograms and chronopotentiograms were obtained for the reversible process Ti(III) $\rightleftharpoons$ Ti(IV) + e. A standard electrode potential of +0.197 V vs a unit mole fraction Ni(II)/Ni electrode was calculated from these studies. No electrochemical reduction of Ti(III) was observed in this melt prior to the cathodic limit.

The electroreduction of bismuth(III) in LiF-BeF_2-ZrF_4 at 500°C results in a one-step reversible deposition of an insoluble product. An n value of 3 was obtained on different indicator electrode materials by voltammetric and chronopotentiometric techniques. A diffusion coefficient for the Bi(III) species of 1×10^{-6} cm^{-2} sec^{-1} was evaluated. No evidence was observed for $Bi^{(3^+-n)}$ intermediate states in LiF-BeF_2-ZrF_4. Iridium appears to be a good choice for an indicator electrode both in terms of inertness and long-term surface reproducibility in the molten salt.

Techniques have been developed so that gases can be bubbled into melts contained in windowless cells for gas-melt interactions. The spectrum and chemistry of Ce^{3+} and Te^{2-} have been studied in fluoride melts. The analytical usefulness of the Ce(IV)-Cr(III) reaction has also been considered. Further spectral studies of Cu^{2+} in LiF-BeF_2 have been made leading to a determination of the solubility of CuO in that melt when contained in a SiO_2 cell. Spectral studies have confirmed the existence of dissolved Li_3Bi in molten LiCl or LiBr and have inferred the nonexistence of a corresponding lead plumbide in molten LiCl.

4. NUCLEAR AND RADIOCHEMISTRY

The study of trace element profiles through a coal-fired steam plant has continued with samples of coal, ash, slag tank, and gas from the Allen Steam Plant in Memphis, Tennessee. Neutron activation analysis (NAA), atomic absorption (AA), and spark-source mass spectrometry (SSMS) are the principal techniques used. In the Cooperative Isotopes Program a number of requests for nuclear data have been answered, nuclear data updated, isotope products evaluated, and counting methods tested. In applied NAA a number of small cooperative ventures such as a study of tagging elm bark beetles, determination of mercury and other elements in blood, tissue, etc., and assistance in training students in NAA techniques were carried out. The feasibility of detection and identification of explosives by 14-MeV NAA was evaluated.

Special measurement problems included a search for beta decay of ^{96}Zr (indicated half-life is $\geqslant 3.6 \times 10^{17}$ years), a number of round-robin comparisons, and determination of ^{235}U in fission monitors. The fission product behavior in HTGR coolant circuits continued to be studied with analysis both in situ and of removed dust. The fission product release from reactor fuel microspheres has also continued to be studied. Sensitivities for a number of elements at the photon activation analysis facility at ORELA were determined, and the HFIR activation lab has been used to determine air-filter impurities. Abundances of a number of elements and cosmogenic radionuclides were determined in Apollo 15 rocks, soil, and special samples. The program concerned with effects of radiation on analytical methods was completed, with a number of findings that help delineate the overall problems in evaluating effects of alpha and gamma radiation on certain indicators and reagents.

5. SPECTROMETRY AND PHYSICS METHODS

This group has continued its studies of ionization by looking at the desorption of uranium ions and neutrals from carburized rhenium filament surfaces. A value of the work function of the composite rhenium-carbon surface was determined as 5.84 eV, about 0.4 eV higher than the work function of pure rhenium. A method for rhenium analysis in Re-W alloys was developed using the surface ionization-isotope dilution technique. Other developments of the group involve the redetermination of krypton in the earth's atmosphere and the determination of the possible ^{236}U content in some natural minerals.

In the past year approximately 1000 samples were analyzed on the low-resolution mass spectrometer. A majority of these came from the body fluids and cigarette smoke programs. Additional support was given to many groups in the Biology Division, both in analysis and mass spectra identification from our library. In

conjunction with low resolution, high-resolution mass spectrometry provided invaluable assistance in solving many problems in the organic field. During the year the high-resolution instrument was interfaced with the IBM 1130 computer, which allows us the capability of accurate mass assignments.

The two analytical techniques used most by the X-Ray Physics Group for routine analysis and special projects during the last year were scanning electron microscopy (SEM) and photoelectron spectroscopy. With the SEM we are able to take high-resolution photographs that provide very detailed physical descriptions of the specimen of interest. Simultaneously, we can do qualitative and quantitative elemental analysis of minute areas of the specimen by recording x-ray fluorescence spectra excited by the electron beam of the microscope. With photoelectron spectroscopy, used especially for low z elements and valence state studies, we can do qualitative and quantitative surface analysis. Every element of atomic number higher than 2 can be studied.

In the area of x-ray fluorescence, we are attempting to achieve higher sensitivity in heavy element detection by x-ray-induced fluorescence, and we are attempting to evaluate proton-induced (1 to 5 MeV) x-ray fluorescence as an analytical tool. A monochromatic x-ray source instead of the traditional white radiation will result in much better peak-to-background conditions, which will improve the quantitative capability. A variety of specimens that have been analyzed by other methods will be studied.

During the past year many spectrometry techniques have been used to support various environmental programs. We also have conducted analytical development work and performed trace analyses for the Environmental Protection Agency. Some of the more significant problems which were looked at in the past year are mentioned below. Lead was determined in gasoline by surface ionization isotope-dilution mass spectrometry using the established SiO_2 gel technique. This method uses enriched ^{204}Pb as the isotope spike. Cadmium and mercury have been analyzed in a variety of matrices by isotope dilution spark-source mass spectrometry using ^{106}Cd and ^{196}Hg as the isotope spikes. Trace metal analyses have been done on energy sources such as coal and oil. Up to 50 elements are qualitatively determined by scanning the entire mass range; accurate analyses, if desired, are obtained by isotope dilution spark-source mass spectrometry. Cadmium, lead, and zinc were analyzed on samples from the Purdue-ORNL cadmium study. Types of samples received from Purdue include tissue, hair, litter, soil, and vegetation.

Spark-source mass spectrometry continues to be the "work horse" for analyzing impurities in radioactive samples. These include radioactive products from the Isotopes Division and the transuranium elements from TRU programs. In connection with the Chemical Technology Division's $^{233}UO_2$ project for BAPL, certification was obtained for many elements, including mercury and the halogens. The capacity for spark-source mass spectrometry has been increased by the addition of a high-resolution MS-702R instrument. This machine has a mass resolution of about 10,000 using a 0.0005-in. slit.

The mass spectrometry service laboratory reported over 18,700 isotopic results this past year, up slightly over 5% from the previous year. These included radioactive and stable elements principally from the Chemical Technology and Isotopes Divisions. Over 40 different elements were analyzed in connection with the Isotopes Division's production programs. In addition, gas samples of all types from various groups in the plant were analyzed.

6. METHODS DEVELOPMENT AND SPECIAL PROJECTS

This group assists all groups within the service laboratories and is responsible for the development and evaluation of methods for the analysis of nonroutine samples. In this capacity, the group works in cooperation with research and development groups of other divisions in a continuing effort to establish and support analytical development programs within the service laboratories. Our activities in the past have been directed in the area of reactor fuels and materials analysis. However, during the past year, we have increased our involvement in the areas of environmental and ecological analysis. In addition to these activities, the group assignments include special projects such as the preparation of inorganic materials which are not commercially available, recycling of toxic laboratory materials, and the quality control program within the service laboratories. We are also engaged in research and development studies leading to new, practical separation methods for pollution abatement of toxic metals.

The methods for the analyses of reactor fuel and materials included: uranium and plutonium in oxide microspheres and fuel sticks; gas release and helium in irradiated B_4C; oxygen in salts by high temperature fluorination with $KBrF_4$; protons in fluoride salts by IR spectrophotometry; and uranium nitride round-robin analyses for U, N, C, and O. In addition, the analyses of environmental and biological materials included methods for the determination of carbon, nitrogen, and

sulfur in ecological materials by reductive pyrolyses chromatography and element selective detectors; the determination of total organic carbon in aqueous solutions; determining methyl mercury in fish tissue and nitrosamines by gas-liquid chromatography and mercury by cold vapor atomic absorption spectrophotometry; and determining diethylenetriamine pentacetic acid in urine. Solvent extraction with amines was successfully employed for the removal of mercury from effluents of the chloralkali industry.

Inorganic preparations included the synthesis of: alloys of gold; Heusler alloys doped with ^{61}Ni; Ni_3Ga alloys doped with iron; compounds of the rare-earth elements with nitrogen sub-group elements (phictides); and chromites of the form $NiFe_xCr_{2-x}O_4$. The salvaging of expensive stable isotopes from various matrices included: ^{63}Dy, ^{170}Er, and ^{154}Sn in ThO_2; ^{57}Fe from an alloy containing 5 at. % Si; and Ir from alloys containing refractory metals.

PART B. SERVICE ANALYSES

The process laboratories performed some 140,000 analyses during the past year. This 12% increase from last year was accompanied by a 4% decrease in personnel.

The General Hot-Analyses Laboratory was combined with the High-Level Alpha Radiation Laboratory and the Radioisotopes-Radiochemistry Laboratory this past year. Their major analytical efforts were directed toward the LWBR and the TRU programs. There has been an increasing number of analyses for environmental programs.

The General Analyses Laboratory continued to check and make refinements on methods used in boron carbide specifications. A new ion exchange resin was found to give good separation on nucleosides. Work continued to increase in numbers of environmental samples analyzed. Most of this work was done by atomic absorption and pyrolysis-gas chromatography.

The Radiation Control and Safety program continues to improve. We had only 12 medical treatment cases this year compared with 23 last year. Measures to improve industrial safety were taken. Three unusual accidents occurred during the year.

The Quality Control Program started two new projects: one for environmental type samples and one for the LWBR program. There was a decrease in number of control samples this past year.

PART C. ENVIRONMENTAL ACTIVITIES

Participation in environmental activities increased. Air quality, biological indicators of pollution, ecology and analysis of trace contaminants, and a collaborative project with Purdue University on cadmium in the environment are programs in which the Division has substantial participation. Five members are also assisting in writing environmental impact statements.

Part A. Analytical Research and Development

1. Instrumentation and Advanced Methodology

H. H. Ross, Head
R. W. Stelzner, Assistant

D. J. Fisher[1]
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NEW INSTRUMENTATION

Spectrochemical analysis. A relatively new excitation source, a radiofrequency furnace (RFF), was constructed for the direct analysis of solids and evaporated solutions by atomic emission and adsorption spectroscopy. An induction-heated graphite crucible serves both as a means of thermal vaporization and atomization; the atomized sample is mainly excited by a helium plasma which is formed by an rf field. After fabrication, the system was examined to determine the feasibility of quantitatively analyzing traces of cadmium in various matrices which are of immediate or potential interest. Among the samples analyzed were tobacco condensates and ashes, freeze-dried bovine liver (NBS standard), dried orchard leaves (NBS standard), coal, fly ash, bunker oil, and gasoline. The technique requires little or no sample preparation, and solid microsamples in the weight range of 0.10 to 2.0 mg can be analyzed directly in many cases. However, the inhomogeneity problems involved with such a technique often defeat the advantages achieved by it.

The results obtained thus far are very encouraging. The absolute sensitivity of cadmium is 5×10^{-12} and 10^{-11} g for atomic absorption and atomic emission techniques, respectively. The relative sensitivity is 5×10^{-7}% for solutions and 5×10^{-6}% for solids. The accuracy is better than 8% at the 10^{-5} to 10^{-7}% range, calculated from certified and uncertified values given by NBS standards and from values obtained by other techniques (spark MS). Experimental reproducibility varies from 2 to 10% and depends on the complexity of the matrix involved.

The most important features of the RFF system are (1) the capability to analyze trace elements at very low levels and (2) the short analysis time due to the simplicity (or complete absence) of sample preparation. The RFF is especially adaptable to routine work where large numbers of samples are to be analyzed. If the system proves itself as useful for the analysis of other trace elements as it has for cadmium, it will provide the Laboratory with an efficient analytical instrument, capable of performing tasks which usually require much more sophisticated and expensive equipment.

We have developed a new photometric amplifier system to support our analysis and research activities in trace-level absorption and emission photometry. Basically a dc amplifying system, the instrument was designed for three types of applications: (1) flame emission, (2) flame-excited atomic absorption, and (3) flameless atomic absorption photometry (AA).

For emission techniques, the gain of the amplifier may be varied from 10 V/μA to 10 V/nA as practical limits. The signal may be filtered, averaged, or integrated. The photocurrent level is displayed on a front panel meter. There are provisions for a record input amplifier with fixed gain should it be desirable to use a second signal source for another analysis.

The flame-excited atomic absorption mode is not fully implemented, but provisions exist for adding the necessary circuitry. The instrumental problem associated with this technique is the subtraction of that portion of the signal resulting from extraneous flame

1. Technical staff.
2. Senior Research Advisor.

emission from the desired photocurrent. Mechanical chopping to screen the hollow-cathode source and various modulation techniques may be used to facilitate the desired separation of emission and absorption signals. Each of these methods requires specialized data acquisition and processing circuitry that can be added as required. Cadmium and zinc will probably be the first elements determined by flame-excited AA with this instrument.

The determination of mercury by flameless AA presently accounts for the bulk of the analytical AA work. The instrument was also designed to make this determination as automatic as possible. Only two controls, "reset" and "operate," are required to be activated in order to obtain the necessary analytical data for the determination of mercury. In the "reset" mode a long time constant memory amplifier acquires the "100% T" level. In the "operate" mode this signal becomes the reference signal for a log ratio conversion circuit. The active input of the log amplifier is connected to the photo signal amplifier. The log ratio may be further amplified with a maximum sensitivity of 100 V/decade (absorbance). The actual photocurrent may be observed on a panel meter or recorded from rear panel connectors. The time integral of the log ratio is displayed on a digital panel meter and is also available at the rear panel as an analog signal. The manner in which the mercury determination is performed makes this a desirable form of readout. Since the mercury sample has only fleeting residence in the absorption path, the output of the log ratio amplifier starts from and returns to zero. The displayed integral therefore acquires a steady value. After recording this value, the integrator is cleared, and a new value for 100% T is collected. A "wait to operate" warning is extinguished when the new value of 100% T has been acquired. The operate and reset switches may be operated from rear panel connectors with DTL/TTL "low" levels or by momentary grounding of the switch line. The digital panel meter has BCD output coding. Thus, all signals and facilities are available for automatic control and/or data acquisition.

The instrument has been placed into operation only recently, and as yet data are unavailable for assessment of its field performance. Overall accuracy is expected to be about 2%.

Electrochemical analysis. We have developed an electrochemical air monitor in cooperation with the Air Programs Office of the Environmental Protection Agency. Preliminary work on this monitor was reported previously.[3] The monitor is useful for determining a variety of species electrochemically, but its present implementation is for the determination of chlorine and chloride (HCl) at the 10- to 1000-ppb level in air. Chlorine is determined by direct reduction at a platinum electrode in 6 *M* H_2SO_4 electrolyte. Chloride is determined by oxidation to chlorine, followed by reduction to chloride in a closed system. A fully automatic program sequence is utilized to (1) acquire and store a voltage corresponding to electrolyte-contained impurities, (2) subtract this voltage from that obtained in the presence of air, (3) generate coulometrically a standard sample of chlorine and determine it as chlorine and/or chloride, and (4) find, display, and store for permanent record the ratio of the signal obtained for the air sample and that obtained for the standard.

With only minor modifications the monitor could be applied to the analysis of much higher chlorine/chloride levels; that is, it could serve as a source monitor. Extensive use of plug-in circuit cards for the electronic portion of the monitor simplifies modification and/or updating of the design. To achieve maximum sensitivity, only one liter of H_2SO_4 is consumed per day in the present design. We feel that this rate of electrolytic consumption could probably be reduced substantially. Also, digital calculating capabilities which have become available could be combined advantageously with the monitor to increase its accuracy and to improve its data-handling efficiency.

The ORNL model Q-2943A cyclic voltammeter mentioned in the previous Annual Report[4] has been completed, checked out, and delivered to the Energy Programs Group. This is the fifth in the series of cyclic voltammeters originally designed for electrochemical research in molten-salt electrolytes. With the completion of this instrument we have also completed the preparation of electrical and mechanical drawings. In addition, the check-out and test procedure has been amended to include procedures for checking and calibrating Module E, the added differentiator/integrator module. We have also designed and built a less-elaborate first-derivative plug-in module to be used with the voltammeter.

The prototype Q-2943 (in use by Reactor Chemistry Division) was recently converted to the Q-2943A design by the Instrumentation and Controls Division. We

3. W. D. Shults et al, "Environmental Activities," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971,* ORNL-4749, p. 1.

4. D. J. Fisher et al, "Instrumentation Research and Development," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971,* ORNL-4749, p. 43.

served as consultants during the conversion. The Q-2943A design is principally a high-scan-rate instrument (0.005 to 500 V/sec). For our work with the air monitor,[5] the need developed for a slower scan instrument. We designed and built a scan control unit for the ORNL model Q-4010 coulometric titrator. The scan control unit plugs into the titrator's bin in a spare location. The integrator normally used for integration of titrator current serves as the scan integrator. The quality of the integrator (Q-3094) permits very slow, linear scan rates (less than 1 mV/min).

During the development of the air monitor, we needed a source of stable, constant currents for a number of our studies, as well as for the coulometric generation of chlorine. We designed and built an inexpensive supply that will deliver from 10 pA to 4 mA with a stability of ±0.1 pA/day. It can be powered by ±12 or ±15 V dc, making it usable in a standard NIM[6] bin.

R. H. Busey, Chemistry Division, requested a method whereby a constant current source and timer could be synchronized with a precision of ±1 msec. The currents to be switched varied from 1 to 200 mA, and the experiment duration was to be in the range of 1 sec to 30 min. The current source was a Hewlett-Packard model 6181B and the timer a Monsanto model 100A. We designed a circuit which was subsequently fabricated by the Instrumentation and Controls Division. A preselect feature was incorporated which permits the selection of experiment times from 1 to 9999 sec in increments of 1 sec. Should other time intervals be required, the circuitry is compatible with operation from 10 μsec to about 1 year. The apparatus is now in use.

ANALYTICAL ACTIVITIES IN THE TRANSURANIUM RESEARCH LABORATORY

Research activities at the Transuranium Research Laboratory are aimed at application and development of new techniques and instrumentation for analyzing and studying the properties of the transuranium elements. Support activities involve applications of diverse analytical techniques which require use of TRL facilities.

Analytical support for TRL programs has continued. Carbon, hydrogen, and nitrogen analyses were run on a number of solid organometallic compounds of the actinide and lanthanide elements. Recently, we cooperated in the preparation of high-quality, electroplated specimens of uranium, americium, and plutonium oxides for projects in the Chemistry Division.

During the last year, we collaborated in the development of an improved coulometric cell for controlled-potential analysis. This cell incorporates several new features which allow higher accuracy and precision, greater reliability, and faster titration rates. The coulometric cell is sealed from the atmosphere to prevent leakage of oxygen which causes high results in most coulometric titrations with a mercury electrode. The titration vessel is a 60-ml threaded glass bottle which is screwed into a threaded Teflon cap. A glass paddle stirrer driven by a Bodine motor stirs the solution. A mercury seal is incorporated into the Teflon cap to prevent oxygen leakage. Argon gas admitted to the cell is vented through a bubbler. Tank argon is used for sparging the solution; the argon is purified by passing it through copper packing at 550°C.

Bridges for the counter and reference electrodes are made from cation exchange membrane (AMF-103) heat sealed to polyethylene tubing. Resistances of the order of 20 to 50 Ω are obtained for bridges made from this membrane. The resistance of these bridges is lower by about a factor of 10 than the resistance of bridges made from unfired Vycor. The lower bridge resistances allow higher currents and faster titration rates.

The cell has been evaluated using the titration of uranium in sulfuric acid solutions. Important advantages of this cell as compared with the conventional cells are:

1. Deoxygenation of the solution is very rapid. No evidence for the presence of oxygen could be found after sparging for about 1 min at an argon flow rate of 200 cm^3/min.
2. Precision and accuracy are at least as good as found with conventional mercury coulometric cells. In work performed so far, titration results agree with standard values within 0.1% for 5 mg of uranium.

A method for the absolute chemical analysis of californium was developed and used to determine precisely the half-life of ^{249}Cf by an absolute specific activity measurement. The analysis method was based on a micro-complexometric titration of californium(III) with ethylenediaminetetraacetic acid (EDTA). A similar

5. W. D. Shults et al, "Electrochemical Air Monitor," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971,* ORNL-4749, p. 1.

6. Standard Modular Nuclear Instrument System, AEC TID-20893.

titration was done previously on curium to determine the half-lives of ^{246}Cm and ^{248}Cm.[7]

For the chemical analysis, we used a new electronic system for performing the controlled-current coulometric titration. This system employed a digital current integrator for the electrolysis current in the coulometric cell. The potential of the solution was monitored with an amalgamated platinum electrode during the course of the titration. This potential was also digitized and fed into a multichannel analyzer on the pulse-height axis. A titration curve was obtained in which the number of increments of integrated current were recorded for each potential increment of the indicator electrode. Titration curves recorded in this manner have a minimum at the end point, which allows accurate location of the end point and improves the precision a factor of 2 over the analog readout system used previously. Although this system was developed specifically for the californium analysis, it has application to all other coulometric titrations.

The electronic and chemical systems were initially evaluated using rare-earth ions as "stand-ins" for californium. Then, eight titrations were made on about 4 mg of high-purity ^{249}Cf. The uncertainty in these titrations was 0.5% (relative standard deviation). High-precision alpha counting was performed on the assayed ^{249}Cf solution by C. E. Bemis of the ORNL Chemistry Division. A half-life of 350.6 ± 2.1 years was obtained from these measurements. Further work is presently under way to determine the half-lives of ^{250}Cf and ^{251}Cf, using the chemically analyzed ^{249}Cf solution for isotope dilution.

Work was continued this year to determine if divalent actinides can be prepared and, if so, to measure the potentials of the actinide (III)-(II) couples in nonaqueous solvents. Using conventional dc polarographic techniques, we have obtained definite evidence for the existence of a divalent oxidation state of californium. Polarograms of californium(III) perchlorate in acetonitrile at millimolar concentrations show two well-defined reduction waves with potentials at −1.00 and −1.43 V vs aqueous S.C.E. The two waves are attributed to reduction of Cf(III) to Cf(II) and Cf(II) to Cf(O). This work has been published.[8]

Further work is presently under way to obtain the absorption spectrum of divalent californium in acetonitrile. We are attempting to electrolytically reduce Cf(III) to Cf(II) in a combination spectrophotometric-electrolysis cell and to simultaneously obtain the spectrum. This work is being done with H. A. Friedman of the Chemical Technology Division.

For some time, we have been interested in developing specific ion electrodes for uranium and plutonium. This year, three types of electrodes were examined for this purpose. One type, the PVC membrane electrode,[9] appears to be quite promising for detection of uranium. The membrane for this electrode is prepared by incorporating uranyl salt of di(2-ethylhexyl)phosphoric acid into a matrix of polyvinyl chloride (PVC). Semi-log calibration plots obtained with electrodes prepared with this membrane are linear from about 5×10^{-4} to 10^{-1} *M* uranyl chloride. The response of the electrode is rapid; steady potential readings are obtained within a few seconds. Further work is under way to determine the utility of this electrode. We are also interested in the possibility of using this type electrode for other heavy elements.

COMPUTER APPLICATIONS

Programming for mini-computers. A new 12-bit, 8K ND-812 computer has been installed for analysis of x-ray spectra from the scanning electron microscope. In general, the software supplied by the manufacturer, Nuclear Data, Inc., has been satisfactory for the x-ray analyses. However, the users of the instrument wanted the energy readings to be directly in energy units instead of channel number. A simple programming change accomplished this conversion. Although the supplier had indicated that a general computing language was to be available for this computer, the appearance of a "bug-free" version of this language has been long delayed. Therefore, to increase the usefulness of this small computer a "translation" of FOCAL[10] was written for the ND-812. Since many features of computer instructions and addressing are quite different in the ND-812 from that of the PDP-8 family of computers (for which FOCAL was written), it would be more correct to describe the process as an implementation of the principles of FOCAL in the instruction set of the ND-812. The process of assembling the program

7. J. E. McCracken, J. R. Stokely, R. D. Baybarz, C. E. Bemis, Jr. and R. Eby, "Determination of the Half-Lives of ^{246}Cm and ^{248}Cm by Absolute Specific Activity Techniques," *J. Inorg. Nucl. Chem.* **33**, 3251 (1971).

8. H. A. Friedman, J. R. Stokely, and R. D. Baybarz, "Polarographic Evidence for the Divalent Oxidation States of Californium," *Inorg. Nucl. Chem. Lett.* **8**, 433 (1972).

9. G. J. Moody, R. B. Oke, and J. D. R. Thomas, "A Calcium-Sensitive Electrode Based on a Liquid Ion Exchanger in a Poly(vinylchloride) Matrix," *Analyst* **95**, 910 (1970).

10. Trade mark of the Digital Equipment Corp.

was aided greatly by the availability of a special version of the PALFTN assembler originally written for PDP-8 code.

The resulting conversational, interpretive language has been given the name "ORCAL" and has been published as ORNL-TM-3697. A short summary was also published in *Chem. Instrum.* 3, 345 (1972). In general, except for some minor differences, programs written for FOCAL can be run with ORCAL. The ORCAL language has been made available to Nuclear Data, Inc., and has been distributed as a part of their software package to a number of their customers. A considerable number of questions from such customers is evidence that others have also found ORCAL highly useful.

We have recently obtained the use of another ND-812 computer with which we will investigate the use of ORCAL with specially written function patches for observing plasma-excited spectra which have a relatively short life (1 to 3 sec). This type of approach has been very successful, using FOCAL on the PDP-8, and should prove to be even simpler on the ND-812 because of the greater ease with which patches can be inserted into ORCAL.

An 8K PDP-8/E computer has been obtained to interface to analytical instruments in the analytical laboratory operated in the Environmental Sciences Division by the General Analysis Group. The instrument for which a computer interface seems to offer the greatest benefit is a Perkin-Elmer 403 atomic absorption (AA) spectrophotometer, since it has the heaviest load of samples. Using the meager information in the operating manual observing the oscillographic signal wave forms, we determined that a very simple interface could be used requiring only three connections to the spectrophotometer; this should leave normal operation of the instrument undisturbed.

This approach uses the chopped signal from the Perkin-Elmer amplifier ahead of the adc circuitry. On this basis, a special version of FOCAL was written that incorporates a function patch which measures the reference beam intensity, the dark current, and the sample beam intensity, averaging 64 readings of each one (in about 1.2 msec) and then repeating the cycle 64 times (about 1.05 sec). Thus each value stored is the average of 4096 readings. These averages are deposited directly into variable locations. A FOCAL program was written that converts these intensities into absorbances, which are then fitted to a cubic equation for a calibration curve. When samples are run, the cubic equation is solved by a trial-and-error technique to yield concentration values. A special function will allow the calibration constants to be retained from one set of samples to another until a new calibration is run. The programs which should allow this approach to be implemented have been completed and parts of them tested. They will be tested on the AA spectrophotometer as soon as all the necessary hardware is available.

We have updated our PS/8 operating system on the 8K PDP-8/I with the acquisition of OS/8, and added to the software with a BASIC compiler, a PS/8 FOCAL compiler, and a TECO-8 text editor and corrector. OS/8 allows file-oriented, device-independent operation of the computer with a choice of BASIC, FOCAL, or FORTRAN high-level languages. A Sykes Datatronics, Inc. Compu/Corder 100 cassette-type digital recorder will furnish the bulk storage on magnetic tape needed for efficient operation of the OS/8 system.

The initial phase of a study of the signal-to-noise (S/N) ratio at successive points on the polarographic current vs time (i,t) curve has been completed. The instantaneous current curve for a 5- to 6-sec mercury drop time is divided into 200 equally spaced (i,t) data points at 25-msec intervals. Each value of the current is the average of 128 analog-to-digital converter measurements acquired in exactly 1/60 sec. Signal enhancement is achieved by discrimination against both random and 60-Hz noise. The single-precision data for each point is stored rapidly in core and is then relocated on the disk later at a slower pace. Twenty curves for 20 successive mercury drops can be stored for subsequent calculations and x-y recorder plotting. These 20 curves represent about ½ million current measurements acquired in a time span of about 2 min.

The S/N is assessed by determination of the standard deviation of the measured currents at corresponding times on the 20 curves. Synchronization is provided by software detection of the fall of the mercury drop. Relative standard deviations were found to range from about 30% at the start of drop life to about 0.3% near the end. We are writing new machine language subprograms for insertion into the FOCAL compiler of the 8K PDP-8/I computer to provide increased data storage for a longer drop time, and for 40 (i,t) curves. The new data will enable us to more accurately measure exponent values on the wave form, in addition to S/N ratios.

We have written a machine-language patch to the FOCAL compiler of the 8K PDP-8/I to allow us to investigate the technique of computer-operated pulse polarography. Electrochemical cell current is sampled and averaged during a 1/60-sec interval just prior to application of a pulse and again during the last 1/60 sec of pulse life. Subtraction of the two current values produces a value for storage in the FOCAL table of

variables. This differential mode of pulse polarography will be tested on Cd^{2+} solutions.

Programming for the DEC 10 time-shared computer. The long-awaited time-sharing service on the DEC system 10 became available during this year, and despite some frustrations has proved to be very useful for some of the computational jobs in the Division, which are typically relatively small and require little CPU time. While our first efforts on the DEC 10 were with the AID and BASIC languages, we soon found that the availability of double-precision operation in FORTRAN made this the language of choice. Actually, with the very flexible editor TECO, FORTRAN on the DEC 10 is almost as flexible as BASIC or AID.

Our first job on the DEC 10 was setting up a program to fit experimental data to a cubic-parabolic equation. This was set up first in AID, where it was found that the lack of double precision could lead to errors with some approaches to the problem. However, in FORTRAN, a general determinant solution for an *n*th degree equation was set up and has been used routinely by personnel from the General Analysis Laboratory for data from several different types of analyses.

A program written in ADVANCED BASIC language was developed to calculate air quality indices from Council on Environmental Quality data. Levels for SO_2, NO_2, and TPM (total particulate matter) for 89 cities in the USA are entered from the remote terminal keyboard. The text string and numerical data are then typed out for verification and editing. Once accepted, a table of the three indices for each city is printed out. The program is stored on the DISK and on DECTAPE. It has been transferred successfully into another user's disk area for input of information from a remote terminal located at Y-12.

The DEC 10 has also proved useful for assembling programs for our small computers. The PAL 10 assembler available as a systems program will assemble a program as complex as FOCAL in 30 sec and was highly useful for the PDP-8/E programming just described.

Since it is desirable to have available a rapid means of analyzing gamma spectra (from a sodium iodide spectrometer) when a shorter turnaround time is desired than is normally obtained from submission to the IBM 360 system, we have investigated the possibility of running the ALPHA program on the DEC 10. This program, written originally by E. Schonfeld, resolves sodium iodide gamma spectra by means of a matrix inversion against a standard library of spectra of pure radionuclides counted under the same conditions. As normally run on the IBM 360, 460 K words of core are required, so it is obvious that to run in the 20 K available to time-sharing users on the DEC 10 requires some changes. A very large part of the computer space is occupied by the library, so along with the other changes required to make ALPHA compatible with DEC 10 FORTRAN, it was changed so that only standards for radionuclides actually being sought would be read into core from the DEC 10 disk file. Also, the number of channels examined was cut down to include only those covering the more common radionuclides. It was found that with spectra of 340 channels a library of up to 16 radionuclides could be accommodated. For duplicate samples, CPU time of 12 to 25 sec is required. A paper tape produced directly from the nuclear data analyzer can be read into the DEC 10, and, after conversion to proper format, the analysis is completed with a teletype printout showing the most essential data in a matter of 2 or 3 min. A more complete printout from the DEC 10 line printer follows in 1 to 2 hr.

To check the operation of this version of ALPHA as well as to study the capability of ALPHA in resolving a pair of radionuclides usually not considered resolvable by sodium iodide spectra, we examined a sample of separated ^{95}Zr and followed the growth of the ^{95}Nb daughter. Zirconium-95 has two gamma rays at 724 and 757 keV (0.43 and 0.546 branching ratios respectively), while ^{95}Nb has a single gamma peak at 766 keV. Sodium iodide spectra of ^{95}Zr and of mixtures with ^{95}Nb show only a single peak as might be expected from the resolution for sodium iodide; for an equilibrium mixture, this peak has an apparent peak energy of 742 keV. On spectra taken over a period of two months, ALPHA is able to resolve the ^{95}Zr and ^{95}Nb components, and the curves plotted for the activities of the two components follow the theoretical decay and growth curves. The activity values obtained for ^{95}Zr are within the errors of counting statistics when corrected back to zero time. These data demonstrate very effectively the utility of ALPHA as revised for the DEC 10 and also confirm the resolving capability of the ALPHA program.

Long before the DEC 10 became available, we anticipated that it would be of great value in handling the voluminous data produced by the Tobacco Smoke Analysis Program. This has indeed been shown to be the case. We have completed the processing of data to be used in a meeting of the Tobacco Smoke Analysis Working Group. This involved the production of approximately 270 tables (up to 15 columns for 23 cigarettes) with 10 copies each. These tables were taken from approximately 65 input files, and 85 output files were produced and saved on DECTAPE for possible later correlation studies. The DEC 10 has been almost

ideal for this operation; although the data are very voluminous, the computation in general did not exceed 5 sec per table. The flexibility of the DEC 10 allowed trial runs with modifications to the programs being made without waiting out the long turnaround time for the IBM 360 system.

Originally we expected that experimental data for the tables would be entered via teletypewriter, but it proved better to punch the data on cards which could be read into the computer. This procedure gave more opportunity for checking the data before entry, as well as significantly reducing the computer connect time. The calculations involved in this work were rather simple: a matter of computing the average, the variance, and an estimate of the standard error on each group of data. But also included were tests for rejection of outliers and tests for selection of one group of analyses in preference to another or alternatively retaining both. These tests, along with a variable number of observations and several variations in units, made the final program for producing the tables quite complex.

GeMSAEC HEAVY METALS ANALYSIS

We have initiated a study to determine the feasibility of using the GeMSAEC (centrifugal photometric analyzer) for the determination of micro amounts of heavy metals. Under investigation at present are methods for cadmium, zinc, and copper. Both cadmium and zinc form highly colored complexes with the water-soluble reagent PAR, 4-(2-pyridylazo)resorcinol. The determination of copper is being studied by its catalytic effect on the reaction between ferric and thiosulfate ions. As little as 0.05 μg of copper causes a measurable increase in the speed of the decolorization of the formed complex. Another study being planned is the determination of vanadium, based on its catalytic effect on the rate of oxidation of gallic acid by persulfate in acid solution.

PHOSPHOR SCREENS FOR X-RAY DETECTION

During the past year, we have continued our work on the fabrication and testing of flexible phosphor screens for x-ray detection as previously described.[11] This work was carried out for the U.S. Army and had as its objective the development of three different types of screens for specific applications:

1. a high-sensitivity fluoroscopic screen for real-time visual observation,
2. an improved intensification (photographic) screen to match the spectral characteristics of Polaroid film, and
3. a new type of phosphorescent screen that can be used to store an x-ray image for a short time (20 to 30 sec) and can be erased at will for reuse.

The development program has been concluded; as a result of our work we have completed screens that meet the desired specifications for types 1 and 2 and partially succeeded in meeting those for type 3.

All of the flexible screens were fabricated using the plastic "sandwich" technique that has been described previously. Minor variations were made in the physical and optical parameters of the sandwich system, but the resulting screens continued to exhibit the desirable characteristics of flexibility, durability, uniformity, and hermeticity. We did note, however, that screens with very thick phosphor layers suffered a loss of resolution and uniformity.

The work on the fluoroscopic screen was completed last year, and the details of the fabrication and response functions will not be repeated here. However, it should be noted that this type of screen has now been tested under field conditions and found to be acceptable. A large number of duplicate screens were constructed and submitted for further testing and life studies. We do not expect the results of these tests to be available for some time.

Our work on the photographic intensification screens has yielded a number of useful types. Most of these use rare-earth phosphor systems; of particular interest are screens that employ oxysulfide-type phosphors such as Gd_2O_2S:Tb, Y_2O_2S:Tb, and Gd_xYyO_2S:Tb. Occasionally, we have produced screens with blended phosphors [using $Ba_3(PO_4)_2$:Eu] that have proved valuable with certain types of photographic film. As an example of what we have been able to achieve, it is interesting to note that with one type of screen prepared with a blue-emitting rare-earth phosphor and Polaroid 3000 speed film, speed increases as high as 230 have been measured as compared with the unscreened film. In addition to the speed increase, a somewhat better contrast ratio was obtained. Of course, the screen-film combination produces significantly reduced definition, but this is about the same as when using conventional intensification screens.

Our work on the phosphorescent screen was only partially successful. We were able to produce a screen that would hold an x-ray image and could be erased

11. W. S. Lyon et al, "Cerenkov Counting and Phosphor Screens," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4749, p. 31.

(with heat) when desired. However, screen sensitivity was the major problem that we were unable to solve. During the course of this program we tested over 80 phosphor materials plus various blends. The results showed that when sensitivity was high, retention time was short. Conversely, long retention screens proved to be rather insensitive. Screens that were supplied to the Army employed phosphor types that showed the best compromise between the sensitivity and retention parameters.

2. Bio-Organic Analysis

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The Bio-Organic Analysis Group was recently formed by combining the Bioanalytical Group with the Organic Analytical Section of the Methodology Group. As such, the work summarized here represents in part the inputs of G. Goldstein and W. D. Shults, the previous group leaders.

BIOANALYTICAL PROJECTS

Biochemistry of Human Variants Group. Metabolic Defects Screening Program. The role of the Analytical Chemistry Division in this program was terminated at the end of the calendar year. Work on this project was devoted to continuation of the studies on the thin-layer chromatographic separation of amino acids in general, as well as of indoles, imidazoles, and carbohydrates in wine. We compared various methods for the separation and detection of these classes of compounds. For indoles the best solvent system was isopropanol:water: ammonia (20:2:1). We achieved good separations of seven urinary indoles using chromatography in shaped areas after deureation of the sample. No estimate of sensitivity was made. The best solvent system for imidazoles was acetone:acetic acid:water (70:10:20). We found that chromatography in shaped areas was also preferable, but that it was not necessary to remove urea. As little as 0.25 μg of several imidazoles added to 20 μl of urine could be detected. Chromatography of both indoles and imidazoles was done on 100-μ Avicel layers. Chromatography of carbohydrates on Avicel with an isopropanol:water (4:1) solvent gave as good a separation as any method so far reported, but the sensitivity was too low to detect normal amounts of urinary sugars.

Cancer screening program. We are continuing to contribute to this aspect of the Molecular Anatomy (MAN) Program. A laboratory was obtained and equipped with a liquid nitrogen freezer capable of holding 90,000 blood serum samples. Various computerized storage and retrieval systems were studied, and several hundred sera from both normal and cancer patients were obtained. We have helped to obtain electrophoresis patterns for many of these sera. Acrylamide gels in various concentrations and forms, including slabs and disks, have been used. We have also obtained patterns on a number of these sera using cellulose membrane material in conjunction with a Beckman microzone electrophoresis instrument. Staining and destaining procedures have been established using the stains coumassie blue, amido blue-black, and ponceau red. We have also attempted to use various fluorescence materials to mark the separated protein bands. Detection procedures using Ouchterlong-type agar immunoplates with positive sera and rabbit antisera were also established. This laboratory is being held in readiness in anticipation of future activities.

1. On leave of absence. Present address, Biochemistry Department, University of Washington, Seattle.
2. Special assignment.
3. Technical staff.
4. Methods Development and Special Projects Group.
5. Senior Research Advisor.
6. ORAU Summer Trainee from Dickinson State College, Dickinson, N.D.
7. Student Participant, Union Carbide Cooperative Education Program, Southern University, Baton Rouge, La.
8. Student Participant, Union Carbide Cooperative Education Program, Tennessee State University, Nashville.

Chemical aspects of GeMSAEC development. A miniature GeMSAEC fast analyzer has been developed by the Biochemical Separations Systems Group of the Chemical Technology Division. We have been adapting existing clinical tests to this system. The system is designed to use 10 to 25 μl of sample with 100 μl of reagent. Rotors are still under development and are designed to be of a disposable nature, possibly making the system useful for radiochemical determinations. We have established simple tests for the determination of uranium and thorium by the arsenazo III method. We have found that various routine clinical tests run on blood sera are equivalent to those for the larger fast analyzer system. Additional methods being developed for the GeMSAEC system include an acid phosphatase enzyme determination, an inorganic phosphorus determination with a special fast reaction-rate program, and studies on multichemistry determinations from a single rotor.

Bioanalytical electrophoresis. High resolution and novel techniques. Polyacrylamide gel electrophoresis permits very highly resolved analytical separations of biologically important macromolecules. Body fluids and tissue extracts can be analyzed. However, its routine use for large numbers of samples is restricted because of several problems. These problems can be separated into four categories: (1) reproducibility, (2) band identification, (3) sample handling, and (4) data processing. The development work in analytical electrophoresis in the MAN Program has been carried out with these problems in mind. The ultimate goal of this development effort is to make possible the routine use of high-resolution polyacrylamide gel electrophoresis for clinical and screening purposes. We are involved in the development of high-resolution electrophoretic methodologies, studies of novel electrophoretic techniques, and the application of electrophoresis to complement other efforts that constitute the MAN Program.

We are studying immunosubtractive electrophoresis. In this technique the specificity of antibodies is employed for the identification of bands separated by polyacrylamide gel electrophoresis by subtracting the band prior to electrophoretic separation. In brief, the steps involved are as follows: (1) The immunoglobulins (IgG) from an antiserum to a given protein of interest are separated by ion exchange chromatography. (2) The separated IgG is then mixed with the sample, and the mixture is electrophoresed. The component of the IgG sample, which is an antibody to the protein of interest, combines with it forming a precipitate. Because the precipitated protein does not migrate during electrophoresis, it is subtracted from the electrophoretic pattern. One can subtract and thereby identify a band without sacrificing the high resolution associated with gradient polyacrylamide gel electrophoresis.

The major problem we have encountered in applying the immunosubtraction technique is the conversion of the antibody into a form that is not mobile electrically while still remaining active chemically. Because the IgG fraction contains many antibodies peculiar to the donor animal's immune system, in addition to the specific antibody caused by the challenge, there is a potentially extreme amount of interference in the gamma region of the immunosubtracted sample. Thus it is evident that the IgG containing the specific antibody must be immobilized. We are now studying this possibility with some promising, but preliminary, results. The immobilization problem would appear to be twofold: first, one must form an IgG-support complex that does not dissociate; second, the complex should not undergo a significant amount of exchange of miscellaneous proteins from the sample with the bound IgG.

We are also examining the technique of isoelectric focusing. In this technique a pH gradient is developed along the separating medium during electrophoresis. Subsequently a protein constituent migrates to a point along the gradient where the pH is the same as the isoelectric point of the protein. The protein accumulates and bands because it has no charge and can migrate no farther. We have considered preparative schemes based on the nonelectroactivity of proteins at their isoelectric point. Exploratory studies on isoelectric focusing in gels have been carried out. A study was initiated to determine the minimum amount of Ampholine necessary to obtain a satisfactory separation of proteins by the technique; it employs a synthetic mixture of proteins chosen because they have visible color and a wide range of isoelectric points. One can readily see when equilibrium is attained. The following observations were made:

1. The time required to reach equilibrium varied with the Ampholine concentration. A gel with an Ampholine concentration (volume of Ampholine per total volume of gel) of 0.04 required 6 hr or more to reach equilibrium, while a gel with an Ampholine concentration of 0.008 required less than 1 hr.
2. Sharp bands appear very quickly with no Ampholine present in the gel. However, these bands also converge rapidly.
3. The absolute distance between the protein band of highest and lowest isoelectric point decreases with Ampholine concentration for a given electrophoresis time on gels of a given length.

It is important to note that in the above study the samples were mixed with the gel solution before polymerization. The sample components were distributed homogeneously throughout the gel before electrophoresis. During electrophoresis they migrated from this homogeneous distribution to form a band. This opens the possibility that a sufficiently concentrated protein sample could act not only as the sample but also as the Ampholines.

Mixing the sample with the gel solution before polymerization allows the direct evaluation of the extent to which the gel matrix restricts the migration of a given protein. By the conventional method the sample is loaded at one end of the gel and then migrates through the gel during electrophoresis. The distance that a given protein migrates is a function of both charge and size. One can never be certain whether minimal migration is due to very small charge or very large size. For example, in a typical pH-9 electrophoresis system employing a 7.5% polyacrylamide gel, both α_2-macroglobulin (mol. wt 800,000) and chymotripsinogen A (mol. wt 25,000) band very near the gel origin. The smaller molecule migrates little because of a very small charge. The macroglobulin is very highly charged but migrates very little because of restriction by the gel matrix. However, if the sample is homogeneously distributed throughout the gel and subjected to isoelectric focusing, a greatly restricted macromolecule cannot form a band.

We have now acquired considerable experience with the gel rotor which permits the simultaneous casting of 500 cylindrical gels, and we feel that this rotor will contribute significantly to the solution of the reproducibility problem mentioned previously. Five hundred gels have been poured in as little time as 10 min, but 15 min appears to be optimum. The time required from preparation to cleanup is about two man-hours. Gels that are either gradient, stepped, or homogeneous in polyacrylamide concentration may be prepared with equal ease. Gels prepared in this manner have yielded good electrophoretic separations both in this Laboratory and at the University of Alabama Medical Center in Birmingham (laboratory of G. Cline).

We have been applying electrophoretic techniques to the characterization of human placental antigens. The object of this work is to isolate and characterize as many antigens as possible that are peculiar to pregnancy and the placenta. At least five such proteins may exist. Our present approach to this work is outlined in the general steps listed below:

1. Crude fractionation and concentration by "salting-out" precipitation.
2. Fractionation by ion exchange and/or affinity chromatography.
3. Routine electrophoretic analysis of individual fractions.
4. Examination of each fraction for the possible presence of an antigen of interest by immunodiffusion techniques.
5. Immunoelectrophoresis of fractions containing antigens of interest.
6. Further purification of individual fractions if necessary.
7. Careful characterization of purified antigens by various electrophoretic techniques (isoelectric point, number and molecular weight of subunits, mobility, type of protein, etc.).
8. Further characterization and immunochemical studies as larger samples become available.

New approach to prenatal diagnosis. In families where there is risk of serious genetic disease, the only way to prevent the birth of many hopelessly defective children and, at the same time, provide the parents with the possibility of having a normal child of their own is through prenatal diagnosis and selective abortion. Unfortunately, present methods for in utero detection of suspected metabolic disorders cannot be initiated prior to 12 to 16 weeks' gestation, when the minimum quantity of amniotic fluid for preparation of cell cultures becomes available. There is a further delay of 3 to 6 weeks for cultivation of the cells in sufficient quantity for the necessary enzyme assays. Meanwhile, the risk of major complications increases severalfold for abortions deferred into the second trimester. This, along with other considerations such as time limits for legal termination of pregnancy and the prolonged emotional burden, provides strong incentives for earlier detection of these untreatable diseases.

As a possible basis for earlier diagnosis, we have investigated the feasibility of measuring enzyme levels in individual cells, isolated from amniotic fluid according to cell type, viability, morphology, and other criteria. In the course of this preliminary work, we have devised a tentative method for determining a variety of enzymes, depending on the specific substrates used. The basic problems involved in cell handling, photometry, standardization, and preservation of fresh cells for a posteriori studies have also been solved, within the limits of our present facilities. As the elucidation of metabolic defects progresses and substrates for characteristic enzymes in various diseases become available, the number of potential applications of the ultramicro

method will increase. Current work is aimed at refinement of the assay procedures along with correlation of cellular morphology and normal enzyme levels, preparatory to further evaluation in the monitoring of selected high-risk pregnancies.

The ultramicro method is based on physical isolation of the desired cell from a microliter specimen of amniotic fluid, using micrurgical techniques, followed by washing and extraction or incubation in a measured volume of substrate, usually about 0.3 or 0.9 nl, depending on the enzyme. The reaction is terminated by removal and evaporation of the supernatant and taking up the residue in a measured volume of buffer for the photometric measurement. Photometry is done in 0.08 nl hanging drops, 54 μm in diameter, using a standard fluorescence microscope or modified cytological microscope, both equipped with photomultipliers. Light absorption measurements are used with substrates derived from *p*-nitrophenol or 4-nitrocatechol, and fluorescence measurements are used with 4-methylumbelliferyl substrates.

Enzymes assayed by these methods in the femtomole cell^{-1} hour^{-1} range include acid and alkaline phosphatase, aryl sulfatase, β-glucuronidase, and hexosaminidase (1 fmole hr^{-1} = 1.6×10^{-11} International Unit). To the extent that we have examined these reactions in detail, the conditions are in conformity with established practice regarding enzyme kinetics. Although single cells can by analyzed, small groups (e.g., three cells for glucuronidase and five for hexosaminidase) are used for biological averaging and/or reducing the incubation time, which is usually 2 to 4 hr. Volume measurements are reliable to 2 to 3% and photometry 3 to 5%. Overall precision has not been established, but we have observed relative standard deviations averaging about 10% within runs for different cells, indicating that, with careful sampling, it should be possible to report the results on a "per cell" basis. This avoids the necessity of a separate protein determination, weighing of frozen-dried cells, or other additional measurements.

We are not unaware of the difficulties encountered by others who have been unsuccessful in doing enzyme assays for prenatal diagnosis with noncultured material. Without regard to any of the criteria adopted here, these workers have invariably based their results on the entire suspended fraction in the amniotic fluid, of which probably less than half consists of viable cells of fetal origin. Debris from various sites is usually present, and maternal blood cells are often encountered. Our approach avoids these and several other uncertainties associated with the analysis of both cultured and noncultured cells.

Use of primary amniotic cells for diagnosis presupposes that biochemical defects are expressed at that stage of development, and this is the case in several diseases. No one knows to what extent advancing gestational age is accompanied by quantitative developmental changes in enzyme patterns for most other disorders.

Since the ultramicro method requires less than one-thousandth of the volume of amniotic fluid now used for cell cultivation, the prospects appear favorable, in some diseases at least, for developing techniques that will both eliminate the need for cell cultures and encourage earlier amniocenteses. In cases where this can be achieved, the time required for a prenatal diagnosis will be substantially shortened. Furthermore, the foregoing methodology will be immediately applicable to fetal biopsies, which are already under serious discussion, whenever the necessary operative techniques are perfected. When this occurs, the possibilities for prenatal diagnosis and, hopefully, intrauterine therapy will be significantly enlarged.

TOBACCO SMOKE CHEMISTRY

We have continued to give primary attention to the analysis of the smokes generated by the National Cancer Institute (NCI) experimental cigarettes. The scope of our responsibilities in this area has expanded to include considerations of sample generation procedures in use here and by other contractors, studies of the reliability of the specified procedures, and data handling and treatment. We are also sharing the responsibility for defining procedures for the correlation of biological and chemical results.

The chemical facility, originally established for the sole purpose of providing data for specified compounds, is now acting as a general support facility. Smokes of cigarettes other than those incorporated in the NCI bioassay schedules are now being analyzed. Smokes, condensates, and condensate extracts derived from cigarettes containing ammonium sulfamate as a paper additive have been studied. We have concluded additional studies on marijuana smokes, including determinations of the active cannabinols. Procedures are being readied for a study of cigarettes containing selective filters. We are presently involved in a study of the quantity and quality of the smokes generated for eventual dog inhalation experiments to be carried out by another NCI contractor. Procedures have been developed which allow the incorporation of new smoke components in the regular analytical schedule. Research and development activities have expanded considerably

to provide the broader base needed for the new study areas.

National Cancer Institute experimental cigarettes. We continue to be responsible for the chemical characterization of the smokes delivered by experimental cigarettes presently undergoing biological characterization by other NCI contractors. A larger number of components are presently being determined on a semiroutine basis here than are determined regularly at any other smoke laboratory. The chemical components semiroutinely determined in the past year were: total particulate matter, water, nicotine, and tar in the particulate matter; acetaldehyde, acrolein, formaldehyde, oxides of nitrogen, hydrogen cyanide, carbon monoxide, carbon dioxide, and acidity in the gas phase; water, acetone, nicotine alkaloids, nicotine, phenolics, phenol, *o*-cresol, *m* + *p* cresol, weak acids, very weak acids, phenanthrene, benz(a)anthracene, and benzo(a)pyrene in condensates. We also consider cigarette characteristics. Cigarette weight, pressure drop attending a standard puff, and puffs required to reach a 23-mm butt are regularly determined.

The first series of cigarettes (23) was characterized a second time during this report period. Since each result is the average of four determinations and some analyses were repeated to ensure reliability, this corresponds to approximately 3000 determinations. Analyses of special cigarettes and analyses performed in research activities are not included in this figure. Condensates generated from the second series of NCI cigarettes (25) were also analyzed. At least two additional complete analyses are scheduled for these cigarettes. We are preparing for studies of the smokes delivered by the new series as well as smokes delivered by a pilot batch of cigarettes, which will constitute the third experimental series.

The analytical facility has been improved. An Aminco-Aire temperature and humidity system is now in operation to provide superior environmental control for the cigarette conditioning and smoking laboratory. There is a high-speed digital balance in operation for weight-selecting cigarettes. A standard pressure-drop tester is in regular use for determining the resistance-to-draw of selected cigarettes. An additional gas chromatograph is in operation which partially relieves the sample backup.

We have begun an in-depth study of the reliability of the procedures in regular use. The availability of data for each parameter on each cigarette obtained 12 to 18 months apart allows an assessment of both procedure and scheduling. Informal collaborative studies with industry laboratories have been found very helpful. Discussions with visiting scientists highly experienced in smoke chemistry have confirmed the essential reliability of procedures in use here and have helped to define promising procedural modifications.

Special studies. Cigarettes prepared using ammonium sulfamate-treated paper first received attention because analytical data suggested a lowered benzo(a)pyrene (BaP) concentration in the generated tar. Subsequent work suggested that BaP deliveries were not significantly reduced. Data obtained by mouse skin-painting bioassays revealed that the biological activity of the tar is reduced when compared with cigarettes with the same formulation in the absence of ammonium sulfamate. We have studied selected components in the smokes generated by a control cigarette and two cigarettes containing different levels of ammonium sulfamate. Condensates and condensate extracts prepared elsewhere were submitted for study. All of those components which constitute the regular assay facility, with the exception of gas-phase acidity and including isoprene, were measured. Our findings confirmed that there is no significant difference in BaP deliveries by treated cigarettes. With the possible exception of acetaldehyde, acrolein, and formaldehyde, the treated cigarettes delivered the same amount or greater amounts of each component than the control on a per cigarette basis. We have not, as yet, discovered a chemical explanation for the observed biological response. Final conclusions may not be possible. The cigarette manufacturer suspects an error in the production method for one or more of the cigarettes. Further studies are postponed pending an evaluation of the cigarettes.

We have reanalyzed the smokes delivered by marijuana cigarettes. The chemical composition of the smokes and condensates is not dramatically different from tobacco smokes when the standard components are examined. An evaluation of the data awaits comparison with similar data generated elsewhere. No conclusion about the potential health hazard is possible until the results of biological assays, carried out elsewhere, are available.

Data have been made available by three industry laboratories for comparison with that generated here. One collaborative study involves the analysis of smokes from three specially prepared cigarettes – a charcoal-filter cigarette, the same cigarette with charcoal cavity empty, and a nonfilter cigarette. A second laboratory has forwarded an in-house monitor cigarette and resulting data on selected compounds. A third has forwarded results on phenanthrene, benz(a)anthracene, and benzo(a)pyrene in condensates from NCI cigarettes. Agreement has ranged from exceptionally good to unac-

ceptably poor. Procedures which provide considerable disparity in results are presently under study.

We are cooperating with A. D. Little, Inc. (Cambridge, Mass.) and the Veteran's Administration Hospital (East Orange, N.J.) research staffs on problems associated with dog inhalation studies to be carried out for the NCI. The system of exposure used in previous studies, though successful in eliciting a biological response, is considered incapable of providing strictly interpretable results. Determinations of the actual levels of exposure are not possible. We have initiated chemical studies to estimate the quantities of smoke delivered by simulated dog-smoking puff parameters. Preliminary results suggest that given deliveries of certain components under given conditions are not significantly different from those found with standard parameters. As expected, we found a very large difference in deliveries over the range of puff characteristics observed during dog smoking. A device for the mechanical generation of smokes for exposing chickens, developed at A. D. Little, Inc., has been suggested as a possible alternative to direct dog-smoking tests. We are involved in the construction of a number of these devices for pilot studies and in a study of the smokes delivered by the device.

Acetaldehyde, acrolein, and isoprene. Acetaldehyde and acrolein are of particular interest in characterizing the biological insult of smoke exposure because of their demonstrated relationship to impaired ciliary clearance. Recently we became interested in isoprene as a possible secondary measure of isoprenoids in smoke condensates. Terpene and aliphatic hydrocarbons may play a role in tumor promotion.

The procedure we developed for the determination of acetaldehyde and acrolein involves smoking a carefully selected cigarette through a gas-sampling loop, routing each puff to the head of a gas chromatography column maintained at $-75°C$, and chromatographic separation and quantitation of the compounds after the cigarette is consumed. Approximately 20 other compounds are visualized in the chromatogram. We have demonstrated the possibility of determining isoprene at the same time acetaldehyde and acrolein are determined. Relative deliveries of isoprene have been determined for the first series of cigarettes. Correlation with biological activity appears promising.

Although excellent for the determination of relative deliveries, the system caused us considerable difficulty when we attempted to obtain absolute deliveries. The calibration problem appears to have been solved by adopting a suggestion from Dr. A. W. Spears of Lorillard Corporation. We prepared acetaldehyde or acrolein standards by adding the organic liquid to a 20-liter carboy containing air. The mixture was allowed to equilibrate overnight. An evacuated Saran bag was placed inside the bottle with a glass tube leading through a stopcock to the outside. A second tube with a stopcock was connected to the cigarette holder of the smoking machine, and this conveyed the sample to the gas chromatograph or to water-filled gas-washing bottles for colorimetric analysis. The Saran bag inside the bottle filled with air as the sample was removed, thereby maintaining the pressure in the carboy at 1 atm absolute. We took samples which were roughly equivalent to the acetaldehyde and acrolein in a monitor cigarette.

The colorimetric analysis is based on the formation of hydrazones by the combination of an acidic solution of 2,4-dinitrophenylhydrazine and the aldehyde. The microgram equivalent of the peak area was computed by dividing the gas chromatographic peak area by the colorimetrically determined quantity of aldehyde generated by the same procedure. Using this calibration factor we find acetaldehyde and acrolein deliveries of 1017 and 109 μg, respectively. Agreement with the values reported by our collaborator, 1005 and 111 μg, respectively, is excellent.

Analyses for acetaldehyde, acrolein, and isoprene are now carried out by comparing peak sizes with those generated by a reference cigarette. The relative deliveries are then converted to absolute values following colorimetric calibration. We have not yet devised a system for determining absolute deliveries of isoprene.

Sulfur compounds. We are continuing research on the determination of sulfur compounds in cigarette smokes by flame-photometric detection gas chromatography. Particular emphasis is being given to the quantitative determination of the major sulfur gases – H_2S, COS, and SO_2. A smoking system has been developed which promises to provide samples adequately representative of a cigarette's total delivery to allow quantitation by analyzing a single puff (see "smoking machines," below). We have found Porapak P, suggested by researchers at Brown and Williamson Company, to be the best chromatographic packing for the analysis of the sulfur gases. Although columns of Porapak P require less conditioning between runs than all others studied to date, they do not completely solve the problem of solute absorption. Columns reported to be useful for the separation of H_2S, COS, and SO_2 in environmental samples have been tested and found unsuitable. We plan to seek a better chromatographic separation column.

Previous work at this laboratory suggested that the generally accepted composition of the sulfur compo-

nent of smokes was in error. We have applied the now more sophisticated system to the study of smokes and confirm earlier contentions. Hydrogen sulfide and carbonyl sulfide deliveries differ by a factor of 2, with hydrogen sulfide being the larger component. It was generally held that 5 to 20 times more carbonyl sulfide was produced than hydrogen sulfide. It has also been reported that as much sulfur dioxide is produced as hydrogen sulfide. We have confirmed our contention that very little, if any, sulfur dioxide is present in fresh smokes. An improved chromatographic column may be necessary to establish a concentration limit for sulfur dioxide.

Recent work elsewhere suggested that as many as 35 sulfur-containing compounds are present in selected cigarette smokes. We have not been able to confirm this finding as yet. Although further work is planned, our feeling at present is that the large number of species visualized may be an artifact. Programmed temperature studies carried out here to date reveal the presence of only 15 components.

We have applied the sulfur detection system to a survey of the polycyclic aromatic hydrocarbon fractions isolated for analyses. We find evidence of at least 12 sulfur-containing compounds in the phenanthrene subfraction. Work is under way to assess the possibility that these components, not previously reported in condensates, are artifacts of the sample preparation procedure. Evidence that the boiling point ranges of the gas-phase components and condensate components overlap suggests that the compounds are smoke products.

Component profiling. Free fatty acids. We have maintained interest in the method developed here for the profiling of whole-smoke particulate matter and condensate. The unfractionated sample is dissolved or suspended in pyridine, reacted with a silylation agent, and an aliquot is chromatographed. Approximately 40 peaks representing the major components of the sample are visualized. We noted that relatively large peaks were present in the region corresponding to that for trimethyl silyl esters of fatty acids. Interest in free fatty acids as possible tumor promoters encouraged us to examine the possibility of modifying the profiling technique to obtain quantitative estimates of the acids. The work also tests the quantitative reliability of the profiling concept.

We find that the acids of interest, palmitic, linoleic, linolenic, oleic, and stearic, can be quantitatively removed from standard filter pads with pyridine. An aliquot of the extract is silylated and injected into a 6-ft OV-101 gas chromatography column operated at 190°C. The fatty acids are visualized as three peaks – palmitic; linoleic, linolenic, and oleic; and stearic. The identities of the peaks have been confirmed by combined GC-MS. Total free fatty acids, the parameter of interest, is simply obtained by summation. At least eight determinations can be made in a single working day as compared with three days per sample by existing procedures.

We have applied the procedure to the determination of free fatty acids in the particulate matter from the NCI cigarettes and await correlation with biological results to consider adopting this analysis in routine work.

Metal content. Along with the analyses for many organic constituents in tobacco smoke and condensates it seems prudent to at least monitor some of the metals, particularly those metals that are considered toxic, that might be present. The major facilities of the Division are oriented toward inorganic analysis, and there are available a number of different techniques for performing the desired analyses. Our attention is focused on the metals Hg, Cr, Ni, Cd, and Cu. The limitations, sensitivities, ease of analysis, cost of analysis, and the relative advantages and disadvantages of activation analysis, spark-source mass spectrometry, x-ray fluorescence, and atomic absorption are being compared.

Preliminary results from the mass spectrometric survey of condensates suggest the possibility of serious metallic contamination during processing. A study of the complete series of condensates (23) is under way to better establish the nature of the problem. Analyses of the condensates for mercury levels by atomic absorption revealed mercury levels to reside in the low-ppb range. A recent report suggesting unusually high-gas-phase particulate-matter ratios of nickel in smokes has prompted a reexamination of the possible presence of nickel carbonyl. These studies are to be initiated shortly. The experimental work on inorganic components of smoke samples is being carried out by inorganic analytical chemists in this Division – J. A. Carter, Y. Talmi, C. Feldman, and T. Handley.

Polycyclic aromatic hydrocarbons. The quantitative determination of ppm levels of phenanthrene, benz(a)-anthracene, and benzo(a)pyrene continues to be the most challenging analytical problem of the program. The problem is complicated not only by the small quantities present but also by the large excess and multitude of other organics present, and many isomeric polycyclics present. We have intensified our research into the characteristics of the procedure in response to frequently low recoveries and fair to poor agreement with collaborators.

The sampling procedure has been modified. We now obtain samples from more dilute acetone suspensions and remove both water and acetone by controlled rotary evaporation to dryness. The addition of benzene to the suspension was found to be most effective in codistilling water. Excellent consistency has been observed in the dry-weight determinations. Unfortunately, agreement between gravimetric dry weights and dry weights determined by calculation after acetone determinations is only fair. The acetone procedure is suspect, and we are presently examining it.

It has been possible to greatly enhance recoveries by modifying our extraction procedure. Extraction times are now longer. We have added an additional extraction where necessary, and monitor the recovery regularly at the completion of extractions. The florisil and alumina column procedures have been studied with regard to recovery and found to be good. Greater care is given to evaporative concentration procedures to eliminate losses at these stages. Overall recovery is now consistently 75%.

Additional improvements have been made to the initially specified procedure. The alumina column elution procedure has been modified to provide a cleaner phenanthrene subfraction for gas chromatographic analyses. Acetylated chromatography paper is now treated in-house rather than relying on the poorly reproducible commercial papers. We have tested minor adjustments in scheduling and included convenience devices, mechanical shaker, auto pipetter, and new column designs, which greatly improve the efficiency of the two-week analysis.

Since phenanthrene (Phen) and benz(a)anthracene (BaA) are finally quantitated by gas chromatography (GC), we have continued our studies of GC procedures. We have demonstrated that the BaA peak is approximately 90% pure as it elutes from the column and that silicone columns, considerably more stable than the polar Apiezons in use, may be used for the final measurement if the present sample preparation procedure is used. A column designed at Lorillard Research has been constructed and tested as an alternative for existing systems. The column allows the simultaneous determination of the three polycyclic aromatic hydrocarbons of interest plus as many as 20 other polycyclics.

Dibenz(a,j)acridine. Interest has been expressed in the possible role of dibenz(a,j)acridine (DbAc) as a tumor initiator in cigarette smoke condensate. We have tested the possibility of determining DbAc in the samples generated for polycyclic aromatic hydrocarbon (PAH) analyses. Although DbAc is a nitrogen heterocyclic and basic, it does appear in the neutral fraction using our analytical procedure and is transferred with the PAH throughout the extraction steps. DbAc is held tightly by florisil in a very narrow band at the top of the column. Our data indicate that DbAc is retained by the alumina column at least until BaP elutes and can be removed from the alumina with benzene or acetone. It is our present opinion that DbAc may be determined by modifying the existing PAH procedure, but that isotope dilution will be necessary for strict quantitative work.

Monohydric phenols. Most commonly used procedures for the analysis of phenol and the cresols are not capable of resolving *m*-cresol from *p*-cresol. We also found that 2,6-xylenol interferes with the *o*-cresol determination using our column and the previously specified column. Trixylol phosphate and tricresyl phosphate columns are known to resolve the cresols from each other and from the other smoke phenols when employed in capillary columns. We have demonstrated that it is possible to employ standard 6-ft columns of trixylol phosphate and obtain useful separations. The quantitative aspects of the chromatography require further study. We are encouraged to learn that a similar system has stood the test of routine use elsewhere.

Considerable difficulty was experienced with the stability of the Casterwax columns used for phenol determinations. Pretreating the solid support with approximately 1% phosphoric acid has eliminated the problem.

Smoking machines. A six-port smoking machine was designed and built; this greatly extends sample generation capabilities. The machine features the use of a single filamatic pump to smoke six cigarettes in sequence. Each cigarette is puffed once per minute at 10-sec intervals. Preliminary results suggest that the device will be applicable to the generation of selected gas-phase samples as well as the particulate sample generation for which it was designed.

A modified version of a "hexapuffer" (C. H. Keith, Celanese Corporation, Charlotte, N.C.) for sample averaging was also designed. The device is used for studies of the sulfur delivery of cigarettes and may be applicable to other analyses, notably carbon monoxide. The machine consists of a 6-way gas sample valve with a 5-ml loop placed exactly in the middle of a 205-ml copper tubing trap. The input to the trap consists of a hexagonal turret with six ports, each of which is equipped with an orifice to control the volume of the puff to 35 ± 0.5 ml. The six ports are connected to the trap via a common manifold and a Skinner valve. A 60-sec timer with cam-actuated micro switches controls

the duration of the puff and the reevacuation of the trap via the third port of the Skinner valve. Cigarettes are lighted in sequence, one each minute. A stepping switch recycles the puffing-evacuation sequence through six puffs and, on the seventh puff, actuates the six-way gas sample valve, dumping the contents of the loop to the gas chromatograph. If a cigarette requires more than eight puffs to burn to a 23-mm butt length, a switch that bypasses the stepping switch allows any number of puffs to be taken prior to actuation of the stepping switch. This feature ensures that the sample is taken from the middle puff of any cigarette.

Sampling condensate suspensions. Although the precision observed for most analyses is good, the average results from lot to lot of submitted sample varied significantly. The variability is too great to be attributed entirely to analytical error. Sampling procedures – those used in-house and by the contractor supplying samples – are undergoing study. We find that the removal of condensate by transfer pipette from a stirred 50%-acetone suspension is subject to error; the size of the sample taken influences its composition. It appears questionable to compute the dry condensate composition from the analyses of small water-acetone samples and apply the values to large PAH samples. The sampling procedure used previously also afforded the opportunity to obtain inhomogeneous samples because the exact position of the pipette relative to the slurry could not be controlled. Consequently, a new sampling procedure was developed. Condensate samples are now thawed and diluted to no more than 25% dry condensate with acetone. The suspension is transferred to a separatory funnel through a side arm. The suspension is thoroughly mixed with a mechanical stirrer while samples are withdrawn through a Teflon stopcock. No change in dry condensate composition with sample size or time of sampling (level in flask) has been observed.

The manner in which samples are taken by the contractor supplying condensates has been changed. Previously, the contractor concentrated the condensate, distributed the thick slurry into small-mouth bottles by pouring from a graduated cylinder, and simply forwarded one of the bottles to ORNL. Samples are now taken from a dilute suspension prior to concentration and distribution, and the dried condensate is forwarded for study. Preparations are under way for an experimental study of the influence of previously used sample preparation procedures on lot-to-lot variability.

Data handling and treatment. M. T. Kelley and G. Wilson of the Division are cooperating with us on the statistical and logistics problems of handling the large volumes of data generated. Preliminary formats have been devised for the presentation of data to data analysis subgroups of the NCI and for final selection and presentation of results. D. Gosslee of the Mathematics Division has been extremely helpful in defining statistical approaches to the study and correlation of data.

TOBACCO SMOKE INHALATION BIOASSAY METHODOLOGY

We have continued to work closely with P. Nettesheim and his staff in the Biology Division toward a viable inhalation bioassay to test the carcinogenicity of cigarette smokes. Progress of primarily a biological nature is not, of course, summarized here. Those facets of the work which are summarized do, however, include a very substantial input from the biologists.

Smoke generation–exposure devices. The success of this project relies heavily on the availability of characterized, reliable smoke generation-exposure machines. The problem is complicated by the requirement that smokes must be generated using standard puff characteristics. The development of proper machines and coordination of their fabrication are continuing.

Three complete machines designed here are in routine use for biological experiments; they feature standard puff characteristics to generate smokes and allow ten hamsters to be exposed to 10% smoke aerosols for intermittent periods. Presently we employ an exposure protocol of 30 sec of fresh smoke followed by 30 sec of fresh air, with the cycle repeating until one or more cigarettes are consumed.

The design of the exposure side plates was modified to accept an improved version of the animal containment tubes (see below), and the filamatic puffing mechanism was changed to allow a single pump to operate two exposure units. Two such double units, allowing the exposure of a total of 40 hamsters, are scheduled to be put into service within the month. The exposure chamber on the commercially obtained Hamburg II machine was also modified to provide superior smoke exhaustion and to accept our animal containment tubes.

Extensive use has allowed a preliminary assessment of the operating characteristics of our (ORNL) device and the Hamburg II device. Little or no trouble has been experienced with the puffing mechanism of the ORNL machine, but the Hamburg II system appears to be subject to possibly serious pumping and mechanical malfunction. Both machines have certain advantages. A thorough consideration of machine characteristics awaits a chemical study of the aerosols produced. We

are also preparing to evaluate and construct a particularly flexible machine concept developed elsewhere.

Mouthpiece-cannula development. The inhalation program was initiated to test the concept of intratracheal cannulation as a means of increasing lung dosage. Small laboratory animals, being obligatory nose breathers, were thought to minimize lung dosage by effectively trapping much of the inhaled particulates in the nose. The singular problem which must be overcome to make intratracheal cannulation practical is the development of a tolerable cannula and means (mouthpiece) to hold the cannula in place. The recommendations and testing by the biology group have been critical to the success of this development.

Cannulas of various dimensions and materials such as polyethylene, lycra, and stainless steel have been considered. A special consideration is the need to carefully shape the tips of the cannulas to minimize damage during insertion. The biologists report that, from all evidence to date, insertion poses little problem with regard to injuring the animal. Maintaining a cannulated animal for more than 2 hr has continued to be a problem. It is felt that the injuries result from internal bruising and/or cutting when the animal moves. More flexible materials for constructing cannulas may be an answer to this problem. The mouthpiece in common use is one developed by the biologists. A sacrificed hamster is used to make rubber mouthpieces molded to conform to the interior of the mouth. Some difficulty was experienced with seeing the cannula around the large mouthpiece, thus making insertion difficult. We designed several mouthpieces to minimize the insertion problem – an aritificially molded mouthpiece with a hole in the middle for visibility, and several convoluted metal-ring mouthpieces with pivoting cannula attachments. Later work eliminated the visibility problem with the rubber mouthpiece. We are now in search of mouthpiece designs which minimize tongue compression and damage to the interior of the mouth.

The possibility of selective absorption of smoke components by the cannula itself is of concern in choosing the proper construction material. We have examined the uptake of the smoke labels hexadecane (C_{16}) and dotriacontane (C_{32}), presumably a measure of particulate matter, by respirating cannulas positioned in place of hamsters. Cannulas of the same inner diameter but of stainless steel, Teflon, polyethylene, and lycra were "smoked." Stainless steel removed the least C_{16} and C_{32}. Polyethylene and lycra absorbed the greatest amount of C_{16}, whereas Teflon and lycra absorbed the most C_{32}. Absorption of C_{16} was generally much greater than C_{32}.

Animal containment tubes. Animals must be maintained exterior to the smoke chamber to minimize contact between the fur and smoke. Deposition on the exterior of the animal produces an artifactual uptake through skin absorption and orally by preening. The animals must be positioned to inhale the aerosol during normal breathing. The problem is complicated with cannulated animals because excessive struggling can product internal injuries.

With the help of the biologists, we designed and coordinated the fabrication of two types of containment devices. The first is a three-part assembly consisting of a body tube, hinged collar, and face piece. The animal is collared, placed into the body tube, the face piece is attached, and the animal is "plugged" into the machine. Steps have been taken to eliminate the problems of severe eye pressure and gnawing on the machine side plate. A second containment tube has been developed that is a single-piece assembly featuring hinged, slanted collar. The new device appears to make the hamsters more comfortable and lessens vigorous movement. Both devices are in routine use, with selection depending on the type of experiment planned.

Radiolabeled cigarettes. Accurate determinations of lung deposition requires the reproducible preparation of cigarettes containing ^{14}C-dotriacontane (C_{32}) or ^{14}C-hexadecane (C_{16}). Other labeling compounds could be used, but the preparation technique remains critical. We have examined several alternatives for the preparation of such products – hand rolling cigarettes prepared from filler which has been sprayed uniformly with label, hand syringe injection of the label in a volatile solvent into the butt or whole cigarette, and machine injection via syringe. The mechanical device was designed and constructed in-house. The mechanical introduction of the labeling compound seems to be the most reproducible.

The characteristics of the ^{14}C-containing cigarettes had to be determined before lung deposition experiments could be fully interpreted. We confirmed reported work that the C_{32} and C_{16} were associated primarily with the particulates. Chemical and biological studies demonstrated an insignificant contribution to the final measurements by gas-phase products. We have demonstrated a close relationship between the quantities of C_{32} and total particulate matter generated from whole-cigarette-labeled products. Butt end deposition C_{16} was found to be an unsatisfactory technique. The bulk of the label was carried into the smoke during the last three puffs.

Lung deposition methodology. A procedure has been established for the measurement of particulate matter

deposited in the lungs and other organs of hamsters. This procedure is based on the assumption that the deposition of an added ^{14}C-labeled compound, which is representative of a class of compounds found in tobacco smoke particulate matter, will parallel the deposition of the particulate matter as a whole. We have confirmed that dotriacontane, when added to cigarettes which are subsequently smoked, is recovered mainly from particulate matter. Consequently, deposition studies involving the use of ^{14}C-dotriacontane were begun, and studies of ^{14}C-hexadecane were continued. Labeled compounds were injected along the axis of the cigarettes to a depth of 60 mm by a mechanical syringe device. Reproducibility of labeling from cigarette to cigarette was good, with a precision of 5% or better. Reproducibility of labeling along the axis was also good, as measured by slicing the cigarette into segments and extracting the label or by measuring the label collected on filter pads on a puff-by-puff basis.

The labeled alkane hydrocarbons are recovered from the hamster organs by dissolving the tissue in ethanolic-potassium hydroxide and then counting the ^{14}C in an aliquot of the sample solution by means of a scintillation spectrometer. The aliquot must first be bleached with hydrogen peroxide, but neutralization is not necessary. We tested a number of scintillator solutions using secondary scintillator solvents, but the highest counting efficiency was obtained with a standard toluene scintillator solution even though the final counting solution is not homogeneous. Counting efficiencies for ^{14}C in the various tissue solutions ranged from 0.70 to 0.80. Blood samples are treated in essentially the same manner as the tissue samples. Approximately 90% of the label is recovered, and the precision averages about 5%. Small organs such as trachea, larynx, and esophagus can be counted directly in the scintillator solution without solubilization.

A total of 25 tobacco smoke inhalation experiments on hamsters have now been carried out, as well as several experiments involving intratracheal injection of the labeled compounds alone. These experiments were designed primarily to establish the effectiveness in using a cannula to deliver the smoke directly to the lungs. The experiments also served to establish the best method for handling the control animals, to compare deposition from the gas phase with deposition from whole smoke, and to study the loss of label from the lungs and its course in some of the other organs. The results of the tests indicate that the use of a cannula does increase the deposition of particulate matter in the lungs by a factor of 2 to 3 over the deposition in the lungs of nose-breathing animals when calculated on the basis of percent of total matter deposited in the body.

Determination of benz(a)pyrene in tissue. A method is under development for the determination of low-microgram amounts (10 μg and less) of benz(a)-pyrene (BaP) in mammalian tissue. The tissue is digested in ethanolic-potassium hydroxide, and the BaP is extracted into petroleum ether. A turbidity forms when the extract is evaporated, and this interferes with the ultraviolet spectrophotometric determination of the BaP. However, this turbidity does not interfere with the fluorescent spectrophotometry. The background fluorescence of the tissue solution does, however, limit the sensitivity by a factor of possibly 50 when compared with pure BaP solutions. On the other hand, this sensitivity is still more than adequate because difficulties have been found in attempting to extract quantities of BaP less than 0.1 μg from tissue solutions. In these tests, solutions of previously digested organs were used and standard BaP solutions added. Recovery ranged from about 85% at the 0.1-μg level to about 95% at the 10-μg level.

Nasal filtration. A series of experiments has begun to determine the influence of nasal filtration on the composition of the smoke reaching the lungs of experimental animals. The study serves the dual purpose of acquiring definitive chemical data on the efficiency of nasal trapping and assessing the possible effect of cannulation on the quality of the smoke reaching the target organ.

A preliminary study of the effect of nasal filtration on gas-phase components is now complete. The hamster was surgically prepared by the biologists to allow normal respiration while providing access to the upper respiratory tract of the intact animal. Smoke was drawn through the nose via the trachea and its composition compared with smoke drawn through a cannula. Approximately 40% of the acetaldehyde and acrolein were removed by the nasal turbinates. Now we are establishing procedures to examine nicotine, additional gas-phase components, and the profile of particulate matter components following nasal filtration.

MISCELLANEOUS STUDIES

Simultaneous determination of carbon, nitrogen, and sulfur in solid ecological materials by hydrogenation and element-selective detection. As a result of our continuing development program, we now have a simultaneous determination for carbon, nitrogen, and sulfur, and an individual determination of phosphorus in ecological materials. A platinum catalyst and hydrogen reactant are used for the simultaneous reduction of C, N, and S to their respective hydrides, and a pure SiO_2 catalyst is used for the reduction of P to PH_3.

The effluent stream from the pyrolyzer is split: one portion passes to a flame photometric detector which responds to H_2S and CH_4, and the other portion passes to a Coulson electrolytic conductivity detector which responds to NH_3. We have analyzed forest floor litter, grasses, seeds, tree leaves, insects, tree saps, and forest dry fall for C, N, and S. We were able to determine P, but only in lipid-rich seeds, insects, or in soil extracts (inorganic P). This method is now in routine use for the determination of C, N, and S in ecological field specimens.

Characterization and purity of biochemical compounds. The data collected in the Analytical Chemistry Division on the purity of commercially available nucleotides, nucleosides, and bases for the National Academy of Sciences–National Research Council Committee on Specifications and Criteria for Biochemical Compounds have been published.[9] Of the 85 compounds tested 29 met specifications for designation as "NRC grade," and 6 others tentatively met specifications.

The Committee is also interested in establishing specifications for labeled compounds, and we have been examining the specific activity and labeling pattern of ^{14}C-labeled purines and pyrimidines by mass spectrometry. The results of our specific activity measurements are shown in Table 2.1. In two cases the manufacturer's quoted specific activity is 15 to 20% too low. The positions of the ^{14}C atoms, determined by examination of the mass fragments, were found to be consistent with both the method of preparation and manufacturer's designation in all cases. We plan to continue this work since it appears that mass spectrometry is the best method for specific activity measurement, and that we will be able to elucidate the labeling pattern of the more complex nucleosides and nucleotides.

Table 2.1 Specific activity of ^{14}C-labeled purines and pyrimidines by mass spectrometry

Compound	^{14}C (at. %)	Specific activity (mCi/mmole)	
		Found	Quoted
Adenine-2-^{14}C	37.3(±0.5)[a]	23.3	19.8
Adenine-8-^{14}C	89.9(±0.6)[a]	56.0	56
Cytosine-2-^{14}C	48.9(±0.4)[a]	30.5	25
Thymine-2-^{14}C	86.1(±0.7)[a]	53.7	53
Adenine-^{14}C (U)	96.8(±1.0)[b]	302	287

[a]At. % of designated carbon.
[b]At. % of all carbons.

9. Gerald Goldstein, A. L. Nussbaum, D. G. Soll, and Mayo Uziel, "Nucleotides and Related Compounds," pp. 149–83 in *Specifications and Criteria for Biochemical Compounds,* National Academy of Sciences, 1972.

3. Energy Programs

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ANALYTICAL DEVELOPMENTS FOR THE MOLTEN-SALT REACTOR PROGRAM

In-line chemical analysis of molten fluoride salt streams. Automated analyses for U(III) in $LiF-BeF_2-ZrF_4-UF_4$ (65.4-29.1-5.0-0.5 mole %) in the NCL-21 thermal convection salt loop were continued. Analyses for the percent of the total uranium present as U(III) for the first 3600 hr of loop operation were largely made by unattended operation of the computer-controlled voltammetric system that was described in the previous report.[5]

The original measurements on the salt after it was loaded into the loop showed that the concentration of U(III) was about 0.02%. As the salt circulates through the loop, chromium dissolves from the Hastelloy-N tubing and slowly reduces the U(IV) to U(III). Over one period of about two months when the melt was not disturbed, the U(III) concentration increased at a constant rate of about 0.11% per month. This reaction continues until equilibrium is established between the U(IV)/U(III) and Cr(II)/Cr(0) systems.

During the first 3600 hr of loop operation the Hastelloy-N corrosion specimens were inserted into the loop at three different times. Except for the first time when the U(III) concentration was already at a low value, this operation caused the U(III) concentration to decrease by as much as 0.2% in a few hours. We also observed a decrease in U(III) concentration on one occasion when a shielded electrode assembly[5] was installed in the loop. The ease with which the U(III) can be oxidized in this loop emphasizes the difficulty that is encountered in trying to perform this type of analysis on samples that are withdrawn from a molten-salt system. The oxidation of the U(III) also provides an explanation for the lower-than-expected results which we obtained in attempts to apply this technique to the hot-cell measurement of U(III) in MSRE samples.[6] Despite all precautions taken, the contamination introduced during the sampling and transfer of the samples must have been at least equivalent to that observed during the introduction of the corrosion specimens into the present loop.

We have observed that the U(IV) reduction waves obtained with the shielded and unshielded working electrodes are displaced by 29 to 30 mV from one another, resulting in appreciably different U(III) analyses. We have shown that this is due to an IR drop in the salt in the nickel tube and should be eliminated by placing the reference electrode inside the shielding tube with the working electrode.

The voltammetric technique will also be used to determine other melt constituents such as corrosion product ions. In the reducing melts that have been present in the loop, the equilibrium concentration of Fe(II) and NI(II) is negligible while all of the chromium is present in the ionic form. In fuel melts Cr(II) is the most difficult of the corrosion products to measure because its reduction potential is so close to that of U(IV). One of the proposals which we have made but not demonstrated is that chromium can be determined by a stripping technique. This technique is based on the fact that metallic chromium – the reduction product of

1. Student Guest, University of Tennessee, Knoxville.
2. Student Guest, Denison University, Granville, Ohio.
3. ORAU Graduate Participant.
4. Consultant, Professor of Chemistry, University of Tennessee, Knoxville.
5. A. S. Meyer et al., "In-Line Chemical Analysis of Molten Fluoride Salt Streams," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4749, p. 10.
6. J. M. Dale, R. F. Apple, and A. S. Meyer, *MSR Program Semiannu. Progr. Rep. Feb. 28, 1970*, ORNL-4548, p. 180.

Cr(II) – is deposited on the electrode, whereas U(III) – the reduction product of U(IV) – is soluble and diffuses back into the melt. Thus, if the electrode is held at a potential that is sufficiently cathodic to reduce both U(IV) and Cr(II), the U(III) will rapidly approach a steady-state concentration at the electrode surface while chromium metal is continuously deposited. When the electrode is electrolytically stripped by an anodic scan, the contribution of U(III) should be independent of reduction time, while the stripping current from the chromium metal should increase with plating time.

We have obtained stripping curves for chromium at the 100-ppm level in the salt. When the stripping currents were integrated with the voltammeter and plotted vs plating time, a straight-line relationship was obtained. In theory the slope of the integrated current vs plating time curves should be proportional to the concentration of chromium in the melt. Although we have observed gradual increases in the slope of such curves that may correspond to increases in the concentration in the melt, we have not accumulated sufficient analytical data to establish the analytical validity of this technique.

The results of the ratio measurements have in general shown excellent reproducibility and have been consistent with the known factors of loop operation. Although the establishment of accurate calibrations for the determination of corrosion products remains to be solved, this experience gives us considerable confidence that this relatively simple transducer system can be widely applied to other test systems and ultimately to in-line streams.

We are currently in the process of installing a voltammetric analysis system on the Coolant Salt Technology Facility, a large engineering loop which will contain $NaBF_4$-NaF (92-8 mole %), the proposed coolant for the Molten-Salt Breeder Experiment. We plan to analyze the salt for corrosion products and the reducible proton species. Work on the reduction of the proton species at a hollow palladium electrode is described in another part of this section.

Theoretical considerations of the voltammetric in-line determination of uranium(III). The present method for determining the uranium(III) concentration in the MSRE fuel involves the measurement of the potential difference between the equilibrium potential of the melt and $E_{1/2}$, the voltammetric equivalent of the standard potential of the U(IV)/U(III) couple.[7] The equilibrium potential of the melt E_{EQ} is the potential of an inert platinum wire immersed in the melt and depends upon the U(IV)/U(III) ratio. The standard potential $E_{1/2}$ is the potential on the U(IV) reduction wave at which the concentrations of U(IV) and U(III) are equal. The relationship between E_{EQ}, $E_{1/2}$, and U(IV)/U(III) is given by

$$E_{EQ} = E_{1/2} + \frac{RT}{nF} \ln \frac{\mathrm{U(IV)}}{\mathrm{U(III)}} .$$

Because the voltammetric circuit uses E_{EQ} as a reference potential, we can consider it to be zero, and

$$-E_{1/2} = \frac{RT}{nF} \ln \frac{\mathrm{U(IV)}}{\mathrm{U(III)}} .$$

Evaluation of $E_{1/2}$ with respect to E_{EQ} then permits the U(IV)/U(III) ratio to be calculated.

Nicholson and Shain[8] have reported a solution to the boundary value problem that can be applied to this system. They found that for a reversible couple where both species are soluble $E_{1/2}$ corresponds to the potential on a theoretical reduction wave where the current is 85% of the peak current. The experimental U(IV) reduction wave, however, from the NCL-21 thermal convection loop also involves the reduction of chromium which could adversely affect the potential at which the 85% point occurs. For this reason it was of interest to compare the theoretical reduction wave with the U(IV) reduction wave from the experimental system.

The potential E of the working electrode during a voltammetric scan is represented by

$$(E - E_{1/2})n = (RT/F)(\ln \gamma\theta - at) ,$$

where

$$\gamma = \sqrt{D_0/D_r},$$
$$\theta = \exp\,[(nF/RT)(E_i - E_{1/2})] ,$$
$$at = nFvt/RT .$$

The term $\gamma\theta$ is a constant where D is the diffusion coefficient of the oxidized or reduced species and E_i is the initial starting potential of the voltammetric scan. The term at is a variable where v is the voltage scan rate and t is the time elapsed after the scan is started. All other terms have their usual significance. The current i

7. H. W. Jenkins, D. L. Manning, G. Mamantov, and J. P. Young, *MSR Program Semiannu. Progr. Rep. Feb. 28, 1969*, ORNL-4396, p. 201.

8. R. S. Nicholson and I. Shain, "Theory of Stationary Electrode Polarography," *Anal. Chem.* **36**, 706 (1964).

through the working electrode during a voltammetric scan is represented by

$$i = nFAC_0 \sqrt{\pi D_0 a}\, \chi(at).$$

The term $\chi(at)$ is a function of at, A is the electrode area, and C_0 is the concentration of the U(IV) in the melt.

The expression

$$2\sqrt{\delta}\left\{\chi(1)\sqrt{k} + \sum_{i=1}^{k-1} \times \sqrt{k-i}\,[\chi(i+1) - \chi(i)]\right\} = 1/[1 + \gamma\theta \exp(-at)]\ ,$$

where $\delta = (at)/k$, defines the relationship between the values of χ and the variable at, where k is the serial number of the particular value of χ being evaluated. To get a true theoretical current-potential curve one must solve for the values of χ at small voltage intervals, since each successive value of χ depends upon all of the previously determined values. A program was written for the PDP/8I for the numerical evaluation of the χ values over an 800-mV range at 2-mV intervals. This gave δ a value of 0.025. The initial potential E_i was 500 mV anodic to $E_{1/2}$, making $\ln \gamma\theta = 6.29$.

Evaluation of the current expression where $A = 0.418$ cm^2, $C_0 = 0.282$ moles liter^{-1}, $D_0 = 5.62 \times 10^{-6}$ cm^2 sec^{-1}, and v = 0.1 V sec^{-1} gives

$$i = 53.69\, \chi(at) \text{ mA}$$

for the potential defined by at. The derivative current expression is

$$di/dt = \Delta i/\Delta t = 53.69\, \Delta\chi(at)/\Delta t \text{ mA sec}^{-1}\ ,$$

where the values of $\Delta\chi(at)/\Delta t$ are the incremental slopes between the 2-mV intervals of the successive values of χ. By proper substitution of the values of $\chi(at)$ and $\Delta\chi(at)/\Delta t$, these two expressions were used for the construction of the theoretical current-potential curve and its derivative.

In Fig. 3.1 the experimental waves are represented by the solid lines, and the theoretical waves are represented by the points which are plotted at 10-mV intervals. One observes the expected deviation in the region where Cr(II) is reduced (−0.4 to −0.5 V) both on the normal and derivative waves. The experimental derivative peak is lower because the Cr(II) reduction causes the normal wave to rise less sharply in this region. However, the

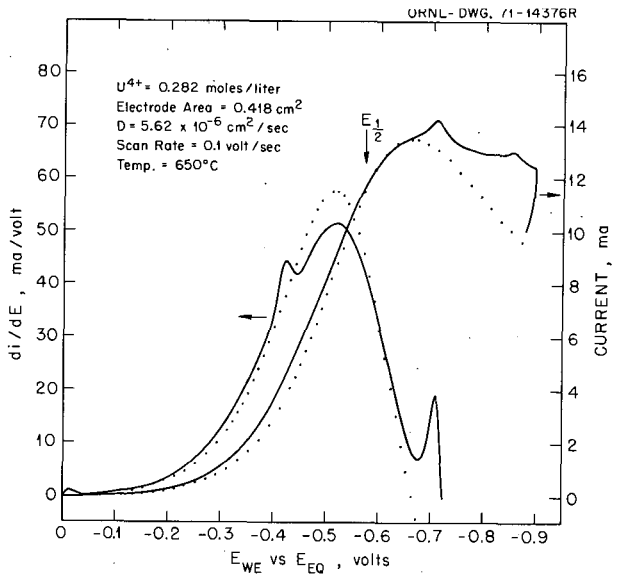

Fig. 3.1. Current-voltage wave and derivative for reduction of U^{4+} to U^{3+}; theoretical points (.) and experimental curve (–).

potentials at which the two derivatives show a maximum agree to within 5 mV, and there is good agreement between the experimental and theoretical values of $E_{1/2}$. We conclude that the chromium reduction does not affect the current-potential curve for the U(IV) reduction at the $E_{1/2}$ potential and that the method for determining $E_{1/2}$ is valid.

Voltammetric studies of protonic species in molten $NaBF_4$-NaF (92-8 mole %). We have continued studies on the voltammetric behavior of protonic species in molten $NaBF_4$ at an evacuated palladium tube electrode.[9] The initial studies were conducted with the melt contained in a graphite cell enclosed in a silica jacket. However, to eliminate any effect of silica and to achieve higher melt temperatures, a nickel cell enclosure was fabricated. Both graphite and copper cells have been utilized. Voltammograms recorded at palladium or palladium-silver (75:25) alloy electrodes revealed a well-defined wave at about −0.1 V vs a platinum quasi-reference electrode. The wave conforms to a reversible one-electron reduction by voltammetric and chronopotentiometric criteria. By electrolyzing at a potential beyond the peak potential of the wave, an increase in pressure was observed inside the electrode. This is evidence that the wave is due to the reduction of protons with part of the resultant hydrogen diffusing

9. A. S. Meyer et al., "In-Line Chemical Analysis of Molten Fluoride Salt Streams," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4749, p. 15.

through the palladium. We first believed that it would be possible to relate the pressure measurements to the protonic content of the melts under controlled electrolysis conditions. Experience with different electrodes, however, has revealed that the "porosity" to hydrogen among the electrodes is not necessarily constant, and, also, pressure measurements at a given electrode will change (usually decrease) with time in the melt. Nevertheless, it is still possible to collect gas samples by this technique for measurement of isotopic ratios of hydrogen.

Our first assumption was that the voltammogram resulted from the reduction of –OH as $NaBF_3OH$ at the palladium electrode. However, the voltammetric results were consistently low when compared with infrared data. Also we observed that the wave height of the voltammogram can be significantly reduced by cooling the top of the nickel cell enclosure and returned to the original value by heating. We now believe that the protonic species yielding the voltammetric wave is in equilibrium with a vapor species that can be condensed at cooler temperatures. Moreover, no marked variation in the BF_3OH^- concentration as measured by IR pellet technique appeared to be associated with significant changes in the reduction wave. We have also noted that when the vapor species is removed by sweeping with helium the wave decreases, but recovers slowly after the sweep is discontinued. This suggests that the more electroactive species may be replenished via slow reactions of a more stable protonated component.

To explain these results we have postulated reactions such as

$$2NaBF_3OH + NaBF_4 \rightleftharpoons Na_2(BF_3)_2O + HBF_3OH \rightleftharpoons \text{vapor},$$

$$NaBF_3OH + 2NaBF_4 \rightleftharpoons Na_2(BF_3)_2O + NaF + HBF_4 \rightleftharpoons \text{vapor},$$

in which the melt equilibrium strongly favors the $NaBF_3OH$ species. To be consistent with our observations, the diffusion coefficient of the more active species must be higher than the 10^{-6} cm^2 sec^{-1} typical value in fluoride melts, so that the active proton concentration is lower than we suspected.

To test these hypotheses, we added crushed chromium metal to a fluoroborate melt and followed the voltammetric wave and the BF_3OH^-. Pertinent observations at 500° are recorded below.

Time	Proton wave height, μA	H as $NaBF_3OH$, ppm
~1 hr	3300	52
4 hr	500	42
1 day	Not detected	32
2 days	Not detected	29
8 days	Not detected	24

Of interest here is that after eight days, the BF_3OH^- level has decreased approximately one-half, whereas the voltammogram, for practical purposes, was lost within the first day. This appears to be additional evidence that the voltammetric and infrared techniques are not observing the same protonated species. Thus the protonic species present and their associated equilibria now appear to be more complex than our original concepts. We are continuing these studies, however, and attempts will be made to evaluate the diffusion coefficient of the electroactive protonated species so that the concentration of this substance can be determined.

Infrared spectral studies of molten and solid $NaBF_4$-NaF. There is still some confusion as to the chemical reactions and stable species of H, B, F, and O that exist in $NaBF_4$-NaF (92-8 mole %). Progress in our understanding of these melts has been made, however. Molten $NaBF_4$-NaF is to be the coolant for the proposed MSBR, and the presence of combined oxygen and hydrogen can affect its corrosiveness and uptake of tritium which is formed in the reactor fuel. From infrared studies of $NaBF_4$-NaF melts, described in the previous reporting period, we had established the existence of the BF_3OD^- ion in the melt. This and related work is presently in press.[10]

As in the past, the melt spectral studies are being carried out in cooperation with J. B. Bates and G. E. Boyd of the Director's Division. This year we completed the design and fabrication of a small LaF_3-windowed cell (2-mm path length and approximately 0.1-ml volume) and associated furnace for use in spectral studies of $NaBF_4$ melts. With the use of this cell and furnace we observed the position of the BF_3OH^- absorption band in molten $NaBF_4$-NaF to be 3640 cm^{-1}. A number of studies of the reaction or exchange of D_2 or H_2 (as a stand-in for T_2 and H_2) with solute species in molten $NaBF_4$-NaF were carried out, but the small size of the LaF_3-windowed cell has

10. J. B. Bates, J. P. Young, M. M. Murray, H. W. Kohn, and G. E. Boyd, "Stability of BF_3OH^- Ion in Molten and Solid $NaBF_4$ and NaF-$NaBF_4$ Eutectics," *J. Inorg. Nucl. Chem.*, in press (1972).

caused problems with such studies in this cell. Our most definitive results have been obtained from experiments in which either D_2 or H_2, independently, can be diffused through nickel thimbles (0.004-in. wall) into the melt contained in a SiO_2 cell at a temperature of approximately 425°C. The presence or absence of the BF_3OD^- ion and its change in concentration is followed spectrophotometrically by its characteristic IR absorption peak at 2690 cm^{-1}. Under our experimental conditions, if D_2 is diffused into this melt some BF_3OD^- ion is formed initially, but its concentration levels off within 10 to 15 min, and no further change in that peak is seen if the diffusion is continued. If H_2 is first diffused into the melt (2 hr) and then D_2 is allowed to diffuse into the melt, no BF_3OD^- absorption is seen. These results in the SiO_2 apparatus suggest that D_2 does not exchange with the BF_3OH^- ion, but rather that D_2 (or H_2) is capable of reducing some species in the melt. One of the ultimate products of this reduction is BF_3OD^- (or BF_3OH^-). If D_2 is used first, the BF_3OD^- is seen; if H_2 is used first, the reduction is complete and no BF_3OD^- is seen when D_2 is subsequently introduced.

We have seen similar but less reliable results when the melt is contained in a LaF_3 cell. The usefulness of the $NaBF_4$ coolant salt in trapping hydrogen isotopes (tritium) is not necessarily based on an exchange reaction with BF_3OH^-, even though this has been a favorite mechanism. The studies carried out here do indeed demonstrate a chemical reaction of diffused hydrogen isotopes with the melt. It is only required to identify this chemical oxidant in this process or to develop some catalyst which will make isotopic exchange more favorable. This demonstrated lack of exchange in melts, coupled with an unsatisfactory correlation between the results of the deuterium exchange technique[11] and the infrared pellet technique in the determination of combined hydrogen in samples of $NaBF_4$, has led to a discontinuance of the isotopic exchange method. Based on present knowledge, the apparent exchange we observed in the earlier studies was probably caused by a side chemical reaction or exchange with a species other than BF_3OH^-.

Additional conformation of the original calibration[11] of the infrared method has been obtained by mixing known quantities of solid $NaBF_3OH$ with solid $NaBF_4$-NaF and melting these mixtures in vacuum-tight crimped copper containers maintained under isothermal conditions. In these tests $NaBF_3OH$ additions corresponding to 25 ppm of hydrogen or less were recovered quantitatively. Lower recoveries of larger additions (e.g., 40 ppm) are probably caused by the separation of a volatile proton-containing species which does not completely reequilibrate with the salt when it solidifies. Indeed, under nonisothermal conditions, a tan-colored viscous liquid can be condensed on a water-cooled surface (see also the section on Electrochemical Studies of $NaBF_4$). This liquid fumes in air and was shown by NMR analysis to contain essentially equal molar quantities of H and F. From the NMR chemical shift, it is indicated that the hydrogen is not ionic. Thus the liquid cannot be HBF_4 or HBF_3OH but might be $BF_3 \cdot H_2O$, $BF_3 \cdot 2H_2O$, or a compound of BF_nOH_{n-3}.

Although a very careful technique is followed, it is not possible to melt apparently low hydrogen containing $NaBF_4$ or $NaBF_4$-NaF mixtures without causing the BF_3OH^- concentration to increase by about 15-ppm hydrogen based on IR pellet analysis. It appears that this increase is caused by some other form of proton, most likely H_2O, that is converted to BF_3OH^- on melting. If the 20-ppm hydrogen-containing salt is ground in air and again melted, a further increase of 15 to 20 ppm is observed. From a consideration of spectral and electrochemical results, there are at least three kinds of protonic species that can find existence in molten or solid $NaBF_4$. This fact undoubtedly is a partial cause of our inability to obtain a precise analytical determination of hydrogen in these salts by the several methods available.

Voltammetry of chromium(III) in molten $NaBF_4$-NaF (92-8 mole %). A voltammetric study is under way on the reduction characteristics of chromium(III) added as Na_3CrF_6 to molten $NaBF_4$-NaF. The melt is contained in a graphite cell enclosed in a nickel apparatus to maintain an inert atmosphere. A cover gas of helium is maintained under static conditions at approximately 5 psi. Enough Na_3CrF_6 was added to give approximately 410 ppm of Cr(III), assuming all the reagent dissolves. Chemical analysis of melt samples taken at 440 and 500°C revealed a chromium(III) concentration of 200 and 300 ppm, respectively.

The chromium reduction wave [Cr(III) → Cr(0)] was observed at approximately −1.0 V vs a platinum quasi-reference electrode at platinum and palladium indicator electrodes. The waves were reasonably well defined; limiting current values at platinum (~0.1 cm^2) were 500 and 1100 μA at 440 and 500°C, respectively, at a scan rate of 0.1 V sec^{-1}. Scan rate studies revealed that plots of peak current (μA) vs scan rate (V $sec^{-1})^{1/2}$ were linear to about 10 V sec^{-1}. From the

11. A. S. Meyer et al., "Spectrophotometric Study of Protonated Species in $NaBF_4$," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4749, p. 13.

slope of the line the diffusion coefficient of the Cr(III) species can be evaluated, and at 400°C was found to be about 2×10^{-6} cm^2 sec^{-1}.

Attempts to record chronopotentiograms were not successful; apparently the potential of the chromium reduction is too close to the melt limit to record meaningful transition times.

It has also been observed that as the temperature of the melt is increased, the apparent potential limit occurs at less cathodic potentials. Thus it may become difficult to resolve the chromium wave at temperatures of the order of 600°C. Attempts will be made, however, to accomplish this, and different indicator electrode materials will be screened in an effort to establish optimum conditions.

Electroanalytical studies of titanium in molten LiF-NaF-KF and LiF-BeF_2-ZrF_4. We carried out electroanalytical studies on the behavior of titanium in molten LiF-NaF-KF (46.5-11.5-42 mole %) and LiF-BeF_2-ZrF_4 (65.4-29.6-5.0 mole %). Titanium is present in the structural metal (Hastelloy N) of the molten-salt reactor, and from free energy considerations should be somewhat more reactive than chromium.

Initial attempts to keep a stable solution of titanium(IV) added as K_2TiF_6 to LiF-NaF-KF contained in a graphite cell were not successful. The disappearance of Ti(IV) but not Ti(III) with time suggests that the Ti(IV) is slowly reduced by the graphite material.

Subsequent experiments were carried out in a platinum cell using platinum electrodes. In this cell, stable solutions of titanium(IV) could be kept for several weeks. The Ti(IV) → Ti(III) voltammograms at about +0.15 V vs a Ni/NiF_2 (saturated) reference electrode were well defined and reproducible. The peak current was proportional to the concentration of Ti(IV) and to the square root of the scan rate to about 1 V sec^{-1}. The Ti(III) → Ti(0) voltammogram at −1.45 V vs Ni/NiF_2 (saturated) reference electrode was preceded by what appears to be a predeposition wave, probably due to alloying of titanium with platinum. Alloy formation is supported by the large separation between anodic and cathodic peak potentials for this wave. The determination of n from the ratios of the voltammetric peak currents and limiting currents from polarograms constructed from current-time curves gave $n_2/n_1 = 3$.

Chronopotentiograms for the reduction of Ti(IV) to Ti(III) were reasonably well defined. Parameter $i\,\tau^{1/2}$ values (τ = transition time) were constant from 1 to 10 mA. Excellent verification of $n = 1$ for the first wave was achieved from the ratio of the voltammetric $i_p/v^{1/2}$ and chronopotentiometric $i\,\tau^{1/2}$ parameters. For this evaluation of n, the concentration of electroactive species, diffusion coefficient, and electrode area do not need to be known.

The initial voltammetric studies in molten LiF-BeF_2-ZrF_4 were undertaken using K_2TiF_6 as the solute; however, the results of titanium(IV) reduction were greatly complicated by the observed instability of Ti(IV) in the melt. White deposits were found to collect in the cooler part of the electrolytic system after K_2TiF_6 was added to the melt. The volatilization of titanium tetrafluoride from the melt was confirmed in a separate experiment in a closed stainless steel vessel provided with a cold trap; the volatile product collected was identified as TiF_4 by x-ray analysis.

Voltammetric studies of the oxidation of titanium(III) in molten LiF-BeF-ZrF_4 at 500° were then initiated since TiF_3 was expected to be stable in the melt at this temperature. The sublimation point of TiF_3 is 930°C in vacuo.

Well-defined linear sweep voltammograms for molten LiF-BeF_2-ZrF_4 containing Ti(III) were obtained at a sheathed glassy carbon electrode. Similar but less well-defined waves were obtained at an unsheathed platinum electrode. The wave corresponds to the anodic oxidation of Ti(III) to Ti(IV). This was the only wave observed upon addition of TiF_3 within the potential limits of the melt, +1.5 to −1.5 V measured at platinum vs the nickel(II) (saturated)/ nickel reference electrode (LaF_3 membrane type). These potential limits correspond to anodic dissolution of platinum and the reduction of Zr(IV), respectively. A plot of i_p vs $v^{1/2}$ resulted in a straight line which is indicative of a simple charge transfer reaction. The concentration dependence of i_p was also linear.

The standard electrode potential E^0 for the Ti(IV)/Ti(III) couple may be estimated from the $E_{1/2}$ for the process Ti(III) ⇌ Ti(IV) + e in molten LiF-BeF_2-ZrF_4 at 500°C. The $E_{1/2}$ is +0.380 V with respect to the Ni(II) (saturated)/Ni(II) reference electrode. However, an extrapolation of a Nernstian plot of the nickel couple to unit mole fraction of nickel(II) gives a potential that is 183 mV more anodic than the potential corresponding to saturation point of nickel(II). Applying this correction of −183 mV to relate the potential of the reference electrode to the potential of a unit fraction Ni(II)/Ni couple, E^0 for the Ti(IV)/Ti(III) couple in molten LiF-BeF_2-ZrF_4 at 500°C is estimated as +0.197 V (vs a unit mole fraction Ni(II)/Ni electrode).

The chronopotentiograms recorded at a sheathed glassy carbon electrode were reasonably well defined. The product, $i_0\,\tau^{1/2}$, at current densities from 0.04 to 0.16 amp cm^{-2} was found to be reasonably constant at

0.060 ± A $sec^{1/2}$ cm^{-2}. Transition times were in the range 0.1 to 2.3 sec.

Further verification of $n = 1$ for the Ti(III) oxidation was accomplished again using the ratio of the voltammetric $i_p/v^{1/2}$ to the chronopotentiometric $i\ \tau^{1/2}$. This relationship for the determination of n is given at 500°C as

$$\frac{i_p/v^{1/2}}{i\ \tau^{1/2}} = 1.96\, n^{1/2}\ ;$$

an n value of 0.9 was determined by this method.

For chronopotentiometry, the half-wave potential for a reversible charge transfer corresponds to the potential at one-fourth the transition time. This value was found to be about +0.40 V vs a Ni(II) saturated/Ni reference electrode and agrees reasonably well with the +0.380 V voltammetric value. From our voltammetric and chronopotentiometric studies, we believe this electrode reaction conforms to a reversible Ti(III) → Ti(IV) oxidation process and that this reaction could be used to monitor any buildup of titanium(III) in a flowing salt stream.

Electrochemical studies of bismuth(III) in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ at 500°C. Because the fuel in the proposed MSBE will be contacted with streams of molten bismuth in the reprocessing system, traces of bismuth may become a significant impurity in the fuel. We have, therefore, performed voltammetric and chronopotentiometric studies to characterize the reduction behavior of bismuth ions.

The linear sweep voltammograms were well defined for the reduction of bismuth at pyrolytic graphite, platinum, iridium, and silver indicator electrodes. Reverse scans indicated possible alloy formation between bismuth and platinum, and also bismuth and silver. No evidence of alloy formation was observed at pyrolytic graphite and iridium electrodes. Of the indicator electrodes tested, the iridium electrode gave results that were most reproducible. This material appears to be an excellent inert electrode for electroanalytical studies in corrosive melts.

The peak-shaped voltammogram corresponds to the reduction of Bi^{3+} to metallic bismuth at approximately +0.1 V vs a Ni/NiF_2 (saturated) reference electrode. Plots of i_p vs $v^{1/2}$ were linear to about 5 V/sec with slightly downward curvature at the faster scan rates. This suggests that the electrode reaction is becoming quasi-reversible at the faster scan rates.[12] The concentration dependence of i_p was linear over the concentration range of about 10 to 200 m*M* Bi(III). It was also discovered that for appreciable periods of time (days), stable solutions of Bi(III) in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ could not be maintained in either graphite or copper cells. However, the bismuth solutions appeared to be more instable in graphite. The mechanism for the bismuth instability is not yet resolved.

Chronopotentiograms recorded at an iridium electrode (~0.1 cm^2) were well defined. The ratio of forward to reverse transition times was unity, indicating the reversible deposition of an insoluble substance.[13] The values for the diffusion coefficient evaluated from voltammetry and chronopotentiometry were 1.08 and 1.03×10^{-6} cm^2 sec^{-1}, respectively.

Verification of $n = 3$ for the bismuth reduction was carried out using the ratio of the voltammetric $i_p/v^{1/2}$ to the chronopotentiometric $i\ \tau^{1/2}$. This equation for the determination of n at 500°C for the deposition of an insoluble substance is given as

$$\frac{i_p/v^{1/2}}{i\ \tau^{1/2}} = 2.69\, n^{1/2}\ ;$$

an n value of about 2.9 was obtained.

A report describing this work has been accepted for publication in *High Temperature Science.*

Spectral studies of solute species in molten fluoride salts. As a continuing effort in the Division, we carry out various spectral studies of molten fluoride salt systems to investigate possible analytical applications and to gain insight into the chemistry of those melts which are related to interests of the MSR project. Studies are carried out in BeF_2 based melts (of direct interest to the MSR) and in fuel salt and alkali fluoride melts, which provide a change in solvent character and are also of interest in developing general knowledge of molten fluoride solution chemistry. Two further papers have been written, one published[14] and one accepted[15] for publication, in which our views are given on the formation and stability of high oxidation states of

12. Paul Delahay, "Reversibility and Irreversibility of Electrode Reactions in Oscillographic Polarography," *J. Phys. Coll. Chem.* **54**, 630 (1950).

13. W. H. Rienmuth, "Chronopotentiometric Potential-Time Curves and Their Interpretation," *Anal. Chem.* **32**, 1514 (1960).

14. F. L. Whiting, G. Mamantov, and J. P. Young, "Spectral Studies of O_2^-, NO_2^-, and CrO_4^{2-} in Molten LiF-NaF-KF and of O_2^- in Liquid Ammonia," *J. Inorg. Nucl. Chem.* **34**, 2475 (1972).

15. F. L. Whiting, G. Mamantov, and J. P. Young, "Electrochemical Generation and Spectrophotometric Study of Solute Species in Molten Fluoride Media," *J. Inorg. Nucl. Chem.* in press.

several solute species in the presence of O^{2-} and/or F^- ligands in fluoride melts. This year we have demonstrated that it is possible to bubble gas into melts contained in windowless spectral cells without losing the melt. It is therefore possible to combine the bubbling of gases (F_2 or ClF_3), coupled with anodic oxidation, to further examine the preparation and properties of high oxidation states of solute species in various molten fluoride salts.

In cooperation with F. F. Blankenship, S. Kirslis (Reactor Chemistry Division), and S. Katz (Chemical Technology Division), we are studying the possibility of using the reduction of Ce(IV) to Ce(III) with the subsequent fluorimetry of Ce(III) as an analytical method for determining the reducing power of amenable melts. Katz and Pitt[16] have described this technique as a very sensitive means of determining organics in aqueous solution, and we have considered using this in an inorganic melt.

As a general analytical scheme the possible determination of reducing power by Ce(III) formation from Ce(IV) seems of value; either spectral absorption or fluorimetric measurements could be made. An interesting reagent for use in such a scheme would be CeO_2. Based on analogous chemical behavior, one might guess that CeO_2 would be very insoluble in fluoride melts, while Ce(III) would be soluble even in the presence of O^{2-}. Several preliminary studies have been carried out in the solvent LiF-NaF-KF and LiF-BeF_2-ZrF_4. In either melt it was found that Ce(III) was sufficiently soluble for use in this scheme. The absorption spectra, in either melt at 500°C, in the spectral region of 600 to 200 nm, consists of three peaks located at 292, 244, and 224 nm. The spectrum corresponds to the absorption spectrum seen for Ce(III) in CaF_2 crystals.[17] No fluorescence of the melt has been observed, but the solidified salt did fluoresce. The molar absorptivity of the most intense peak at 292 nm is estimated to be 700 liters $mole^{-1}$ cm^{-1}. Addition of CeO_2 to a melt of LiF-NaF-KF generated some Ce(III) which was seen spectrally; at equilibrium some undissolved CeO_2 still remained. Based on the absorbance of the 292-nm peak, 3 micro equivalents of some material in the salt was oxidized. Under our experimental conditions, down to 0.1 μmole of Ce(III)/g of sample could be determined by absorption spectral measurement. The method was originally proposed to be considered as an alternate method for determining very low concentrations of U(III). We envision that its use as a general reducing power indicator might be of more use, either by melt absorption measurements or melt or solid fluorescent measurements. The evidence to date would indicate that CeO_2 is not as strong an oxidant in these melts as, for example, MnF_3, but CeO_2 should be strong enough to oxidize Ni^0, Fe^0, etc., that might be present in such melts and that in the past have created problems in analysis when present with Ni^{2+} and Fe^{2+}.

Tellurium is a fission product of the fuel burnup in molten-salt reactors and has been implicated in some stress cracking that has been observed in the metal alloy which has been used in the MSRE. Because of this interest in Te, spectral studies of the various oxidation states will be carried out. Initially only Te^{2-} or Te^0 have been considered. It has been found, spectrally, that both ZnTe and Na_2Te are soluble in LiF-NaF-KF and that Na_2Te is soluble in molten LiF-BeF_2. The spectra of the resultant rose-colored solution probably arises from the Te^{2-} ion and consists of a moderately broad peak at 520 nm and a very intense absorption in the ultraviolet below 350 nm. The spectra are similar but not identical to that reported by Gruen et al.[18] for Li_2Te and Cs and Te in melts that were essentially chloride media. We do not know the sensitivity of the absorbance peak at 520 nm but estimate the molar absorptivity to be between 25 and 50 liters $mole^{-1}$ cm^{-1}. The solubility of either telluride, therefore, is believed to exceed 1000 ppm in LiF-NaF-KF at 525°C. The dissolved Te^{2-} ion is reasonably stable in an inert atmosphere at least for 24 hr, but has been found to be easily oxidized by exposure of the melt to air, possibly an oxidation via O_2, or by the addition of Fe^{2+}.

C. Bamberger and C. Baes, Reactor Chemistry Division, have collected thermodynamic data on LiF-BeF_2 melts in contact with SiO_2. In cooperation with them we plan to use spectral measurements of melts in silica cells to calculate the free energy of formation of CuF_2 and CuF in molten LiF-BeF_2 (SiO_2 cells). As part of this study we have determined the solubility of CuO in LiF-BeF_2 (contained in a SiO_2 cell) to be approximately 2100-ppm Cu^{2+} at 500°C under a partial pressure of SiF_4 of 500 mm. The solubility was calculated from a separate determination of the molar

16. S. Katz and W. W. Pitt, Jr., "A New Versatile and Sensitive Monitoring System for Liquid Chromatography: Cerate Oxidation and Fluorescence Measurement," *Anal. Lett.* **5**, 177 (1972).

17. P. P. Feofilov, "On Absorption and Luminescence Spectra of Ce^{+++} Ions," *Opt. Spectry.* (USSR) 6, 150 (1959).

18. D. M. Gruen, R. L. McBeth, M. S. Foster, and C. E. Crouthamel, "Absorption Spectra of Alkali Metal Tellurides and of Elemental Tellurium in Molten Alkali Halides," *J. Phys. Chem.* **70**, 472 (1966).

absorptivity for Cu^{2+} in $LiF\text{-}BeF_2$ (11 liters $mole^{-1}$ cm^{-1} at 500°C) and the equilibria absorbances seen when CuO was contacted with the solvent melt.

Spectral studies of Li-Bi or Li-Pb alloy in contact with molten lithium halides. In a proposed reprocessing scheme for MSR fuels, the molten fuel contacts Bi-Li alloy to remove certain fission product metallic ions via reduction. The alloy is then contacted with chloride melts in the removal of the fission product metals. In cooperation with L. Ferris' group, Chemical Technology Division, we undertook spectral studies of Li-Bi alloys in contact with molten LiCl or LiBr and spectral studies of an alternative processing alloy, Li-Pb in contact with molten LiCl. For these studies samples of the equilibrated melt and alloy were withdrawn, solidified, and transferred into an inert atmosphere box for reloading into a molybdenum windowless cell. The cell was designed so that the alloy was positioned just below the optical aperture of the cell. Thus spectral studies of the melt could be made while it was in contact with the alloy. From our results, Li_3Be seems to be the ionized solute species in either molten LiCl or LiBr near the LiX melting point. The reddish-yellow solution has a featureless ultraviolet absorption peak which appears similar to that obtained for Li_3Bi in molten LiCl-LiF (80-20 mole %).[19] No absorption spectrum, or color, was observed when Li-Pb alloy was in contact with molten LiCl, and it seems probable that no unusual "plumbide" species were present in the salt melt. These results are in line with chemical analyses of other samples of the melts as to the presence of Li_3Bi, or a lithium plumbide.

19. M. S. Foster, C. E. Crouthamel, D. M. Gruen, and R. L. McBeth, "First Observation of a Solution of Li_3Bi, An Intermetallic in Molten LiCl and LiCl-LiF," *J. Phys. Chem.* **68**, 980 (1964).

4. Nuclear and Radiochemistry

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TRACE ELEMENT PROFILES THROUGH A COAL-FIRED STEAM PLANT

The primary purpose of this program is to determine experimentally the trace elements in the influent and effluent materials of a selected TVA coal-fired power plant. A number of toxic elements are known to be present in coal; their ultimate fate following combustion of the fuel is uncertain. We hope to be able to establish the pathways of such elements through the fuel plant and to determine in what part(s) of the waste system they finally stop. This information is of considerable importance in planning slag, fly ash, and gas effluent control and disposal, as well as in understanding the environmental impact of such materials.

Sampling at the Allen Steam Plant was performed by Newell Bolton, industrial hygienist at ORNL, with assistance from the TVA sampling crew during the period January 26–February 2, 1972. A crew of 12 men worked 14 hr/day for two weeks to obtain five complete sets of samples.

During the sampling period the electric output of the generator was held constant at 240 MW. The consumption of coal at this level is about 90.7 metric tons/hr. Sampling of coal and slag was performed by taking grab samples during the course of the test; the air and stack gas samples were obtained by isokinetic sampling, using an ORNL-designed modification of the recently recommended EPA stack-sampling assembly. The ORNL sampling system used an alundum thimble as the primary particulate trap rather than the EPA recommended filter since our experience indicated that the filter would not survive the test conditions at Allen. From the weight of material collected, the total air volume passed through the thimble, and the velocity of the air through the system, one can hopefully calculate the total particulates at a particular time.

Three pre-precipitator and two post-precipitator points were sampled. Pre-precipitator points included the air heater, inlet air, and precipitator inlet. Post-precipitator points sampled were the precipitator outlet and the stack. Two solid samples were also taken: the coal prior to burning and the bottom ash or slag tank following combustion.

The total cubic feet of air per minute through the stack was measured as was the total weight of coal burned per minute. An attempt was made to measure the total weight of slag deposited per minute, but this was unsuccessful; the slag is accumulated in a water tank for 4 hr and then dumped with additional H_2O flushing. Attempts to sample and estimate the solid/liquid ratio gave very erratic results. Thus the slag was calculated by multiplying the percent ash obtained from the proximate analysis of the coal by the total weight of coal and subtracting the total weight of particulates entering the precipitator. The air heater and inlet air samples were found to be unsuitable for profile determinations, and so our profile consisted of the remaining samples. Of the five sets of samples no one set appeared to be without fault. For example, the precipitator outlet thimble in almost every case contained little or no visible sample despite the fact that the weights indicate about 100 mg was collected. The filter samples were broken in several instances, and, during some runs, precipitator blow-by apparently occurred.

So far data have been accumulated on three complete runs by use of nondestructive neutron activation analysis (NAA). Mercury has been determined on all samples by flameless atomic absorption (AA). A number of samples have also been analyzed by spark source mass spectrometry. Table 4.1 is representative of data obtained. The merucry has not been positively located in any of these samples; we think it is in the stack gas, but so far all sampling procedures have been unable to find it. Other than mercury, however, satisfactory material balance is seen in Table 4.1.

1. Energy programs.
2. Technical staff.

Table 4.1. Trace element content of coal and ash from Allen Plant by NAA – Test 9

	Coal CS-16	Slag tank ST-15	Precipitator inlet, fly ash PI-3	Precipitator outlet, fly ash PO-10
		Percent		
Al	1.13	6.6	6.5	3.5
Fe	1.30	10.1	9.2	23.5
Ca	0.40	2.70	1.42	0.49
Mg	0.15	0.41	0.7	0.88
K	0.30	1.27	2.3	1.70
Na	0.073	0.32	0.7	0.28
Ti	0.071	0.30	0.4	0.25
S	4.6			10.5
		μg/g		
Rb	7.4	50	<40	110
Mn	60	418	310	550
V	22	125	200	63
Cl	350		<5	1000
Br	2	<0.5	<1	10
Se	8	34	<80	1900
As	3.8	0.5	32	50
Sb	<0.6	<0.2	20	7
Cs	1.4	8	18	4
Co	3.4	19	21	58
Sc	3.5	22	26	10
La	5.1	42	32	11
Sm	1	8		2
Eu	0.20	1.4	2	1.0
Mo	20	55	1.50	
Ba	79	600	~800	
Cr	23	180		300
Ag	<2	<3		
Hf	4.0	5		
Ta	0.2	2	<5	<3
U	1.34	14	20	7
Th	3	20	30	
W	<5			
Hg[a]	0.068			

[a]Atomic absorption.

The next phase of the program (begun with a sampling on Sept. 5, 1972) involves a study of the ecological effects of the stack particulates. Soil and vegetation were sampled, and these specimens are currently being examined by NAA and AA. The object here is severalfold: (1) to try to establish fall-down pattern of particulates, (2) to study retention of these particulates, (3) to investigate ultimate fate of mercury and cadmium in particulates (as well as other toxic metals), and (4) to relate the results of our stack studies to the overall energy and environmental programs planned for the coming decade.

COOPERATIVE ISOTOPES PROGRAM

Information on radioisotopes. The joint program of the Isotopes and Analytical Chemistry Divisions continues to be concerned with characterization, analysis, and application of isotopes. The information-gathering function of this program furnishes essential data for use by ORNL people, by AEC personnel in isotopes, regulatory, and biomedical fields, and by other AEC contractors as well as by national organizations such as ASTM, NBS, and ANS. At the request of local health physics personnel, suggestions were made with regard to decay schemes for calculations of dose rates to be included in a revision of an ICRP handbook. One of the people engaged in preparation of the "GE Chart" sent information that our half-life values are being used and that agreement with their adoptions is good.

Despite the closing of the Isotopes Information Center on June 30, we have continued to receive and answer inquiries at about the same level as before. These involved, for example, calibration for ^{32}P in biological samples, standard methods for gamma activity and gamma dosimetry, measurement of curie-level ^{24}Na sources, methods for radionuclides in environmental samples, etc.

Practical specific activities were calculated for over 160 radionuclides of present or potential usefulness, produced in accelerators or reactors. For neutron-capture products, effects of target and product burnup were considered. At the same time, half-lives were updated. In answer to a request from NBS, a modernized version of our table of pure-nuclide specific activities was furnished. The specific activities of natural uranium isotopes were recalculated using the latest values of half-lives and the result of a detailed consideration of the abundance of ^{234}U. Experimental values[3] were averaged, discarding three outliers, to obtain 53.1 ± 0.5 ppm (by weight), significantly below 56 in the *Table of Isotopes.* Using the value of 54 adopted by Hyde, Perlman, and Seaborg, the activity of ^{234}U in natural uranium is substantially equal to that of ^{238}U, as it should be, since the two are in secular equilibrium. Therefore 54 ± 1 is recommended.

Barium-133 is useful as a long-lived standard for measurements of intensities of photons of low to moderate energy. Several careful studies have been made of its decay scheme, and the results of one of them differed from the others. We found an error in the calculations of those results, and corrections brought

3. R. F. Smith and J. M. Jackson, *Variations in U^{234} Content of Natural Uranium,* KY-581 (1969).

them into agreement with the others. L. T. Dillman of Ohio Wesleyan University assigned new values of half-life, 10.4 years; K x-ray intensity, 120%; and 356-keV gamma intensity, 62%; and we and M. J. Martin of the ORNL Nuclear Data Group concurred.

Experimental characterization. The latest product of our experimental program of characterization was a paper[4] giving the half-lives of 61 nuclides. Several of the values have important applications; ^{57}Co is used as a substitute standard for ^{99m}Tc (see below); ^{154}Eu and ^{155}Eu can be important contributors to the gamma activity of old waste; and ^{129}I and ^{10}Be are used in some cosmological studies. Two early values for the latter have been recalculated, a new one[5] has been reported, and all are now in the range 1.3 to 1.9 million years, averaging 1.6, in agreement with our determination. Our estimates[6] of the thermal-neutron cross sections of Ca isotopes were confirmed.[7] We found the intensity of the 88-keV gamma of ^{109}Cd to be 3.8 ± 0.1%, using a photon standard from NBS and a disintegration-rate standard from the British RCC; 462 days was adopted as the half-life.

Special problems. At intervals we are asked to assist with process problems. The following are typical. It was desired to have a noninstrumental method for detection of as little as 10^{-5} *M* free HCl in ^{137}CsCl material. Four indicators (one mixed) were tried in "cold" experiments, and two showed satisfactory sensitivities under laboratory conditions. However, their colors were not suitable for viewing through cell windows. We recommend that electrometric pH equipment be installed when feasible. It was found that high and erratic assays of certain ^{90}Sr process samples were due to a trace of unidentified solid. To measure tritium in discharged ventilation air from a processing building, we recommended that a slow stream of air from the discharge duct be passed through a train containing a filter, a flowmeter, a heated CuO tube, a $CaCl_2$ tube (as used by Health Physics), and a Drierite tube (for protection from atmospheric moisture). It is necessary to oxidize the sample, because spontaneous oxidation or exchange of tritium gas is very slow under ambient atmospheric conditions. Neutron activation analysis was suggested for determination of Na in enriched ^{7}Li.

Radioisotope quality control. Most of our quality-control activities are concerned with radioassay and with standards needed for such work. Eleven standards of ten nuclides were obtained during the past year, largely from NBS, and agreement with our previous calibrations was good. Measurement capability for discontinued products must be maintained because they are sometimes required as "special" items, occasionally occur as impurities in other products, and, being available as NBS standards, for example, can be used to support the validity of our calibrations for other nuclides.

Some of our assay and quality-control procedures, plus those used by other countries and by IAEA, were summarized in a report.[8] Two gamma ionization chambers used for assay of some products were checked electrically, a potentiometer was added to one to improve the precision of its readings, and they were recalibrated with a set of ^{60}Co standards.

A ^{67}Ga product was extensively measured by Ge(Li) and NaI(Tl) spectrometry and by 4π ionization chamber. Local results agreed very well with each other, and were 6% lower than those of ORAU, considered adequate. The local assay method was described in writing for ORAU and AEC personnel. The basis for assay, in the absence of a ^{67}Ga standard, was explained, and the effect of assumptions about the decay scheme was discussed. Cobalt-57 has been widely used as a long-lived substitute standard for ^{99m}Tc, an important radiopharmaceutical nuclide. Review of properties, availability, and NBS-traceability of various radionuclides led to our recommendation that the use of ^{57}Co be continued. The suggested half-life is 271 days, the average of our value with two other careful ones.

Users of liquid scintillation counting are gradually realizing that the technique is subject to interferences, such as quenching and chemiluminescence, which are poorly understood and may not be anticipated. In the assay of ^{14}C, we obtained anomalous results by the "standard-addition" method, in which liquid scintillation counting of a sample mixture is first done, followed by addition of a portion of an organic standard from NBS, and then is recounted to determine efficiency. Results were high compared with the accepted method, which uses a separate standard mixture,

4. J. F. Emery, S. A. Reynolds, E. I. Wyatt, and G. I. Gleason, "Half-Lives of Radionuclides – IV," *Nucl. Sci. Eng.* **48,** 319 (1972).

5. F. Yiou and G. M. Raisbeck, "Half-Life of ^{10}Be," *Phys. Rev. Lett.* **29,** 372 (1972).

6. S. A. Reynolds and W. T. Mullins, "Neutron Cross Sections and Flux Monitoring," *Anal. Chem. Div. Annu. Progr. Rep. Oct. 31, 1969,* ORNL-4466, p. 74.

7. F. P. Cranston and D. H. White, "Thermal Neutron Capture Cross Sections in Calcium," *Nucl. Phys.* **A169,** 95 (1971).

8. *Radioisotope Production and Quality Control,* STI/DOC/10/128, IAEA, Vienna, 1971.

and by comparison with mass spectrometry. Although no explanation has been found, the phenomenon seems to be related to that reported by Moghissi,[9] and, privately, by representatives of two reputable radioactivity laboratories. The standard-addition method was therefore abandoned. Tests of various aspects of ^{14}C analysis were made in the course of the investigation. Accuracy of weighing and dilution were confirmed, stability of the counting mixture was tested, effects of components were studied, linearity of counter response was verified, and crude spectra of various samples were compared. Additional tests will be done when NBS issues a new ^{14}C standard later this year.

In investigating discrepancies in the assay of ^{33}P, for which a substitute standard of ^{45}Ca is used, we found that the "carrier-free" ^{33}P was lost from the scintillator mixture. Addition of microgram quantities of phosphate eliminated the losses. Routine tritium analyses were reviewed, and practices were found to be appropriate, except that some organic samples may have given low results because of the presence of water, unknown to the analysts. Such samples can be assayed by addition of a ^{3}H-toluene standard. Recent papers have contained information that deuterium compounds, including D_2O, contain variable concentrations of ^{3}H; D_2O of course is used as starting material for the preparation of many other compounds. We found that a local supply contained 3.8 μCi/ml. Our postulate is that small quantities of neutron-irradiated D_2O, which may contain over 10 mCi/ml, have been inadvertently introduced into some D_2O stocks.

Work with national organizations. Participation in the work of national organizations has increased, with the appointment of S. A. Reynolds as chairman of ANS-16, the Standards Subcommittee of the ANS Isotopes and Radiation Division. Subcommittee members are being sought, and plans are being developed for the group's work. Early tasks are expected to be concerned with standard materials and methods for radioisotopes and standard decay-scheme data. A session on absolute counting is being arranged for the ANS meeting in June 1973. We were asked to advise on the quality control program of the College of American Pathologists, and subsequently participated in the "round robin" on ^{131}I. By invitation, we also participated in discussions of the NBS program and the radioactivity-standards actions of the Atomic Industrial Forum. A list of nuclides was drafted for which decay-scheme data are needed for the NRC standards subcommittee. The list will be submitted to advisors for the AEC-NSF nuclear data project and will be a factor in setting priorities for work in that area. A modernized version of the introduction to the subcommittee's *Guides*[10] was submitted to the university faculty member who has overall responsibility for the revision.

COOPERATIVE PROGRAMS IN APPLIED NEUTRON ACTIVATION ANALYSIS

Elm bark beetle tagging. The European elm bark beetle *scolytus multistriatus (Marsham)* is the carrier that transmits the Dutch elm disease *ceratosystis ulmi (Buisman)* from tree to tree. Little is known of the beetle's habits, movements, and population. We were asked by the U.S. Department of Agriculture (USDA) Northern Forest Experiment Station, Delaware, Ohio, to assist in devising a means of tagging elm bark beetles so that tagged beetles could be released, later recaptured, and identified. In the procedure selected, the beetles were immersed in a gold solution for a few seconds; it was found that this short treatment tagged the beetles with sufficient gold (1.0 to 0.015 μg of gold per beetle) to be measured after a 6-hr irradiation in the Bulk Shielding Reactor (BSR) and 3 days decay. The use of a radioactive tracer was discussed but rejected, as eventually the tagged beetles would be released in populated areas.

Using our procedure workers at the USDA tagged and then released a number of beetles in a controlled area. The beetles were then collected in screen cages covered with a flypaper-like "stickum," as is normally done. It was found that the "stickum" could be removed with a number of solvents, and in all cases most of the gold tag remained on the beetles. Field tests are in progress using many vials of beetles in experiments aimed at determining the composition of certain beetle populations from the ratio of tagged to nontagged beetles.

Determination of mercury and other elements by neutron activation. Neutron activation analysis continues to be a useful tool for the determination of mercury. We have used it for a number of referee samples submitted by outside agencies. Mercury has been determined by activation analysis in fly ash, coal, sediment, fish, dry liver, tuna, wheat, flour, orchard leaves, dried blood, placenta, and hair. Many of these samples have also been analyzed by atomic absorption

9. A. A. Moghissi and M. W. Carter, "Internal Standard with Identical System Properties for Determination of Liquid Scintillation Counting Efficiency," *Anal. Chem.* **40**, 812 (1968).

10. B. Kahn, G. R. Choppin, and J. G. V. Taylor, *Users' Guides for Radioactivity Standards*, National Academy of Sciences–National Research Council, Washington, D.C., 1967.

at ORNL. Table 4.2 lists values obtained on U.S. Bureau of Mines round-robin samples and two NBS standards. The results in Table 4.2 indicate that agreement is very good – both between the two ORNL techniques and between ORNL and the average values obtained elsewhere.

The mercury in dried blood, placenta, and hair is an NSF-supported project from Vanderbilt University and the Environmental Science and Engineering Corporation of Nashville. The concentration ranges of mercury in the tissue are: (1) dried placenta, 0.021 to 0.056 μg/g; (2) dried cord blood, 0.017 to 0.12 μg/g; and (3) hair, 3.64 to 4.9 μg/g.

We have continued in a number of other cooperative programs, some arranged through ORAU and others (funded) through AEC contracts. Among the former are assistance to Dr. Gail Norris of Denison University, who is studying Al in human lung, and instruction and demonstration of NAA lab techniques for a group of ORAU students. The latter were part of a summer study group directed by G. I. Gleason of ORAU. A separate joint research project between Gleason and members of this group was concerned with half-life measurements.

Besides the work for the EPA, Vanderbilt University, and the U.S. Department of Agriculture (mentioned elsewhere), we have also collaborated with a researcher from NASA who was interested in examining small occlusions in moon rocks by NAA, and physicians at a VA hospital in Connecticut who are studying zinc in eye tissue.

14-MeV neutron generator studies. A seven-month program sponsored by the U.S. Army Land Warfare Laboratory, Aberdeen Proving Grounds, was completed. The final report will be published by the Army.

Use of our Kaman nuclear neutron generator for routine 14-MeV neutron activation analysis has steadily declined during the past year. No more than 50 samples of Li, K, Ca_2O, Ta, V, and Nb were analyzed for oxygen. Other elements determined were iron and silicon in coal and coal ash.

SPECIAL MEASUREMENT AND FISSION PRODUCT RELEASE STUDIES

Search for beta decay of ^{96}Zr. The heaviest isotope of zirconium, ^{96}Zr, is energetically unstable for beta decay and possesses a half-life long enough to exist in nature. We attempted to detect the beta decay of ^{96}Zr by the presence of its daughter nuclide, 23.4-hr ^{96}Nb. In the ORNL low-background gamma spectrometer, the coincident gamma transitions from ^{96}Nb make possible both a high-detection sensitivity and an identification of the radionuclide. Accordingly, the spectrometer was calibrated with a sample of cyclotron-produced ^{96}Nb, along with thorium and uranium standards.

A 9.64-g sample of Zr enriched to 57.4% ^{96}Zr was measured for 9573 min, and a background determination was made for 6637 min in the ORNL low-background spectrometer. The data were analyzed by least-squares techniques perfected for the lunar sample analysis program. Thorium at 3.8 ppm and uranium at 0.8 ppm were determined from the data, and gamma rays from these elements seriously impaired our ability to measure ^{96}Nb. In fact, ^{96}Nb was not detected in this experiment, but we were able to set an upper limit

Table 4.2. Results from standard samples run for mercury by NAA and AA

Sample	Mercury (μg/g)		
	NAA	AA	Accepted[a]
USBM P1 coal	0.21 ± 0.021	0.22	(0.196)
USBM P3 coal	0.209 ± 0.006	0.23	(0.176)
USBM P4 coal	0.04	0.04	(0.047)
DRB-C coal	0.279 ± 0.006	0.26	(0.255)
DRB-E coal	0.110 ± 0.001	0.090	(0.135)
NBS 1630 std, coal	0.105 ± 0.03		(0.130)
NBS orchard leaves	0.158 ± 0.005	0.150 ± 0.005	(0.155)
ORNL tuna	0.45 ± 0.01	0.425	
EPA sediment 3	125 ± 10	112 ± 2	(110 ± 21)
EPA sediment 4	46.8 ± 3	43.4 ± 0.5	(43.9 ± 9)
EPA sediment 5	0.055 ± 0.10	0.76 ± 0.025	(0.22 ± 0.38)

[a]Average of round-robin determinations except for NBS 1630 standard, coal, and NBS orchard leaves.

of ≤0.13 dis/min of ^{96}Nb for the sample, from which we infer a half-life of at least 3.6×10^{17} years. This is possibly the longest half-life known for a beta-unstable nucleus.

From theoretical considerations of log ft values for similar cases, we feel that our method may have sufficient sensitivity to make definitive measurement of this half-life, provided that a source of zirconium of sufficient purity can be found.

The sample used here is equivalent to about 200 grams of natural zirconium. A kilogram sample of national zirconium containing thorium and uranium at levels below 0.1 ppm would be a suitable sample for a second search.

This is a cooperative program with E. Eichler and G. D. O'Kelley of the Chemistry Division and J. B. Ball of the Physics Division.

Round-robin determinations. We have participated in a pilot study on radionuclide identification and activity measurement sponsored by the College of American Pathologists. The sample was kindly provided by S. B. Garfinkel of the NBS, and our results were reported directly to the NBS. The other participants included average nuclear medicine laboratories, and the overall objective was to provide data on the ability of nuclear medicine laboratories to identify and standardize an unknown radionuclide solution.

The sample consisted of an unlabeled vial containing an unspecified quantity of a radionuclide in solution. We identified the radionuclide as ^{131}I, with no detectable impurities by Ge(Li) spectroscopy. Our value for the amount of ^{131}I in the vial, 64.2 ± 1.3 μCi, is in excellent agreement with the value 64.67 ± 1.36 determined by the NBS.

^{235}U content of fission monitors. A reliable technique for the nondestructive determination of ^{235}U present in large area foils was devised, using the low-level 5 × 4 in. NaI(Tl) system. Thin foils are placed in close proximity to both the top and bottom detectors in the system. Such an arrangement yields essentially 4π geometry and provides maximum sensitivity for the quantitative determination of total uranium. The method requires a standard assayed by an independent method, yielding precisions of ±1% with counting periods of 10 min per foil at the 1-mg source level. Approximately 30 monitors consisting of three sample types have been measured with the system.

Experiments are being performed to determine the sensitivity for ^{239}Pu and ^{237}Np fission foils.

Fission product behavior in HTGR coolant circuits. We have continued our assistance to the ORNL high-temperature gas-cooled reactor Nuclear Safety Project (coordinated by H. J. De Nordwall). One of our objectives is to define and eventually predict the release and behavior of fission products in HTGR coolant circuits. In meeting this objective, we are conducting a variety of measurements and studies of the Peach Bottom HTGR at Delta, Pennsylvania. We periodically monitor the fission gases in the primary coolant circuit. This determination not only defines the efficiency of the coolant cleanup plant for fission gases, but also provides a measure of that fraction of metallic fission products released to the primary circuit via gaseous precursors. We also periodically determine, during reactor down time, the distribution of fission products in the large ducts of the primary circuit. The primary circuit consists of the reactor vessel, two steam generators, and helium coolant compressors operated in parallel. The large ducts that carry the coolant from the reactor vessel to the steam generators, to the compressors and back to the reactor, range in size from 28 to 40 in. in diameter. We scan these ducts by remote gamma spectrometry, using a collimated Ge(Li) detector, in a manner similar to that described by Houtzeel and Dyer.[11]

In addition, we analyze dust from the reactor's dust collectors and primary circuit gas samplers, which we insert and remove at intervals. Dust samples are analyzed by determining their particle size distribution, composition and chemical nature, morphological character, and radionuclide content. Analysis of gas sampler components including gaseous diffusion tubes, impactors, etc. indicate what fraction of fission products, for example ^{137}Cs, is transported as gases, as well as the total concentration of each radionuclide in the coolant.

Our measurements thus far indicate that most of the radionuclides are transported on dust particles. Although gaseous ^{137}Cs, ^{110m}Ag, and ^{90}Sr exist between the reactor and the steam generators, they have been detected only on dust particles behind the steam generators. Results of tests on dust samples fractionated according to particle size and density indicate that most of the radionuclides are associated with metal- or metal oxide-containing particles rather than those that are mostly carbon. This observation suggests a relatively high rate of reentrainment of fission products that have previously plated out on the primary circuit walls. Results of scans of the large ducts show a gradual decrease of surface plate-out in fair agreement with calculational models.

11. A. Houtzeel and F. F. Dyer, *A Study of Fission Products in the Molten-Salt Reactor Experiment by Gamma Spectrometry*, ORNL-TM-31-51 (1972).

Fission product release. The study of fission product release from reactor fuel microspheres is a cooperative and continuing program[12] with the Reactor Chemistry Division. The release rates of ^{134}Cs, ^{137}Cs, ^{90}Sr, ^{140}Ba, ^{141}Ce, and ^{144}Cl are being measured from several types of castings and matrices in microspheres and bonded beds.

The ^{141}Ce and ^{144}Ce losses were observed upon heating resin-containing sulfur-coated particles, and subsequent tests by washing the particles for 30 min in 50% HNO_3 removed most of the fission products in a large portion of the coated microspheres. Normally there is no loss of fission products from the particle upon washing except traces which are on the surface. This is being evaluated further with different types of coatings and particle matrices.

NEW FACILITIES AND EQUIPMENT

Experiments at ORELA's photon-activation facility. Work continued with the Division's photon bombardment facility at the Oak Ridge Electron Linear Accelerator (ORELA).[13] Simultaneously with the sensitivity survey, performance tests and modifications of the facility were carried out, which resulted in its final analytical readiness.

A. *Systematic survey of photon-activation sensitivities.* Eight elements were added to the sensitivity survey. Table 4.3 lists these results and shows very high sensitivities for carbon, nitrogen, fluorine, and phosphorus, whose reactor NAA is difficult or impossible. Analogous results for oxygen have already been reported.[13]

It is interesting to note the fast-neutron contribution – by (n,p), (n,α), and even (n,γ) reactions – to these data. In fact, the ORELA (with its massive tantalum electron target) was designed as a neutron source for reactor physics experiments. Very schematically, the neutron-production mechanism is

$$e^- + \mathrm{Ta} \rightarrow \gamma\ (\text{bremsstrahlung}),\ \gamma + \mathrm{Ta} \rightarrow n\ .$$

In this process copious fast neutrons are generated, while gamma-ray energies are degraded to values much lower than the original 140-MeV electron energy. This

12. W. S. Lyon et al., "Applied Gamma Spectrometry," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4749.

13. W. S. Lyon et al., "Systematic Survey of Photon Activation Sensitivities at the ORELA," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971*, ORNL-4749, p. 35.

Table 4.3. New photon-activation analysis sensitivities and specific activities at ORELA's Analytical Chemistry Division facility[a]

Element (target)	Reaction	Product nuclide	Measured gamma ray (MeV)	Sensitivity (cpm/μg)	Specific activity (dpm/μg)
C (graphite)	γ,n	^{11}C	0.511	940	4,000
N ($NaNO_3$)	γ,n	^{13}N	0.511	890	3,900
F ($NaBF_3OH$)	γ,n	^{18}F	0.511	5900	26,000
Na ($NaNO_3$)	γ,n	^{22}Na	0.511	0.16	0.76
	n,γ	^{24}Na	1.369	2.4	53
Mg (metal)	$\gamma,p;n,p$	^{24}Na	1.369	7.0	150
			2.754	3.4	
Al (metal)	n,p	^{27}Mg	0.84 + 1.013	3.4	49
	n,α	^{24}Na	1.369	0.79	17
			2.754	0.37	
P (red)	γ,n	^{30}P	0.511	1900	8,200
	$\gamma,2p$	^{29}Al	1.28	6.4	140
	$\gamma,n2p$	^{28}Al	1.78	6.5	170
Ta (metal)	γ,p	^{180m}Hf	0.215 + 0.333 + 0.444	32.0	72.0

[a]Interference-free. For a one-half-life or a 2-hr bombardment (whichever is smaller) with 140-MeV, 30-kW electron bremsstrahlung. Counting in Lucite annihilation sandwich through 1.24-cm Lucite absorber directly placed on a 7.62 × 7.62 cm NaI(Tl) detector.

phenomenon also explains the fact (observed and pointed out before)[13] that sensitivities and potential interferences at our facility are similar to those observed by other authors at lower bremsstrahlung energies.

Sensitivities and specific activities in Table 4.3 are average values for the four irradiation capsules of the spherical "rabbit" at the ORELA facility. Activation differences between these capsules are discussed in Part B. Pure tantalum crystals and bottom-ash (TVA Allen Steam Plant) samples were analyzed in this facility for carbon; the latter showed an unexpected 1.3% concentration. In general, these analyses indicated the need for coincidence counting equipment [or for a Ge(Li) system] to reduce interference in the counting of annihilation radiation – most important in photon activation, as illustrated in Table 4.3.

B. *Performance tests and modifications of the photon-bombardment system.* Some structural changes were introduced in the rabbit sphere of our irradiation facility at the ORELA to improve its performance; that is, to increase its spinning-precessing speed and consequently obtain a homogeneous bombardment of the four samples it carries.

As aerodynamical tests in a mock-up chamber proved satisfactory, an actual 30-sec bombardment was made of four capsules, each containing one phosphorous and one magnesium sample. The reactions $^{31}P(\gamma,n)^{30}P$ and $^{25}Mg(\gamma,p)^{24}Na$ were thus induced, and their radioactive products measured in similar conditions for comparison purposes. The standard deviation for the ^{30}P activity induced in the four capsules was 30.7%, while that for ^{24}Na was 23.1%. This showed that bombardment was not homogeneous for the four capsules; that is, the rotational speed of the sphere was insufficient, during the short bombardment, to ensure irradiation homogeneity. We observed, however, that the standard deviation for the activity ratio $^{30}P/^{24}Na$ in the four capsules was only 6.9%. It is clear, therefore, that irradiation homogeneity is quite satisfactory within each capsule. Because these containers are conveniently large (~2 cc), a standard and a sample can usually both be bombarded in the same capsule. Thus, we consider our system ready for activation analysis and the solution of the above problem somewhat academic.

Physics experiments at the ORELA required the design and installation of a new tantalum target – now encased in beryllium – for the electron beam. This target interfered mechanically with the correct positioning of our bombardment chamber, causing the photon flux intensity to drop by a factor of 7.9; the spinning of the sphere was also affected. Thus, the shape of our transfer system had to be modified to regain satisfactory positioning and performance of the rabbit sphere during bombardment.

The modified system was checked by loading a 10-mCi ^{60}Co source in the sphere and finding its working position in the irradiation chamber – from the outside – with a detector. It was also concluded from this test that the sphere-bombarding position is insensitive to a large range of load variations (82.3 to 124.3 g) and to all the changes in air flow available at our facility. Though these results are quite satisfactory, a new sphere design and a bombardment homogeneity test are being considered to further check the modified facility.

Preliminary analysis of air-filter impurities at the new High-Flux Neutron Activation Laboratory. At the High-Flux Isotope Reactor, we have begun a program to measure concentrations of air particulates (multielement analysis) both in pristine environments and near pollution sources – particularly energy plants. The first experiments will be necessarily aimed at establishing levels of impurities in air-filtering materials, because these are going to determine the analytical detection limits of our instrumental analyses. Table 4.4 exemplifies preliminary results for four elements found in samples of Whatman No. 42 filter paper; they correspond to a 10-min irradiation followed by 3- to 4-hr decay.

Absolute activation analysis was used in these determinations; the necessary thermal and resonance flux data were obtained by simultaneous bombardment of aluminum-diluted manganese (σ_0 = 13.3 *b*, I_0 = 15.6 *b*) and gold (σ_0 = 98.8 *b*, I_0 = 1558 *b*) monitors. The solution of the equations resulting from the flux measurements and the absolute calculations were carried out at the PDP-15 computer. Table 4.4 also

Table 4.4. Results obtained at the HFIR facility

Element	Analysis of Whatman No. 42 air-filter paper		Test of absolute activation analysis method		Error (%)
	Sample 1 (ppm)	Sample 2 (ppm)	Found (%)	Known (%)	
Na	16.8	16.8			0.7
Cl	291	282			1.7
Mn	0.27	0.26	0.0867	0.087	0.9[a]
					–0.3[b]
Br	0.24	0.22			5.6
Au			0.109	0.109	0

[a]Whatman filter analysis.
[b]Test of absolute AA subroutine.

shows satisfactory results of an accuracy test of the absolute activation analysis subroutine, for which known concentrations of manganese and gold in aluminum (monitors) were redetermined. Clearly, the detection limits listed can be easily improved, and the number of determined elements can be increased by adequate combination of irradiation lengths and decay times. This – as well as tests of the absolute-activation-analysis PDP-15 program with complex synthetic samples – will be the next step in our development work.

LOW-LEVEL GAMMA-RAY SPECTROMETRY OF RETURNED LUNAR SAMPLES

Abundances of the primordial radioelements K, Th, and U in Apollo 15 samples, as determined by nondestructive gamma-ray spectrometry. Twenty-two samples returned to earth by the Apollo 15 astronauts have been studied by nondestructive gamma-ray spectrometry. Patterns of primordial radioelement distribution in these materials show subtle differences from the distributors observed at other sites.

Our extensive suite of crystalline rocks is distinguished by its uniformity in primordial radionuclide content. These rocks may be classified as mare basalts, and the chemical uniformity seen here suggests that these samples are characteristic of the basaltic flows which underlie the Hadley-Apennine landing site. The Apollo 15 basalts form a new and distinct group on a plot of the mass ratio K/U vs concentration of K, and they consistently manifest a higher value of K/U for a given concentration of K than the Apollo 12 basalts. The range of K concentration for the Apollo 15 basalts lies between about 300 ppm (K/U = 2200) and 540 ppm (K/U = 3400).

The soils and breccias of Apollo 15 are much higher in primordial radioelement concentrations than the basalts from the same area.

Concentrations of cosmogenic radionuclides in Apollo 15 rocks and soil. We have studied in some detail the irradiation history of lunar samples by measuring the concentrations of radionuclides produced by solar and galactic cosmic-ray bombardment. Our latest results are mostly concerned with nuclides of long half-life, because the samples in question were measured rather long after they were collected. Our suite of samples includes a large group of basaltic rocks with low concentrations of K, Th, and U; thus, weak components of the gamma-ray spectra due to cosmogenic radionuclides can be determined in these samples with less interference than in lunar soils and breccias.

Sample 15379 (58.6 g) is a small basaltic fragment collected with the rake as part of the comprehensive sample at station 7 (Spur Crater). This fragment is a newcomer to the lunar surface, as its ^{26}Al content indicates that it was ejected from depth only 0.8 to 1.3 million years ago.

We have studied a group of samples consisting of soil 15471, and rocks 15475, 15476, and 15495, which were collected 28 m south of the rim crest of Dune Crater (station 4). The ^{22}Na and ^{26}Al data for 15471 are compatible with a mean-sampling depth of about 2 cm, which is in good agreement with field geology predictions. The rocks are all fresh in appearance, and when on the lunar surface were observed to lack either fillets or extensive burial. The ^{26}Al concentration of 15475 is below saturation and indicates that it was ejected onto the lunar surface as recently as 0.7 to 1.1 million years ago. Similar considerations suggest that 15476 has resided on the surface for only 0.8 to 1.5 million years. The exposure of 15495 is difficult to assess; however, it apparently has lain exposed for a minimum of 2.5 million years. Information of this type is useful for estimating recycling rates for determination of lunar erosion.

K, U, and Th concentrations in lunar sample 15382 by nondestructive gamma-ray spectroscopy. Sample 15382 was a small (3.2-g) fragment collected with the rake by Apollo 15 astronauts. Thin-section studies indicated that this fragment had textures and mineralogy similar to KREEP basalts found in lunar soils. From these considerations special efforts were taken to determine the characteristics of the remaining sample of 15382 (2.24 g).

Final values for K, Th, and U showed that 15382 had much higher concentrations than those of other mare basalts collected at Hadley-Apennine. Values in parts per million for K, Th, and U were 4900 ± 500, 10.5 ± 0.5, and 3.1 ± 0.4, respectively, whereas the hypothetical values for KREEP are 5200, 17.2, and 4.5, respectively.

No other known lunar rock type has K, Th, and U concentrations similar to those of KREEP; consequently, sample 15382 could be pure KREEP. Data collected from Apollo 12 and 14 samples suggest that there is about a 30% variation in the K, Th, and U concentrations of KREEP, and sample 15382 is within that range. Of course, one cannot exclude the possibility that sample 15382 is a mixture, but if so the amount of contaminants should be small. If in fact this sample represents original crystalline KREEP basalt, it is obviously an important sample for future study of the mineral isochron and bulk and mineral chemical composition.

In all the aforementioned studies, G. D. O'Kelley of the Chemistry Division is principal investigator; in the

last study E. Schonfeld of NASA, Houston, is a co-investigator.

EFFECTS OF RADIATION ON ANALYTICAL METHODS

The effect of radiation on many of the organic and inorganic compounds used in analytical chemistry has been studied from a "radiation chemistry" viewpoint. However, few studies have been made under the conditions attained when these compounds are used as analytical reagents. As might be expected, the chemical environs of a given compound may and do modify greatly its behavior under the impact of high-energy radiation. Therefore it is impossible to extrapolate from the radiolytic behavior of a reagent in a highly specific "clean" environment to its behavior when used analytically, that is, in a relatively "dirty" chemical environment. It has been one of the major aims of this program to delineate the radiolytic conditions which would cause error in a given method and to find ways to curtail this error when present. The work carried out last year, while still adhering to this objective, has also been concerned with the possible ways in which high-energy light radiation could be used as an analytical tool. Several of the specific projects reported were approached with this end in mind.

The effect of gamma radiation on some organic pH indicators. The effect of gamma radiation on the color intensity of a series of organic dyes, commonly used as pH indicators, has been studied. The dyes are thymol blue, phenol red, methyl red, bromocresol green, and methyl orange. In aqueous medium, at commonly used concentration levels, all the dyes demonstrate ability to indicate pH after gamma doses of 10^3 to 10^4 R. In general, all the dyes show less sensitivity to radiation in neutral or basic media. The indicators, on irradiation, show a pseudo first-order degradation reaction rate which was shown to be the expected radiation effect zero-order reaction rate. Of the compounds studied, methyl orange proved to be the most sensitive to radiation, while bromocresol green is the most resistant to radiation damage. It was found that the addition of small amounts of ethyl alcohol to the medium is effective in decreasing dye radiation damage to a large degree.

The results of this work have been accepted for publication by the *Journal of Radioanalytical Chemistry.*

Effects of alpha radiation on analytical reagents. One of the original objectives of this program was to ascertain the relative effects of the various types of radiation on analytical methods and reagents. With this in mind, a ^{252}Cf neutron source was modified and used in conjunction with lithium to study the effect of alpha radiation on the series of pH indicators mentioned in the above section. It was found that in all the cases studied the effect of alpha radiation on a per unit dose basis is approximately 25 to 35% of that obtained under gamma radiation. It is evident that the active agent in radiation decolorization of many of the color agents used in analytical chemistry is the hydroxyl free radical resulting from the radiolysis of the aqueous medium. The H_2O_2 formed by alpha radiation in aqueous medium in large amounts, as compared with that formed by gamma radiation, is relatively inactive in the decolorizing process. It is hypothesized that the effect of gamma radiation on analytical methods can be considered the limiting value for radiation effects unless H_2O_2 is specifically active in a given case.

The use of radiation in trace analyses. In accordance with the objective of using high-energy radiation for useful purposes in analytical chemistry, a study was initiated using gamma radiation for trace analyses. During the investigation on the effect of gamma radiation on the pH indicators, we noted that the decolorization of the dye (methyl orange) was retarded by traces of Cl^-. On studying this effect more closely, we found that less than 1 ppm of either Br^- or Cl^- could easily be detected by virtue of this protection. However, since the reaction was not specific, that is, any reducing agent would interfere, tests were carried out to see if metal ions could be detected in the same manner. By selection of the proper conditions, it was found that copper can be detected in the sub-ppb range of concentration. Interference studies showed that Cd, Ni, Al, Ba, Zn, and Ca in concentrations equal to or greater than the Cu concentration do not interfere. The program was terminated before the study could be completed.

Post-accident hydrogen generation in a loss-of-coolant accident. Two studies which had been initiated and essentially completed under another program were completed. Two papers on these studies were submitted and accepted for publication, "Post-Accident Hydrogen Generation from Protective Coatings in Power Reactors," by *Nuclear Technology,* and "Post-LOCA Radiolytic Hydrogen Generation in Water-Cooled Power Reactors," by *Nuclear Safety.*

5. Spectrometry and Physics Methods

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MASS SPECTROMETRY DEVELOPMENT

The investigation of the mechanism of surface ionization was continued. Many applications and uses of this technique, both for isotopic analyses and for isotope-dilution analyses, were studied. The desorption of uranium ions and of neutrals from carburized rhenium-filament surfaces has been investigated with a view to improving the ionization efficiency for uranium and other actinide elements.[5]

Rhenium analysis by surface ionization–isotope-dilution method. Investigation of the surface ionization of rhenium from a hot tungsten filament resulted in a method for the determination of rhenium in rhenium-tungsten alloys used to make thermocouples for nuclear reactors. A detailed description of this work has been accepted for publication.[6] Quantitative analysis of rhenium on milligram-size samples of Re-W alloys containing 3 to 25 wt % rhenium has been done by use of the isotope-dilution method. Pure (99.5%) ^{187}Re in perrhenate form obtained from the ORNL Isotopes Division was used as the spike. By pulse-counting techniques, sufficient ion signals can be obtained on a single-filament loading of 5 to 10 μg of rhenium; the relative standard deviation is ±1 to 2%.

Age dating of speleothems. A graduate student, Glenn Thompson from Memphis State University, is doing his masters thesis research at ORNL through the Oak Ridge Associated University's Fellowship Program. His research concerns the dating of speleothems by a combination of the ^{238}U/^{234}U and ^{234}U/^{230}Th dating methods. The uranium will be determined by isotope dilution–mass spectrometry, and the ^{230}Th will be determined by alpha spectrometry with ^{228}Th as the spike.

Determination of the abundance of ^{236}U in tektites. The three-stage high-abundance-sensitivity mass spectrometer described completely elsewhere,[7,8] was used to determine the possible existence of ^{236}U in some natural minerals. This work was done in cooperation with R. V. Gentry of the ORNL Chemistry Division. Large samples of tektites (gadolinites) were processed for uranium through our clean-chemistry laboratory and then were isotopically analyzed by loading relatively large amounts (200 to 300 ng) on to rhenium filaments for surface ionization. The abundance of ^{236}U determined in these samples was reported as $\leqslant 1.5 \pm 1.0$ ppb. Further work in this area will be attempted; the possible existence of ^{244}Pu in nature will be investigated.

Absolute abundance of krypton in the earth's atmosphere. The abundance of elemental krypton in the earth's atmosphere was determined by the isotope-dilution method. A calibrated amount of isotopically altered krypton was added to large known volumes of air and thoroughly mixed. The spiked krypton was then concentrated and separated from the air. The amount and composition of the tracer and the isotopic com-

1. On leave of absence to I.A.E.A., Vienna, Austria.
2. Postdoctoral Presidential Intern Appointment.
3. ORAU Graduate Participant from Memphis State University.
4. On loan to ORNL Civil Defense Project.
5. D. H. Smith, "Mass Spectrometric Investigation of Surface Ionization. X. Desorption of Uranium Ions and Neutrals from Carburized Rhenium," *J. Chem. Phys.* **55**, 4152 (1971).
6. R. L. Walker, "Rhenium Analysis by Surface Ionization–Isotope Dilution Method," *Int. J. Mass Spectrom. Ion Phys.*, in press.
7. A. E. Cameron, W. H. Christie, H. S. McKown, W. T. Rainey, and D. H. Smith, *Analytical Mass Spectrometry at Oak Ridge National Laboratory*, ORNL-4643 (1971).
8. D. H. Smith, W. H. Christie, H. S. McKown, R. L. Walker, and G. R. Hertel, "A New Three-Stage Mass Spectrometer for High Abundance Sensitivity Measurements," *Int. J. Mass Spectrom. Ion Phys.*, in press.

position of the natural krypton had been determined previously; therefore, complete chemical recovery of the krypton was not required. About 1×10^{-4} cc (standard) of krypton was recovered, and the $^{84}Kr/^{86}Kr$ ratio was measured on a static-mode mass spectrometer. From seven samplings the krypton content in air was determined to be 1.102 ± 0.0075 ppm. A report of this work is planned for publication.

Cross-section measurements of ^{85}Kr. Long-term storage and/or disposal of the radioactive noble-gas fission products poses a difficult problem. Perhaps the most important rare-gas fission product is ^{85}Kr. If the thermal-neutron capture cross section were high enough, then the ^{85}Kr possibly could be transmuted into stable ^{86}Kr in nuclear reactors and thus minimize the disposal problem.

Mass spectrometric analyses were carried out on unirradiated and irradiated samples of ^{85}Kr by use of a static, 6-in.-radius, 90°-sector magnetic instrument. The thermal-neutron capture cross section for ^{85}Kr was determined to be 1.66 ± 0.206 b. It was concluded that the burnup of ^{85}Kr in power reactors as a possible means of disposal is not feasible. This work was done in collaboration with Bemis et al. of the ORNL Chemistry Division. The results of this work have been published.[9]

ORGANIC MASS SPECTROMETRY

Low-resolution mass spectrometry. The single-stage mass spectrometer for the analysis of organic samples was used to process approximately 1000 samples during the past year. The Body Fluids Program continues to furnish about 50% of the samples as a result of the effort to identify fractions collected in high-pressure liquid chromatography of urine and blood serum. Mass spectrometry has been of major importance in the positive identification of at least 35 compounds isolated from urine during the year. Several of these compounds have not been previously detected in urine (e.g., 5-hydroxymethyl furoic acid and its glycine conjugate). Increasing use has been made of the gas-chromatograph (GC) inlet system in this program. Many of the fractions collected from the liquid chromatograph contain 5 to 10 components; the GC inlet can resolve most of these into reasonably pure compounds.

Increased use is being made of the library of mass spectra stored on the IBM 1130 magnetic disk. As spectra of known compounds are generated, they are stored on the disk to assist in the identification of future spectra. During this year about 150 new spectra were added to the library, bringing the total to 650.

Several groups in the Biology Division have requested mass spectra either as an aid to the identification of an unknown or to prove the purity of a known material. A large number of samples have been analyzed for biologists interested in genetic defects resulting in changes in compositions of body fluids. This work has been very similar to that done for the Body Fluids Program of the Chemical Technology Division. Much interest has been generated in the study of nitrosamines as carcinogens. We have analyzed many samples of amino compounds and nitroso derivatives that will be used in these studies.

We have been asked for help by Y-12 personnel from many different programs, both production and development. Contaminants and sources of contamination have been identified in several cases (e.g., clean-room contamination and electroplating-bath failure).

A series of high-specific-activity ^{14}C biological compounds were analyzed to check the radiochemical assay. In several cases the specific activity of the compound was found to be higher than that claimed by the manufacturer. This method seems to be very satisfactory, since only the radioactivity of the molecule of interest is measured, not the gross radioactivity, which might be in error due to impurities present.

High-resolution mass spectrometry. The high-resolution mass spectrometer has been interfaced to the IBM 1130 computer and is now in routine use. A 17-stage electron multiplier in current-integration mode is used as the detector; the output signal is digitized at selectable rates up to 10 kHz. For routine operation, resolutions of 10,000 to 15,000 are used (source slit width, 0.001 in.). Masses determined under these conditions are usually accurate to better than ±0.002 amu. Opening the source slits to 0.006 in. produces about an order-of-magnitude increase in sample sensitivity, with a corresponding decrease in resolution to about 5000. No appreciable loss in mass-measuring accuracy is observed for most samples.

Accurate mass assignments in high-resolution mass spectrometry require that a sample with known fragment peaks be scanned simultaneously with the sample. Perfluorokerosene (PFK) is used in our instrument. The computer programs written to process the data from the instrument identify the PFK masses in the scan and assign to each its known exact mass. A second-order least-squares fit is made to these peaks, and the masses of all peaks, PFK, and sample are calculated. The

9. C. E. Bemis, Jr., R. E. Druschel, J. Halperin, and J. R. Walton, "Thermal-Neutron Capture Cross Section and Resonance Integral for 10.7-Year Krypton-85," *Nucl. Sci. Eng.* 47, 371–72 (1972).

accuracy of a given set of calculations can be checked by how well the calculated PFK masses agree with the known values.

Final output consists of a list of the accurate sample masses, PFK masses and their associated ranges, and the standard deviations. The sample masses can be plotted in a notebook-size format by the IBM 1627 plotting attachment, if desired.

During the past year this instrument has been used to attack a variety of problems in the realm of organic chemistry; an example follows.

A recent design change in some cooling towers at the Paducah plant created a perplexing problem. After the towers were modified, the chlorine (used as a bacteriostatic agent and algicide) added to the cooling water caused a precipitate to form that clogged the chlorinator. A sample of the precipitate was submitted to the Mass Spectrometry Laboratory for analysis. Low-resolution mass spectrometry showed that the precipitate was a chlorine-containing compound with possibly as many as 5 or 6 chlorine atoms per molecule. The sample was then subjected to high-resolution mass spectrometry; the spectrum shown in Fig. 5.1 was obtained. This spectrum has had the PFK reference peaks stripped out and is identical with the spectrum obtained in the low-resolution instrument. A partial listing of the measured masses and their corresponding formulas is given in Table 5.1. Only the member of the isotope cluster that contains ^{35}Cl exclusively is listed. This amounts to the lowest mass member of each cluster.

As further proof that these compositions were correct, the calculated (using our computer program ABURD) abundances for each of the isotope clusters were compared with those observed in the spectrum. The agreement between the observed and calculated clusters was such that no doubt was left as to the correctness of the empirical formulas. The calculated cluster for the 329.8-m/e group is shown for comparison in Fig. 5.1.

When given this information, the Y-12 Development people (working with Paducah) pointed out that a number of melamine plastic baffles had been installed as part of the tower modification; the empirical formula of melamine is $C_3H_6N_6$. Small pieces of the baffles and an aqueous extract of the baffles were prepared for mass spectrographic analysis. Both samples gave spectra correct for the melamine monomer. High-resolution mass spectrometry was done on the extract to confirm that melamine was being extracted from the baffles; the results of these measurements for the major fragments are given in Table 5.2.

The mass spectrometric investigation of this incident showed that the precipitation problem was caused by the leaching of melamine from the plastic baffles; the melamine was then being chlorinated to form the

Table 5.1. Partial list of measured masses and corresponding formulas

Measured mass	Corresponding formula	Error	
		mmu	ppm
329.8304	$C_3N_6Cl_6$	−1.2	3.6
295.8701	$C_3N_6Cl_5H$	−0.5	1.7
294.8626	$C_3N_6Cl_5$	−0.1	0.3
245.8916	$C_3N_5Cl_4$	+0.8	3.2

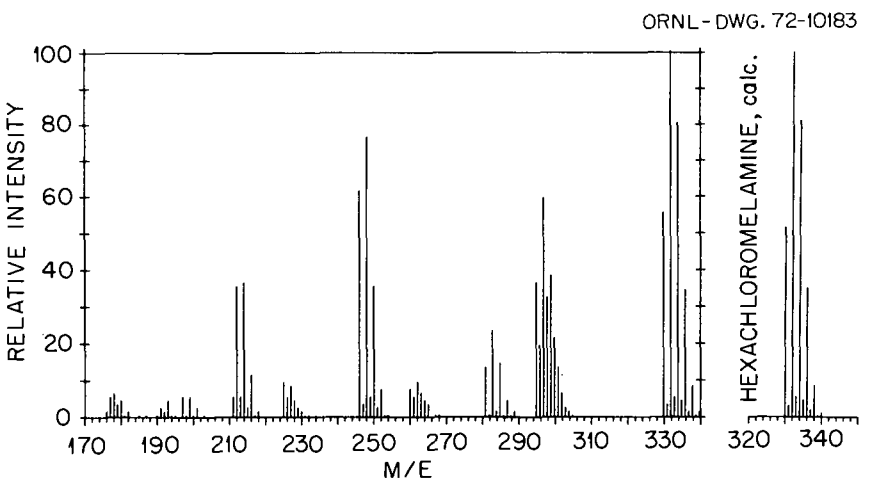

Fig. 5.1. High-resolution mass spectrum of hexachloromelamine.

Table 5.2. Results of measurements for the major fragments

Measured mass	Corresponding formula	Error	
		mmu	ppm
126.0652	$C_3H_6N_6$	−0.2	1.6
85.0506	$C_2H_5N_4$	−0.8	9.4
83.0355	$C_2H_3N_4$	−0.3	3.6

insoluble precipitate. The identification of the precipitate is an example of the type of problem that high-resolution organic mass spectrometry solves quickly and effectively.

X-RAY AND ELECTRON PHYSICS

Scanning electron microscopy. The scanning electron microscope (SEM) is being used so routinely in our group that it has almost completely replaced the optical microscope. For liquids and certain biological specimens, the optical microscope is still the only instrument that can be used; however, for dry solids the SEM is undoubtedly "king." Whenever one wishes to examine an object at an effective magnification greater than 1000X, scanning microscopy is usually the only technique that can be used. Even for lower magnifications (100X or less), the SEM usually provides better images than does the optical microscope because the SEM's depth of field is greater.

The precurser to the SEM was the electron-beam microanalyzer (electron microprobe). With this device, a beam of electrons is focused to a small spot on the surface of the solid to be examined. The energy of the electrons (30 to 50 keV) is high enough to excite x-ray fluorescence of the specimen. The energies of the x-ray photons emitted are characteristic of whatever elements are present and can be measured with crystal spectrometers or with energy-dispersive detectors. In this manner both qualitative and quantitative analyses are possible on an area as small as a square micron. The scanning electron microscope has incorporated the function of the electron microprobe. The combined abilities of physically describing an object by high-resolution photographs and analyzing it point-by-point make the SEM one of the most powerful analytical instruments available. Two examples of problems to which it has been applied follow.

The Metals and Ceramics Division (J. H. Koger) has been continuing its compatibility tests of Hastelloy N with NaK heat-exchanger fluids. Corrosion occurs on the hot side of the heat-exchange loop, and the Hastelloy N specimens lose weight. On the cold side, weight gain occurs. An examination with the SEM showed that the specimen on the hot side corrodes nonuniformly; the surface is undermined by a labyrinth of channels and holes, and the corrosion appears to be intergranular. Both corrosion and deposition occur on the cold-side specimen. The surface was covered with crystallites that had cubic symmetry; growth steps were also seen. Use of the microprobe capability of the SEM showed that iron and chromium are removed from the hot-side specimen and that iron is redeposited on the specimen on the hot side.

The Environmental Sciences Division (T. Cox) has been examining a fungus on tree roots. Tulip poplar trees, prolific in Tennessee, seem to grow faster if there is fungus on their roots. This suggests a symbiotic relationship between the tree and the fungus. One normally thinks of a fungus as being a shapeless glob, but with the SEM we were able to show that the fungus is a well-defined structure of intertwined hollow tubes. The x-ray fluorescence spectrum of the fungus generated by the electron beam of the SEM showed that the fungus was concentrating titanium from the soil.

X-ray-induced x-ray fluorescence. X-ray fluorescence, generated by several different methods, is now being used for analysis. Improvements in instrumentation have greatly improved sensitivity. One such improvement has been developed by C. J. Sparks of the ORNL Metals and Ceramics Division. He has shown that if monochromatic x-ray sources are used to excite fluorescence, the detectability limits of heavy elements are greatly improved. Concentrations as low as 300 ppb have been measured. The monochromator prevents the scatter of white radiation from the excitation source into the fluorescence spectra; this greatly improves peak-to-background conditions. The Metals and Ceramics Division is continuing its development work in hopes of achieving detectability limits as low as 1 ppb. The monochromator for the x-ray source uses pyrolytic graphite crystals that have extremely high diffraction efficiencies.

We hope to improve the reliability of quantitative analysis by using monochromatic excitation sources. The present state of quantitative analysis by x-ray fluorescence is such that one must have standards of similar compositions to the unknowns being studied. That is, empirical standardization must be done for each new matrix analyzed. One of the reasons for this is the difficulty of defining cross sections for white-radiation sources; cross sections are much better defined if monochromatic radiation is used. Our ultimate goal for quantitative analysis by x-ray fluorescence is to

develop an absolute method whereby any matrix can be measured without need for standardization.

Proton-induced x-ray fluorescence. Many workers have shown that the cross section for x-ray excitation by positively charged particles (1 to 5 MeV) is much higher than that for electrons. Also, the degree of bremsstrahlung is much less. Peak-to-background conditions are therefore very good for proton-induced x-ray fluorescence. Experiments at ORNL and at other laboratories where accelerators are available have shown that quantities of elements as small as 1×10^{-12} to 1×10^{-11} g can be detected.

A cooperative effort exists between the Analytical Chemistry Division and the Physics Division to evaluate this technique. The results of analyses will be compared with those obtained by other methods. We have a collection of many environmental pollution samples, already examined by spark-source mass spectroscopy, which we will study by proton-induced x-ray fluorescence. Equipment for these studies is now being fabricated; experiments will begin in October 1972.

Photoelectron spectroscopy. Photoelectron spectroscopy, usually called ESCA, is rapidly entering the stage of a standard analytical tool. It offers the most reliable and practical means of nondestructive surface analysis presently available. As in the case of x-ray fluorescence, the technique is basically a means of elemental analysis. Spectra consist of well-isolated individual peaks that are, in general, unique to individual elements. But in addition to elemental composition, one also obtains information about the chemical states of elements. Small chemical shifts of peaks are seen for elements in different molecular environments. Two examples of problems studied during the past year, utilizing the capabilities of surface analysis and chemical-state determination, are discussed below.

The Environmental Sciences Division (T. Tamura, F. Sweeton) is studying the uptake of heavy metals such as cadmium by clays and soils. The thesis is that the surface of the soils is the important factor; that is, the cadmium is taken up by the clay by adsorption on the surface rather than by incorporation in the bulk. We have studied several specimens of kaolinite and montmorillonite clays containing small quantities (less than 1%) of cadmium. The cadmium peaks were extremely intense – of the same order of magnitude as for pure $CdSO_4$. This means that almost all the cadmium in the clays was concentrated near the surface. The ESCA technique samples only the first few atomic layers of a solid specimen. For a 1% concentration of cadmium to produce the same intensity peak as that of a pure salt, all the cadmium must be segregated near the surface. Other interesting observations were made about the absorbing clays. For both kaolinite and montmorillonite, the silicon peak was greatly broadened, indicating the presence of more than one chemical environment. The silicon peak shape may be related to the amount of cadmium uptake; we reserve the right to alter this interpretation later because more study is needed. For montmorillonite, the calcium peak is greatly broadened, indicating more than one chemical state.

The Metals and Ceramics Division (H. Yakel, J. Brynestad, G. Copeland, R. Knight) is concerned with the characterization of compounds such as boron carbide and boron nitride. These compounds have been used for many years in reactor technology, but they have not been well described in terms of exact chemical composition and crystal structure. We have studied several boron carbide preparations. For some, we found boron to be present in at least three different chemical states; the preparation was obviously not pure boron carbide. Carbon was seen in more than one chemical state. Nitrogen and oxygen were present in large quantities. One of the preparations was subjected to argon etching, which removes outer surface layers. When the specimen was reexamined by ESCA, it was found that the number of chemical states of boron was reduced from three to two. Therefore the chemical composition of the surface of the grains of this preparation differed greatly from that of the surface of the interior grains. There are very few methods of nondestructive analysis for first-row elements such as boron, carbon, nitrogen, and oxygen; ESCA is one of the better techniques. For materials of great use in reactor technology, such as boron carbide and boron nitride, we would propose ESCA as one of the routine tests for quality control.

ENVIRONMENTAL SPECTROMETRY

During the past year, many spectrometry techniques have been used to support the various environmental programs at ORNL. In addition, we have conducted analytical developmental work and have performed trace analyses for the Environmental Protection Agency (EPA).

Lead in gasoline by isotope-dilution mass spectrometry. Lead in gasoline was determined by thermal-emission mass spectrometry, using the technique of isotope dilution. The lead in gasoline was converted from an organic compound to an inorganic form for ^{204}Pb-spike equilibration by refluxing with concentrated HNO_3, followed by complete oxidation with

$HClO_4$. Proof of this oxidation scheme was established by running known amounts of $(C_2H_5)_4Pb$ through the refluxing apparatus under the same oxidizing conditions as those used for the gasoline samples. In making accurate isotope-dilution measurements, two isotopic measurements are required – one before and one after the isotopically enriched spike addition. In nature the isotopic abundance of lead is too variable to rely on average accepted chart values; therefore, the isotopic abundance of lead was measured before and after the addition of the ^{204}Pb spike.

The variation of the isotopic measurements possibly could be used to identify the source of lead in the environment. Lead concentrations were found from 0.035 up to 2.76 g per gallon of gasoline.

Cadmium by isotope-dilution spark-source mass spectrometry. Cadmium may be determined by spark-source mass spectrometry directly in any matrix; however, the results by the direct approach are only semiquantitative. This fact is necessarily so because the average atomic weight, for example, of vegetation is not known nor can it be established easily from the mass spectra, since the fragmentation of organic matter in an rf spark is unpredictable. Therefore, to obtain quantitative cadmium results, an isotope-dilution technique employing spark-source mass spectrometry and cadmium enriched in ^{106}Cd has been developed and used. The success of the technique depends to a great extent on establishing equilibrium between the highly enriched ^{106}Cd and the normal Cd present in the sample. After the ^{106}Cd spike is added, isotopic equilibrium is easily attained in most cases by an acid ($HClO_4$-HNO_3) reflux digestion and oxidation of the organic matter. Thereafter, any technique that permits the transfer of 1 to 10 ng of Cd from the solution to the surfaces of a suitable substrate may be used. Substrates that have been used for the spark-source mass spectrometry are graphite, gold, copper, and niobium.

For very low cadmium concentrations, any suitable extractant may be used to concentrate the cadmium after spiking. High extraction efficiencies are not required, since the analysis at this point depends on establishing a ratio between, for example, ^{114}Cd and ^{106}Cd.

Several gasoline samples from different locales were analyzed for cadmium; the range found was 14 to 28 ppb, except 0.83 ppm for one heavy oil.

Mercury in gasoline by isotope-dilution spark-source mass spectrometry. The general scheme for determining mercury in gasoline is the same as that for cadmium. However, mercury may be lost easily during the oxidation process. Also, it may be incompletely oxidized and, as a result, amalgamate with the copper electrode used. The Hg concentration on a series of gasolines was <0.1 ppm for each sample. Further work is needed to improve the sample preparation for the mass spectrometer.

Metal impurities in heating oil. Heating oils, the primary source of energy in many localities, are very viscous and difficult to sample; therefore, diethyl ether was used in most cases as a solvent in preparing the sample for analysis. Other solvents were tried, but ether proved to be the most satisfactory for transferring the oil samples from the weighing bottles to digestion apparatus or to other containers. Mercury concentration was determined by isotope dilution and was found to be about 5 ppb. Other trace metals of significance include (in ppm) the following: S (>100), V (100), Ni (70), Si (30), Al (20), Fe (20), Pb (3), Ar (2), Mn (1), As (0.7), Se (0.02), and Be (<0.01). These elements were determined on the residue after the low-temperature (450°C) ashing of the viscous oil.

Combustion Improver analyses. Concentrated Combustion Improver (CI), used for more efficient combustion and for smoke and exhaust abatement, was mass analyzed and was also analyzed for manganese by direct-reading emission spectrometry. Solutions of CI in JP-5 fuel were also analyzed for manganese. The CI compound, methylcyclopentadienyl manganese tricarbonyl, in concentrated form is toxic and harmful to the skin; however, the manufacturer states that CI in concentrations in which it is used as a fuel-oil additive presents no health hazard. Mass scans of CI on both the low- and high-resolution organic mass spectrometers were made to verify the compound and, at the same time, to check for the presence of other organic compounds. The mass spectra confirmed a molecular weight of 218 and established the expected cracking pattern. Organic impurities, apparently in low concentrations, were di- and tri-methylcyclopentadienyl manganese tricarbonyl.

For the determination of manganese, the organic matter in the samples was decomposed with HNO_3; the reaction of CI with HNO_3 was vigorous to violent. The manganese was determined by direct-reading (electrical readout) emission spectroscopy. The manganese concentration of concentrated CI was found to be 25.4%, which compares well with the theoretical value of 25.2%. The manganese concentration in JP-5 fuel with the CI additive was 230 ppm.

Fly-ash and coal analyses. Fly-ash and coal samples were analyzed by spark-source mass spectrometry to obtain a scan of the elements present. Over 50 elements were found, and their concentrations were estimated by

this technique. To make the technique more quantitative, ^{57}Fe as an internal standard is used after the iron concentration is accurately established. With this approach, densitometric measurements are used along with computerized relative-sensitivity values.

For the most accurate results, isotope-dilution techniques have been used for cadmium and mercury. The concentration of cadmium in coal has ranged from 0.2 to as high as 0.8 ppm; cadmium concentrations in fly ash are about one order of magnitude higher. The average concentration of mercury in fly-ash samples taken prior to the electrostatic precipitator was 0.12 ppm.

Direct insertion probe for EPA MS-702R. As part of the interagency agreement with the EPA, a direct sample insertion probe for their spark-source mass spectrometry was assembled. The instrument was patterned after the probe used at ORNL for mercury determinations using the isotope-dilution technique.[10] Operating instructions were also provided.

Purdue-ORNL cadmium study. During the past year several samples from Purdue University were analyzed for Cd, Pb, and Zn by isotope-dilution spark-source mass spectrometry. The samples included tissue, hair, litter, soil, and vegetation. In addition to Cd, Pb, and Zn, we have been requested to run general elemental scans on some 45 samples by spark-source mass spectrometry. For soil samples, the Cd, Pb, and Zn concentrations ranged, respectively, from 0.31 to 2.7, 30 to 390, and 80 to 630 ppm. The low results are from agricultural areas, whereas the higher results are from industrial areas.

SPECTROMETRY SERVICES

Spectrochemistry and spark-source mass spectrometry. The spectrochemistry and spark-source mass spectrometry laboratories reported 47,500 results on over 3100 samples. More than 25% of the results were reported to the Isotopes Division, and again – as in years past – the Industrial Hygiene Department of the Health Division supplied a large number of environmental samples of both air and water for trace-metal analyses. These have included urine, blood, fish tissue, coal, ashes, leaves, pine needles, grass, soil, silt, gasoline, cigarettes, and food.

In connection with the Chemical Technology Division's $^{233}UO_2$ project for Bettis Atomic Power Laboratory, certification was obtained by spark-source mass spectrometry for the following elements: Al, B, Br, Ca, Cl, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Si, Th, Ti, V, F, and Hg. The $^{233}UO_2$ product had to be analyzed for mercury by isotope dilution, because part of the mercury was lost by volatilization before Hg^+ ions could be produced by the rf spark. For purposes of quality assurance, the Inspection Engineering, Metals and Ceramics, Reactor, and Operations Divisions continue to supply a large number of alloy samples for specification checks; most of these samples are analyzed with the Paschen direct-reading spectrometer.

The isotope-dilution technique is applied to a large number of waters and solutions, which are analyzed mainly for Hg, Pb, and Cd. The sample probe described previously has continued to be very useful and most reliable.

Radioactive product analyses. Samples with radioactivity requiring special handling have been analyzed. These include ^{33}P, ^{36}Cl, ^{60}Co, ^{67}Ga, ^{90}Sr, ^{137}La, ^{147}Pm, ^{151}Sm, ^{229}Th, ^{230}Th, ^{231}Pa, ^{237}Np, ^{239}Pu, ^{243}Cm, and ^{249}Cf. The products of the curium production program are routinely analyzed.

Thirty-one different metallic elements have been checked for impurities. Alloys of Pt-Rh, Ta-W, Fe-Cr, Sm-Cr, Cu-Au, and many types of nickel-chromium alloys have been analyzed. The compounds analyzed have been BN, B_4C, TaB, Ta_2B, SiC, NaCl, Sc_2O_3, and U_2O_5. Quartz crystals have been analyzed for trace elements.

The installation of the high-resolution MS-702R mass spectrometer is completed, and the check-out shows that the ion-beam current is about twice that called for in the specifications; the mass resolution with a 0.0005-in. source slit is over 10,000. Using the sample probe, several sets of isotope-dilution samples have been analyzed. Other types of samples that have been analyzed are Pt-W-Rh alloys, ThO_2. coal, and quartz powder.

Mass Spectrometry Service Laboratory. This laboratory performs the mass-spectrometric measurements on actinide and stable elements and on gases. Most of the isotopic analyses are for programs in the Chemical Technology and Isotopes Divisions; the majority are from the Transuranium and Stable Isotopes Programs. Welding gases for certification analysis are the major gas samples. More than 18,700 results were reported – slightly over 5% more than during the previous year.

Actinides. Nearly 5700 results were reported on actinide samples last year, an increase of more than 10% over the previous year. The number of samples analyzed for the Chemical Technology Division increased con-

10. J. A. Carter and J. R. Sites, "Determining PPB Mercury Concentrations Using a Spark-Source Mass Spectrometer Sample Changer," *Anal. Lett.* 4(6), 351–55 (1971).

siderably. They accounted for 63% of the analyses, compared with 39% last year. Radioactive samples of 14 different elements were analyzed; they included all transuranium elements through Es and also Bi, Ca, Cs, La, Nd, Sm, and Th. Using the triple-spike method, we continued to make quantitative analyses for ^{148}Nd, U, and Pu in fuel rods for the Metals and Ceramics Division for use in burnup calculations. Determinations were made on ^{249}Cf (>99.999% ^{249}Cf) that was to be used for half-life determinations. The laboratory continues to make isotopic analyses of uranium and plutonium for the Los Alamos Scientific Laboratory. We are again participating in the European "Safeguard" program and are now analyzing samples from the IDA-72 experiment.

We were requested by the Isotopes Division to check the quantity of uranium and plutonium contained in vanadium dosimeter capsules. Quantitative analyses were made by dissolving the entire capsule, then spiking with ^{233}U. Five welded capsules were received that contained 500 to 750 μg of uranium. In only one case have our results differed from their weighted value by more than 1.3%; that one differed by slightly over 3%.

Stable isotopes. Several mass spectrometers used for nonradioactive samples are devoted primarily to the analysis of separated stable isotopes for the Isotopes Division. Isotopic analyses of 40 different elements were made in the past year. Quantitative analyses of two samples of ^{59}Ni were made by isotope dilution, spiking with a known quantity of ^{58}Ni and determining the isotopic ratio. We have also analyzed silicon samples for John Goering of the Institute of Marine Science, University of Alaska, who is studying the uptake of silicon in diatoms by using a ^{29}Si-spike technique.

Gases. Gas samples of all types from various groups in ORNL and the Y-12 plant were analyzed. The number of cylinders certified decreased from about 400 last year to 300 this year. Most work is for argon and helium analysis, but we also run isotopic analyses of Xe, Kr, and H_2. We participated with Y-12 and K-25 laboratories in analyzing a set of helium cylinders with known contaminants. We were the only laboratory able to measure H_2 in the ppm range, and in general had consistent and accurate results. We continually receive a series of samples from D. M. Richardson of the Reactor Chemistry Division from which he is calculating the solubility of hydrogen and deuterium in molten salt. For these samples, we have been able to separate the D_2^+ and He^+ peaks and thus to report both deuterium and helium concentrations.

6. Methods Development and Special Projects

D. A. Costanzo, Head

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REACTOR-FUEL AND MATERIALS ANALYSES

Uranium in urania-thoria microspheres. The uranium content of a series of $^{233}UO_2$-ThO_2 pellets was determined for the Metals and Ceramics Division. These pellets were used by the Bettis Atomic Power Laboratory to define the neutron-absorption characteristics of this LWBR fuel. Nine sets of pellets representing six $^{233}UO_2$ concentrations and three different physical sizes were dissolved. The $^{233}UO_2$ was separated from the thorium by an anion exchange procedure, and the uranium was determined by coulometric titration. The $^{233}UO_2$ content ranged from 0.95 to 5.57%. The evaluation of the procedure used for these determinations indicated a precision of about 0.5 to 0.75%.

Plutonium in plutonia-thoria fuel sticks. In conjunction with a Metals and Ceramics Division contract with Gulf General Atomic to supply a series of $(Th,Pu)O_2$ and PuO_2 fuel sticks, a method for the determination of the plutonium was developed. These fuel sticks were fabricated from SiC-coated particles whose kernels contained either $(Th,Pu)O_2$ or PuO_2. The particles were crushed and screened to 100 mesh, the carbon coat was bumed off, and then the particles were fused with ammonium bisulfate. The plutonium was determined coulometrically. Mass-spectrographic analysis confirmed the completeness of the dissolution of the plutonium from the SiC residue.

Gas release and helium in boron carbide. A method was developed for the measurement of the gas release and the helium content of irradiated B_4C. This work was in support of the Metals and Ceramics Division's B_4C program. The significance of the helium content of the irradiated material is that it gives a measure of the burnup of boron via the $^{10}B(n,\alpha)^7Li$ reaction. The total gas of the sample is extracted under vacuum at 2400°C in a graphite crucible by induction heating. The volume of released gas is measured, and a portion of it is taken for mass-spectrographic analysis. The results obtained for a typical sample are: 6.0 cc/g; H_2, 1.0%; He, 84.5%; H_2O, 1.5%; N_2 + CO, 12.9%; O_2, 0.2%; CO_2, 0.8%. The sample must be heated to above its melting point to release all the gas held in the lattice of the B_4C.

Characterization of uranium nitride. We cooperated in a series of interlaboratory determinations of C, O, N, and U in uranium nitride. Three analytical laboratories (ORNL, Ledoux, and NASA-Lewis) participated to verify and establish the methods and techniques which could be used for the purpose of purchasing UN from commercial vendors to specific chemical specifications. The uranium was determined by a hydrogen-reduction gravimetric method, the nitrogen by a modified Kjeldahl method, the oxygen by an inert fusion method, and the carbon by an oxygen combustion method. The average of the results by the three analytical laboratories for two series of analyses are: U, 94.44 ± 0.04%; N, 5.46 ± 0.05%; C, 376 ± 3 ppm; O, 177 ± 14 ppm. The average value for the mass balance was 99.96%. A paper was published on the chemical characterization of uranium nitride;[1] it describes in detail the evaluation of the methods used in these analyses.

Oxygen in salts by high-temperature fluorination with $KBrF_4$. Renewed interest in determining oxygen in salts in the range 50 to 100 ppm gave rise to the redesign and fabrication of a high-temperature fluorination apparatus. The original method and apparatus involved manometric measurement of the elemental oxygen liberated by the reaction of the oxide-containing salt with potassium bromotetrafluoride ($KBrF_4$) in vacuo at 450°C.[2] Three reaction tubes were operated simultaneously. However, periodic replacement of the $KBrF_4$

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

2. G. Goldberg, A. S. Meyer, and J. C. White, "Determination of Oxides in Fluoride Salts by High-Temperature Fluorination with Potassium Bromotetrafluoride," *Anal. Chem.* 32, 314 (1960).

meant a downtime of 3 to 4 days. The method was further complicated by the need for a volume correction due to the air leakage around the Teflon-gasketed caps of the reaction tubes.

The new apparatus uses two independent reaction systems, each with four tubes, in addition to a gas chromatograph, which replaces the manometer assembly. The $KBrF_4$ can be replaced in one system while the other system is being used for sample analysis, eliminating any downtime. The increase in sensitivity due to the chromatograph makes possible the precise measurement of as little as 2μg of oxygen. Further modification to the reactor cap has reduced the system blank to less than 5 μg of oxygen. It is now possible to analyze up to eight samples per day. The precision of the method is ±10%.

Protonated species in fluoride salts. The Beckman IR-12 spectrometer was used to determine the presence and amount of protonated species (water and/or OH) in $NaBF_4$ or $NaF \cdot NaBF_4$ eutectic proposed as a coolant for MSB reactors. This determination is of interest to the Reactor Chemistry Division, since OH^- can serve as an agent to collect tritium produced in the reactor. The analytically useful band at 3643 cm^{-1} in the infrared spectra of $NaBF_4$ and $NaF \cdot NaBF_4$ eutectic salt containing protonated species is probably due to the BF_3OH^- ion.[3] Approximately 5 to 100 ppm of hydrogen, as $NaBF_3OH$, can be determined in fluoroborate salts by use of the thin-pressed self-pellet technique. This method has been used to determine the hydrogen content of 199 fluoroborate salts during the past year.

The IR-12 was also used to measure the completeness of the substitution of Nb_2O_5 in $(LiF)_2BeF_2$ and in other alkali fluoride salts used to produce M_2NbF_7, by observing the disappearance of the Nb-O stretching peak (~900 cm^{-1}) in their spectra. In addition to the spectra of 15 of these M_2NbF_7 salts, the IR-12 was used to identify six organic compounds or fluorocarbon polymers.

Inert-atmosphere glove box. An inert-atmosphere glove box used for the transfer and weighing of reactive reactor materials was modified for safer operation; a number of backup or safety devices were installed. Double solenoid valves were placed in the vacuum and pressure supply lines. Twenty-pound-pressure relief valves were placed in the gas supply lines. A photohelic gage was installed which deactivates the entire box system by terminating the main power if the pressure or vacuum inside the box reaches a preset limit. Also, an oil-filled bubbler was installed to relieve the pressure inside the box, both positive and negative, in excess of 7 in. of water.

ENVIRONMENTAL AND BIOLOGICAL ANALYSES

Total-organic-carbon analyzer. A Carle model 3000 total-organic-carbon (TOC) analyzer was modified for the determination of total organic material in aqueous systems. The Carle analyzer is designed to measure hydrocarbon species produced by thermal vaporization or fragmentation of the parent compounds. These volatile species are swept by an inert gas stream from the furnace section into a flame ionization detector (FID). Carle states "that with rare exceptions all organic materials are either volatilized or thermally degraded by temperatures of approximately 500°C, and therefore detection closely approaches 100 per cent of the organic content of the samples pyrolyzed." However, the FID has a different efficiency for different hydrocarbon fragments, and certain fragments either give a reduced response (C–O) or no response (C=O). As a consequence, this instrument is ineffective for the quantitative analysis of unidentified organic components.

We have altered the furnace section of this instrument so that the volatile species pass through a reductive furnace packed with nickel metal beads in a hydrogen-helium atmosphere. The fragments are reduced to methane before reaching the FID. A calibration curve obtained with methane is employed.

Preliminary results for aqueous sucrose and citric acid reference materials showed only 10 to 20% recovery. Other investigators have shown[4] that complete recovery is obtained only for species that are volatile or steam-distillable below 500°C, for example, 100% recovery for xylene and only 11% for sodium acetate, even after correcting for the detector efficiency. Many organic species were shown to be nonvolatile under these conditions.

The use of solid oxidizers such as CuO or CoO in the sample boat greatly increased the yield from nonvolatile compounds by first converting the fragments to CO_2 under helium then reducing the CO_2 to methane.[5] Nickel (10%) on alundum, rather than nickel metal

3. J. B. Bates et al., *MSR Program Semiannu. Progr. Rep. Feb. 28, 1971*, ORNL-4676, pp. 94–96.

4. F. T. Eggertsen and F. H. Stross, "Flame Detection Method for Determining Organic Carbon in Water," *Anal. Chem.* **44**, 709 (1972).

5. Y. Takahashi, R. T. Moore, and R. J. Joyce, "Direct Determination of Organic Carbon in Water by Reductive Pyrolysis," *Amer. Lab* **4**, 31 (1972).

beads, is also being used as a catalyst to reduce the volatile species to methane. This work is being continued.

Carbon, nitrogen, and sulfur in ecological materials. Carbon, nitrogen, and sulfur in solid ecological samples can be simultaneously determined in a single test aliquot by reductive pyrolysis–gas chromatography and element-selective detectors.[6] We have analyzed approximately 1000 samples such as leaves, twigs, grasses, seeds, soils, and insects.

The method involves pyrolysis of the solid sample in a hydrogen atmosphere and contacting the fragments with a platinum catalyst, thereby reducing the nitrogen-, sulfur-, and carbon-containing components to ammonia, hydrogen sulfide, and methane respectively. The effluent stream from the pyrolyzer is split–one portion passes to an H_2-air flame equipped with a photometric detector which responds to H_2S and to an ionization detector which responds to CH_4. The other portion passes through a trap for acidic gases (H_2S, HCl, etc.) to a Coulson electrolytic conductivity detector that responds to NH_3.

Typical concentration values obtained for ecological samples range from 0.1 to 5% for nitrogen, 3 to 60% for carbon, and 0.01 to 2% for sulfur. Sample aliquots are normally 0.5 to 2.0 mg. Approximately 25 samples or 75 analyses can be completed in an 8-hr work day. The average coefficient of variation for typical analyses of forest floor litter, for example, was 1.4% for carbon, 5.8% for nitrogen, and 5.5% for sulfur. A paper describing the application of this method to the analyses of solid ecological materials was submitted for publication.

Determination of methyl mercury in fish tissue. Fish tissue samples were submitted by TVA for methyl mercury analysis. The samples were taken from Pickwick Lake, which is known to be relatively high in total mercury. The samples were analyzed for total mercury and for methyl mercury in an attempt to correlate the results for organic mercurial and total mercury.

In the method used,[7] the tissue samples were homogenized in NaI solutions and leached for 24 hr. The resulting methyl mercury iodide was extracted into benzene. Subsequently, the benzene extract was injected into a gas chromatograph equipped with an electron capture detector. The eluted methyl mercury iodide was measured by comparison with reference standards prepared similarly.

Mercury by cold-vapor atomic-absorption spectrophotometer. The cold-vapor atomic-absorption technique[8] was used to determine mercury in a wide variety of biological and ecological materials at the sub-ppb level for members of the Environmental Sciences Division. The 350 samples included fish, twigs, grass, leaves, and moss from various areas of Wyoming and Tennessee and numerous materials from the Allen Steam Plant such as coal, water, fly ash, and various trap solutions.

^{203}Hg-tagged fly ash. A method was developed for tagging fly ash with ^{203}Hg. A solution of ^{203}Hg in dilute nitric acid solution is contacted for 12 hr with a copper wire coil. The elemental mercury deposited on the copper is vaporized in a closed system by resistance heating of the copper coil to a faint red glow and is deposited onto fly ash. The tagged fly ash was used in an Environmental Sciences Division study to trace the pathways of this potential source of mercury pollution in aquatic systems.

Toxic metals in the environment. During this period we began to use our capabilities to support ORNL's growing environmental program. In an NSF-supported project, we are engaged in research and development studies leading to new, practicable industrial separation methods for pollution abatement of toxic metals.

Currently, the major emphasis is on the removal of mercury from effluents of the chlor-alkali industry by solvent extraction with amines. Related studies on the behavior of mercury and cadmium in iodide- and bromide-containing systems have also been made. Details of our work in this program were recently published in the open literature. Our work fits into ORNL's increasing involvement in the area of environmental science.[9,10,11]

Laboratory recycling of toxic materials. A large amount (1735 lb) of mercury was cleaned and recycled

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6. A. D. Horton, W. D. Shults, and A. S. Meyer, "Determination of Nitrogen, Sulfur, Phosphorus, and Carbon in Solid Ecological Materials via Hydrogenation and Element Selective Detection," *Anal. Lett.* **4**, 613 (1971).

7. J. A. Ealy, *A Study of the Extraction and Determination of Some Organo-Mercury(II) Compounds,* M.S. thesis, University of Tennessee, Knoxville, December 1971.

8. W. S. Lyon et al., "Wet-Ashing Organic Matter for the Determination of Mercury by Atomic Absorption," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1971,* ORNL-4749, p. 27.

9. F. L. Moore, "Solvent Extraction of Mercury from Brine Solutions with High-Molecular Weight Amines," *Environ. Sci. Technol.* **6**, 525 (1972).

10. F. L. Moore, "Liquid-Liquid Extraction of Mercury with High-Molecular Weight Amines from Iodide and Bromide Solutions," *Separ. Sci.* **7**, 505 (1972).

11. C. W. McDonald and F. L. Moore, "Liquid-Liquid Extraction of Cadmium with High-Molecular-Weight Amines from Iodide Solutions," *Anal. Chem.*, in press.

during this report period by use of counter-current liquid-liquid extraction column procedure modified from the Hanford method of D. A. Cochran.[12] The mercury, which comes from many divisions at ORNL and Y-12, is pretreated by sparging in 3 *N* HNO_3 before it is put through the column. The processed mercury has been found by spectrographic analysis to be equal in purity to triple-distilled mercury and is being stocked in chemical stores for laboratory distribution. Also, tetrabromoethane used in the gradient-density procedure is being recycled by heating with decolorizing carbon on a sand bath at 100 to 115°C, followed by filtration. The thallous malonate and thallous formate mixture used in the same procedure is being recycled in the same manner except that, after filtration, the mixture is concentrated to a density of approximately 3.6 g/cc by heating on a sand bath at 100 to 115°C.

Nitrosamines by GLC. Nitrosamines are known to be carcinogens, and their formation parameters are being studied by the Biology Division. Primary interest is the formation of nitrosamines by the reaction of amines with sodium nitrite, a preservative added to a variety of meat products. A method was developed to determine nitrosamines which is based on this reaction. After the reaction has taken place, the resulting nitrosamines are extracted into methylene chloride. The resulting extract is injected into the gas chromatograph, using a 5% DEGS column. The flame ionization detector is currently being used.

DTPA in urine. DTPA (diethylenetriaminepentacedic acid) is a chelating agent administered therapeutically for the ingestion of plutonium, americium, and curium. The Health Division requested that we provide a method to monitor the mass balance of DTPA through the urinary tract.

The methods under evaluation are: (1) spectrophotometric titration, (2) polarographic determination of excess bismuth, and (3) coulometric determination of excess bismuth. They exploit the ability of DTPA to preferentially complex with bismuth at pH 2 to 3. All the methods are satisfactory for DTPA in water, but the presence of urine causes many interferences – amines tend to complex with bismuth, and complex organic mixtures interfere with the reduction of bismuth. The most promising method is a coulometric technique whereby the solution is prereduced before excess bismuth is added.

INORGANIC PREPARATIONS

Considerable time in the past year was spent in salvaging some expensive isotopes for the Solid State Division. Among them, ^{163}Dy, ^{170}Er, and ^{154}Sm occurred in several-gram quantities in matrices of ~75 g of ThO_2. Another recovery project was the salvage of 200 g of ^{57}Fe from an alloy containing 5 at. % Si and the subsequent purification of the ^{57}Fe by ether extraction. For the Metals and Ceramics Division, preliminary work has been done on possible methods of recovering iridium from its alloys with such refractory metals as tungsten, niobium, hafnium, and rhenium and on the possible purification of commerical iridium to about 99.99%.

We have made the following compounds for the Neutron Diffraction Group of the Solid State Division: $^{154}SmF_2$, $^{154}SmOF$, ^{154}SmN, YbN, FeS_2, CoS_2, FeF_3, CrF_3, VF_3, and some Ni_3Ga alloys doped with iron. Various heat treatments of these and numerous other alloys were carried out. Compounds made for the Neutron Spectrometry Group included TmTe, PrN, $FeCO_3$, ErN, and TmAs.

Preparations made for the Low-Temperature Nuclear and Solid-State Physics Groups of the Physics Division included a series of chromites of the form $NiFe_xCr_{2-x}O_4$ and a similar series of vanadites. The preparation of completely stoichiometric $NiCr_2O_4$, after the method of Whipple and Wold,[13] was found to be dependent on pH (6.8) and time (<12 hr). The Heusler alloys Ni_2MnSn and Ni_2MnSb, doped with ^{61}Ni, were made. Also, a series of alloys of very pure gold were made that contained 4, 2, and 1 at. % of each of the metals Sc, Ti, V, Cr, Mn, Ni, Co, and Fe; also, a single preparation of $AuAl_2$ was done.

Miscellaneous isolated preparations were made for various groups or purposes. In support of the environmental research programs being conducted here and outside the Laboratory, 200 mg of ^{204}Pb was converted to tetraethyl lead. A simulated moon mineral, $CaAl_2SiO_8$, was prepared in conjunction with the Apollo moon-rock program within the Solid State Division. The compound $NaBF_3OH$, used in reactor studies, has always presented difficulties in preparation due to the relative insolubility of NaF. We successfully prepared it by a procedure that requires semidry conditions.

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12. D. A. Cochran, *Purification of Mercury by Counter Current Liquid-Liquid Extraction,* Hanford Laboratories, HW-84509, (Nov. 16, 1964).

13. E. Whipple and A. Wold, "Preparation of Stoichiometric Chromites," *J. Inorg. Nucl. Chem.* **24,** 23 (1962).

Part B. Service Analyses

The table below gives a summary of the service analyses made by the laboratories of the Analytical Chemistry Division.

Summary of Analytical Work

Group making analyses	Average number in group		Number of results reported																								
			For ORNL divisions																		For others					Total
	Scientists	Technicians	Analytical Chemistry	Biology	Chemistry	Chemical Technology	Directors	Environmental Sciences	Health	Health Physics	Inspection Engineering	Isotopes	Metals and Ceramics	Neutron Physics	Operations	Physics	Reactor	Reactor Chemistry	Solid State	Thermonuclear	Los Alamos Scientific Laboratory	Miscellaneous	Paducah	Stewart	Y-12	
Elemental Spectrometry	2.8	3	563		150	4,430		826	10,100	25	90	12,214	9,196	295	621	20	1695	1289	1867	333		1792			2002	47,508
Mass Spectrometry Service Laboratory	1	3	365		24	3,392				30		6,827	1,830		90	14	240	1305	2		326	3352			970	18,767
Process analyses																										
General Analyses Laboratory	8	15	190	1222	311	30,333		41,221		72		1,726	5,880	278	1,324	38	1816	332	352			635			163	85,893
General Hot-Analyses Laboratory	6	2				6,060		54		20		275	685		1,629			173				5				8,901
High-Level Alpha Radiation Laboratory	10	7	8		20	16,057	2			23		274	258	1	2,415			3				58	13			19,132
Radioisotopes-Radiochemistry Laboratory	3.5	6			37	7,800		109		1559	63	4,034	812	65	5,010	1663	549	945	85			119		151		23,001
Total			1126	1222	542	68,072	2	42,210	10,100	1729	153	25,350	18,661	639	11,089	1735	4300	4047	2306	333	326	5961	13	151	3135	203,202

The table below gives a summary of the numbers and types of analyses performed as part of the Tobacco Smoke Characterization Program sponsored by the National Cancer Institute.

Component	No. determinations in past year
Particulate matter	
TPM	140
Water	140
Nicotine	140
Tar	140
Δ^9THC	12
Cannabinol	12
Cannabidiol	12
Gas phase	
Acetaldehyde	140
Acrolein	140
Isoprene	140
Carbon monoxide Carbon dioxide	150
Hydrogen cyanide	90
Oxides of nitrogen	130
Formaldehyde	130
Condensate	
Water	200
Acetone	200
Nicotine	120
Nicotine alkaloids	120
Colorimetric phenols	120
Phenol	120
o-Cresol	120
m-Cresol + *p*-cresol	120
Titrimetric acids, weak	120
Titrimetric acids, very weak	120
Phenanthrene	120
Benz(a)anthracene	120
Benzo(a)pyrene	120
Stearic acid, palmitic acid, linolenic, linoleic, and oleic acids	100
	3336

7. General Hot Analyses Laboratory

J. H. Cooper

ALPHA AND HOT CELLS

C. E. Lamb

The analysis of radioactive samples continued in support of programs in the Chemical Technology, Isotopes, Operations, and Metals and Ceramics Divisions. The majority of the determinations were on samples from the Pilot Plant's tests and from process evaluation for the LWBR program.

In anticipation of samples from the LWBR program, equipment was assembled, methods were checked, personnel were trained, and synthetic samples were analyzed. As a part of quality assurance, special samples were analyzed. Qualifying certification was received for the determination of total U, O/U, C, and ^{232}U.

Methods for determining bismuth and lead by inverse polarography, bismuth by spectrometry, and lithium by measuring the hydrogen evolved on sample dissolution were added to the group's analytical capability.

Special work included measuring the density of pyrolytic-carbon- and SiC-coated microspheres of PuO_2-ThO_2 before and after removing the carbon coating by combustion. Radioactive Zircaloy-2 specimens were dissolved, and the tritium present was removed by distillation for measurement.

TRANSURANIUM LABORATORY

H. C. Meyer

The Metals and Ceramics Division requested the measurement of the density of particles of SiC and C from coated microspheres of PuO_2-ThO_2. These measurements were made in density-gradient columns, and the densities were calculated by using the computer program of the General Analysis Laboratory. Dissolution of these high-fired microspheres for subsequent plutonium measurements presented a problem. Dissolution was best effected by grinding the microspheres to less than 150 μ and fusing the powder for several hours in ammonium bisulfate.

Samples of process-waste materials from Paducah were analyzed for ^{230}Th. The thorium was separated and purified by lanthanum fluoride precipitation and by TTA extraction. Pulse-height analysis was used to check the purity of the alpha mounts.

Sulfur was determined in samples of curium oxide for the TRU Processing Plant. The oxide was dissolved in aqua regia, and the sulfur was reduced with hydriodic and hypophosphorous acids. The distilled sulfide was measured colorimetrically with *p*-phenylenediamine.

The accuracy of determining ^{242}Pu in TRU process solutions was increased by using isotope-dilution techniques.

RADIOISOTOPES LABORATORY

E. I. Wyatt

Forty-five samples of core drillings from White Oak Lake sediment were analyzed for ^{90}Sr. The highest concentrations were found 40 to 70 cm below the surface of the mud.

A large number of Zr-U alloy specimens were counted for the Metals and Ceramics Division to determine the homogeneity of the alloy. This was accomplished by counting both alpha and beta radiations at the same time in the automatic Low Beta II proportional counter.

Many environmental-background samples were examined for radioactive species. Some came from the site of the J. M. Farley Nuclear Power Plant. These samples included ash from fish, weeds, milk, oyster, etc., as well as soil, silt, and water taken as far downstream as the Gulf of Mexico.

A large number of samples of water from sumps, tanks, and diffusion tubes, as well as samples of the cooling water, were received from the Peach Bottom Reactor. These samples were examined for $^{89,90}Sr$ and ^{3}H content.

Technetium-99 was found in metallic samples from the core of MSRE for the first time.

Gamma-ray spectrometry was used to determine the Pu-Th content of individual batches of fuel microspheres.

We provided support to the HTGR Fuel Program by providing nondestructive burnup analyses on bonded-bed fuel pins. Further, jointly with Charles Sanders of Metals and Ceramics Division, we designed, fabricated, and tested a device for profiling fuel specimens to determine fissile homogeneity. This device rotates and increments the fuel stick above a collimator for a Ge(Li) detector. The device is synchronized with and driven by the ND-3300 analyzer in such a way that the resulting data can be reduced to form a cylindrical profile of one or more fuel materials. To date, measurements have been made on plutonium, uranium, and thorium.

8. General Analyses Laboratory

W. R. Laing

The number of analyses for the Environmental Sciences Division increased 300% to 40,000 determinations. Two new pieces of equipment contributed substantially to this total. A pyrolysis–gas chromatographic apparatus was used to simultaneously measure carbon, nitrogen, and sulfur in 1-mg samples of leaves, twigs, bark, and forest litter. The aliquot was pyrolyzed in a stream of moist hydrogen, and the pyrolysis fragments were reduced to CH_4, NH_3, and H_2S on a platinum catalyst. The three gases were measured independently by a flame-ionization detector, a Coulson detector, and a photometric detector. A Perkin-Elmer model 403 atomic-absorption instrument was placed in service in December and was used for the routine determinations of Na, K, Ca, Mg, as well as trace levels of the toxic metals Pb, Cd, and Zn.

To verify carbon, nitrogen, and sulfur results for some of the environmental samples, assays were made by using some regularly available laboratory equipment not normally associated with this type of analysis. Leco carbon and sulfur analyzers and the Coleman model 14 automatic Dumas apparatus were used with good results. Analysis of the NBS 1571 orchard-leaves standard produced results with a relative standard deviation of 3% and no bias. Values obtained with this equipment were used to calibrate the pyrolysis–gas chromatography apparatus for different types of plant material.

Several determinations – HCl-soluble boron, HNO_3-soluble boron, and free carbon – required in the specification analysis of boron carbide were refined. The changes dealt with the strict definition of the conditions for these leaching procedures. A successful interlaboratory check with LASL and WADCO verified the advisability of these changes.

A production campaign begun in October by the Macromolecular Separations Group and completed in December produced five product-grade beef-liver *t*-RNAs. The progress of the separations and the product purity were checked by aminoacylation and end-group analysis. The emphasis has since shifted to the determination of nucleoside sequences of these *t*-RNAs. An improved ion exchange separation using Aminex A6 resin was developed. Peaks monitored by ultraviolet absorption at 254 nm are sharp and well defined. For the common nucleosides, the analysis is complete in half an hour.

In other work, BF_3 gas trapped in a solution of NaF was determined by reaction with $CaCl_2$ and titration of the released boric acid. Sulfate in cooling-tower water was titrated with $Ba(ClO_4)_2$ solution. Total sulfur in fly ash was measured with the Leco sulfur analyzer. Samples of soil and gravel were leached, and their chloride contents were determined potentiometrically. The Carle total-organic-carbon analyzer was used to measure carbon in water from several woodland locations. Samples of KBF_3OH prepared at ORNL were analyzed for KBF_3OH, KF, KBF_4, and H_3BO_3; their purities were found to be 90 to 100%. Gas chromatography was used to measure nitrosamines and also to measure lithium metal in alkali halide salts.

9. Industrial and Radiation Safety

J. S. Wike

The purpose of our industrial and radiation safety program is to ensure a healthy accident-free environment in which each employee can work. We have experienced both success and failure in our efforts. For instance, only 12 medical-treatment cases are on record for this year compared with 23 for last year. However, one lost-time accident, the first in over 15 years, was suffered in the Analytical Chemistry Division. Regulations governing our safety programs are becoming more stringent because of pressures from environmental protection groups and implementation of the Occupational Safety and Health Act of 1971.

Measures to improve industrial safety were taken during the year. We made an intense effort to clean up our labs and to discard unused chemicals. Improvements were obvious during D. C. Gary's annual safety audit of our Division. We inspected the Division's use of hydrogen to determine whether safety criteria are being met. A central storage rack was constructed outside Corridor B of Building 4500-S to accommodate all surplus hydrogen cylinders in the 4500-S complex. A training program was conducted for temporary employees which included a tour of most of the analytical laboratories in the Division. Emergency procedures are being updated.

Radiation safety is a very vital part of our program. This program has been very successful over the years because of individual respect for the hazards of radiation. Eight new programs in research involving radioisotopes and neutron bombardment were approved. Seventeen radiation work permits were issued for hazardous work areas. All work was completed without incident or overexposure to ionizing radiation.

We witnessed three unusual occurrences in our Division. An inert-glove-box window imploded in Building 3508 due to an instrument failure. A dissolution flask containing perchloric acid and organic material exploded because of a violent oxidation reaction. Operators in each case suffered minor cuts by glass fragments. The inside section of a zinc bromide–filled window at Building 3019B fractured but was replaced following cell decontamination without any loss of cell shielding.

Two new programs will be in effect this year: mercury inventory for the Division will be made, and utility conservation is being reemphasized, with progress reports due each quarter.

10. Quality Control Program

G. R. Wilson

Changes in the types of samples received by the Division's service laboratories have made necessary several changes in the control programs. Control programs for very low levels of Ca, Mg, K, and Na, determined by atomic adsorption and by the colorimetric phosphorus method with the Technicon Auto-Analyzer, were started in April for the Environmental Sciences Division. Control levels for these analyses are being established. In July 1972, new control programs were initiated for the BAPL program. These include the determination of very low levels of nitrogen, fluoride, and chloride, the determination of low amounts of uranium in the presence of large concentrations of thorium, and the determination of high concentrations of uranium in the presence of low levels of thorium. For the General Analyses Laboratory, the control program for the polarographic determination of uranium was reinstated, and a control program for phosphorus in steel was initiated.

The overall quality level decreased from 95% to 93%, and the number of control results decreased from 2225 to 1616. Table 10.1 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 10.2.

Table 10.1. Distribution by laboratory, of control tests for July 1971–June 1972

Laboratory	Number of control results		Quality level[a] (%)	
	Total	Outside fixed limits	1971	1972
General Hot-Analyses	495	11	97.9	97.8
General Analyses	966	90	94.8	97.8
High-Level Alpha Radiation	155	21	90.6	86.5
Total	1616	122	95.1	92.5

[a]Control results within 2S limits.

Table 10.2. Distribution, by method, of control results for July 1971–June 1972

Type of method	Constituent	Number of control programs	Number of control results
Atomic absorption	Calcium	1	8
	Magnesium	1	9
	Potassium	1	10
	Sodium	1	13
			40
Colorimetric	Chromium	1	66
	Iron	1	114
	Molybdenum	1	40
	Nickel	1	61
	Phosphorus	1	22
	Thorium	1	2
	Uranium	1	70
			375
Coulometric	Plutonium	2	107
	Uranium	4	684
			791
Flame photometric	Lithium	1	31
Fluorimetric	Uranium	2	129
Gravimetric	Carbon	2	110
Volumetric	Aluminum	1	10
	Nitrate	2	108
	Thorium	1	22
			140
Total		26	1616

Part C. Environmental Activities

The role of the Division in the environmental programs of the Laboratory continues to expand. Our activities cut across divisional lines and, within our Division, across group lines. Accordingly, these activities are described in various places within this report. They are summarized briefly here.

Participation in the ORNL/NSF Environmental and Technology Assessment Project (ETAP) continued this year. The study concerned with the trace element material balance for a fossil-fueled power plant (TVA's Allen Steam Plant in Memphis) continued, under W. S. Lyon. This project is supported by the ETAP Energy Team. W. D. Shults and G. Goldstein were members of the ETAP Environmental Index Team, Shults working on air quality indices and Goldstein with biological indicators of pollution.

A study of biochemical and biological indicators of environmental pollution was made for the Environmental Indices Group of the ORNL-NSF Environmental Program. The practical use of biological indicators to monitor environmental quality has a long history dating back to the miner's canary as an indicator for methane. A familiar example today is the fecal coliform count as an indicator of pathogenic bacteria in water. Biological indicators have certain advantages compared with chemical analysis of individual compounds in that they are screening agents responding to many different environmental contaminants, are integrators showing cumulative effects over a period of time or over some spatial area, and are direct measures of toxicity. Five classes of biological indicators were considered which are, in order of increasing biological complexity: cell-free preparations, cultured cells, tissues and organs, organisms, and ecosystems. A discussion of the first three classes was presented orally and will be published.[1] A complete annotated bibliography having about 600 entries is being prepared for publication in book form.

A new ORNL/NSF program at ORNL this year is sponsored by the Research Applied to National Needs (RANN) program. The ORNL project – Ecology and Analysis of Trace Contaminants (EATC) – comprises two separate projects which, because of their interdisciplinary nature, have been merged. W. D. Shults is coordinator for analytical tasks in this Project. The GeMSAEC and gas chromatography-microwave emission detector work discussed elsewhere is part of this EATC Project. Other tasks are being conducted in the Chemical Technology, Environmental Sciences, Reactor Chemistry, and Metals and Ceramics Divisions.

We are also collaborating with Purdue University in a study of cadmium in the environment. This is also supported by NSF/RANN. Our function in this study is to provide analytical R & D, assistance, and analyses to the Purdue team to substantiate their analytical measurements. More work of this nature is anticipated.

During the past year, Laboratory personnel have been preparing Environmental Impact Statements for the AEC for various nuclear power stations. These documents are prepared by teams of personnel from many divisions. Five people from the Analytical Chemistry Division have participated in this activity: L. G. Farrar, C. Feldman, R. R. Rickard, W. J. Ross, and W. F. Vaughan.

1. Gerald Goldstein, "Biochemical Indicators of Environmental Pollution," in *Indicators of Environmental Quality*, ed. by W. A. Thomas, Plenum, New York, in press.

Part D. Activities Related To Education

The Division continues to maintain liaison with the academic community through the assistance of its Advisory Committee and consultants as well as affording facilities and superivision for student research and training programs.

This year our Advisory Committee has been composed of:

M. A. Evenson, Professor of Medicine, University of Wisconsin

L. B. Rogers, Professor of Chemistry, Purdue University

S. Siggia, Professor of Chemistry, University of Massachusetts

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

CONSULTANTS

J. A. Dean, Advises and works with the Division as a whole.

Gleb Mamantov, Specializes in areas of electrochemistry and molten-salt research.

GRADUATE THESIS RESEARCH PROGRAM

D. R. Matthews. After completing the requirements for the Ph.D. in chemistry from the University of Tennessee, Mr. Matthews has returned to active duty with the Division. His research was in the application of gas chromatography to the determination of anions in aquatic systems and was performed under the direction of W. D. Shults and J. A. Dean.

J. A. Ealy. A M.S. degree in chemistry was awarded Mr. Ealy this year by the University of Tennessee, and he also has been reinstated as an active member of the Division. The research for his degree involved the analysis of organomercury compounds and was carried out under the supervision of W. D. Shults and J. A. Dean.

J. D. Lodmell. A graduate student from the University of Tennessee, Mr. Lodmell is continuing doctoral research under the direction of W. D. Shults and J. A. Dean in the development of flame photometric detectors for gas chromatography.

J. L. Bowling. A graduate student from the University of Tennessee, Mr. Bowling is initiating doctoral research in centrifugal photometric analysis under the direction of W. D. Shults and J. A. Dean.

G. M. Thompson. A graduate student from Memphis State University, Mr. Thompson is initiating research toward the M.S. degree under the direction of J. A. Carter and Dr. David Lumsden. His research is in the field of uranium and thorium-age measurements by mass spectrometry and alpha spectroscopy.

W. C. Butts. While on leave of absence from the Division, Dr. Butts is studying in the Department of Laboratory Medicine at the University of Washington.

D. C. Canada. Mr. Canada remains on leave of absence while continuing his doctoral program in biochemistry at Purdue University.

D. H. Smith. Dr. Smith has obtained leave of absence to enable him to temporarily join the staff of the International Atomic Energy Agency, Vienna, Austria.

GREAT LAKES COLLEGES EDUCATIONAL PROGRAM

This cooperative program is now in its third year; this year our guest is L. R. Wilson, Professor of Chemistry from Wesleyan University, Delaware, Ohio. Dr. Wilson is working with L. D. Hulett in the X-Ray and Electron Physics Methods Group.

NSF PRESIDENTIAL INTERN PROGRAM

G. E. McGuire. As a representative of this new national program, Dr. McGuire has joined the Division as a member of the X-Ray and Electron Physics Methods Group.

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 1972 high school graduates. H. H. Ross acted as "Dean" for these guests during their visit.

Summer Guest. Dr. Curtis W. McDonald, Professor of Chemistry at Southern University in Baton Rouge, Louisiana, worked with F. L. Moore in the area of solvent extraction.

Pre Co-Op Students.

Karen A. Burges, Southern University, Baton Rouge, Louisiana.

Dianne L. Williams, Tennessee State University, Nashville, Tennessee.

ORAU Summer Trainees.

Rhosus G. Eckles, Mississippi Valley State College, and Vernon J. Gutenkunst, Dickinson State College, worked with R. W. Stelzner and M. R. Guerin, respectively.

Part E. Supplementary Professional Activities

Members of the Division continue to give their time and expertise to serve on professional, civic, and educational boards and committees. These activities are listed below as a part of the Division's overall outreach.

J. A. Carter

Councilor:	East Tennessee Section, ACS

L. T. Corbin

Member:	Committee E-10 Radioisotopes and Radiation Effects, ASTM Subcommittee 1, Burnup Subcommittee 2, Core and Cladding
Vice-Chairman:	Committee C-26, Fuel Control, and Moderator Materials for Nuclear Reactor Applications, ASTM
Chairman:	Subcommittee 5, Test Methods, 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 the Russian Journal *Optika i Spektroskopiya*)
Award of Merit, ASTM:	Fellow, ASTM

D. J. Fisher

Member:	Editorial Board, *Chemical Instrumentation* Advisory Board, Chemical Analysis Monograph Series (Wiley-Interscience)
Chairman:	Association of Indiana University Chemists Advisory Committee

Gerald Goldstein

Member:	Committee on Specifications and Criteria for Biochemical Compounds, NAS-NRC
Chairman:	Subcommittee on Nucleotides and Related Compounds
Member:	Committee on Specifications for Adenine for Use in Anticoagulant Solutions, NAS-NRC
President-Elect:	Tennessee Institute of Chemists, AIC

M. R. Guerin

Member:	Panel 3, Chemistry, International Study Group on Tobacco and Health Research Tobacco Working Group, Lung Cancer Task Force, National Cancer Institute (Data Analysis Subgroup)
Consultant:	Chemical Carcinogenesis Contract Review Committee, National Cancer Institute
Member:	ORNL Ph.D. Recruiting Committee

A. D. Horton

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

L. D. Hulett

Program Chairman:	Sigma Xi-RESA, Oak Ridge Chapter
Member:	Editorial Board, *Journal of Electron Spectroscopy*

M. T. Kelley

Member:	Analytical Specialists Group, Union Carbide Corporation Technology Subcommittee Advisory Board, *The Analyst* Advisory Committee, *Microchemical Journal* Board of Editorial Advisors, *Analytica Chimica Acta* ORNL Instrumentation and Controls Advisory Committee

W. R. Laing

Secretary:	Committee C-26, Fuel, Control and Moderator, Materials for Nuclear Reactor Applications, ASTM Subcommittee 5

W. S. Lyon

Member:	Committee D-5, Coal and Coke Subcommittee on Methodology Task Group on Trace Elements, ASTM Committee E-10, Radioisotopes and Radiation Effects, ASTM Subcommittee 1, Burnup Subcommittee 3, Tracer Application Subcommittee 5, Neutron Dosimetry Collaborating Referee on Mercury Analysis by Neutron Activation Analysis for the Association of Official Analytical Chemists (AOAC) Scientific Committee 25 on Radiation Protection in the Use of Small Neutron Generators, NCRP
Member:	Committee N43-3, Equipment for Nonmedical Radiation Applications, United States of America Standard Institute
Regional Editor:	*Journal of Radioanalytical Chemistry*
Associate Editor:	*Radiochemical and Radioanalytical Letters*

H. S. McKown

Treasurer:	Oak Ridge Section, Instrument Society of America

T. R. Mueller

Chairman:	Analytical Chemistry Group, East Tennessee Section, ACS

S. A. Reynolds

Member:	Committee D-19, Water, ASTM Subcommittee 4, Methods of Radiochemical Analysis Committee E-10, Radioisotopes and Radiation Effects, ASTM Subcommittee 3, Tracer Applications Subcommittee 5, Neutron Dosimetry Task Group on Nuclear Data and Radiation Safety Subcommittee on Use of Radioactivity Standards, NRC Standards Committee, ANS
Chairman:	Standards Subcommittee ANS-16, Isotopes and Radiation Division, ANS
Advisor:	Information Center on Nuclear Standards, ANS

E. Ricci

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

W. D. Shults

Member and Vice Chairman:	Environmental Quality Advisory Board, City of Oak Ridge
Member:	Environmental Quality Committee, East Tenn. Section, ACS
Chairman:	ORNL Graduate Selection Panel
Coordinator:	ORNL-NSF Ecology and Analysis of Trace Contaminants Program

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)
Member:	Editoral Board, *Analytical Letters* ACS Analytical Chemistry Division Executive Committee
Titular Member:	Commission V.7, Analytical Radiochemistry and Nuclear Materials, IUPAC
Chairman-Elect:	Federation of Analytical Chemistry and Spectroscopy Societies

Part F. Presentation of Research Results

Even though the scope of the Division's work has experienced considerable change during the last few years, much basic research and development work continues to accompany our involvement in the newer biochemical fields as well as in continuing programs in such areas as metallurgy, reactor development, and nucleonics. The "multidisciplinary" approach continues to grow in both popularity and effect. Consequently, many of the publications listed below include the names of investigators outside of the Analytical Chemistry Division. These people are designated by an asterisk. The maturity of the Division staff is again demonstrated by the appearance of publications in a large number of professional journals as well as in books, review articles, book reviews, and reports.

PUBLICATIONS

Contributions to Books

AUTHOR(s)	TITLE	PUBLISHER
Carter, J. A.	"The Analysis of Radioactive Samples by Spark-Source Mass Spectrometry," pp. 345–63 in *Trace Analysis by Mass Spectrometry,* chap. 11, ed. by A. J. Ahearn.	Academic, New York, 1972
Goldstein, G., A. L. Nussbaum, D. G. Söll, Mayo Uziel	"Nucleotides and Related Compounds," pp. 149–83 in *Specifications and Criteria for Biochemical Compounds,* 3d ed.	National Academy of Sciences, Washington, D.C., 1972
Ricci, E.	"Charged Particle Activation Analysis," pp. 221–63 in *Advances in Activation Analysis,* Vol. 2, ed. by J. N. A. Lenihan, S. J. Thompson, and V. P. Guinn.	Academic, London, 1972

Articles

Attrill, J. E.	(See Burtis, C. A.)	
Bamberger, C. E.,* R. G. Ross,* C. F. Baes, Jr.,* J. P. Young	"Absence of an Effect of Oxide on the Solubility and the Absorption Spectra of PuF_3 in Molten LiF-BeF_2-ThF_4 and the Instability of Plutonium(III) Oxyfluorides"	*J. Inorg. Nucl. Chem.* **33,** 3591 (1971)
Baybarz, R. D.,* J. R. Stokely, J. R. Peterson*	"Absorption Spectra of Bk(III) and Bk(IV) in Several Media"	*J. Inorg. Nucl. Chem.* **34,** 739 (1972)
Bate, L. C.	"Determination of Mercury in Biological Samples by Neutron Activation Analysis"	*Proc. ANS Topical Meeting on Nuclear Methods in Environmental Research,* University of Missouri, Columbia, Aug. 23–24, 1971
Bemis, C. E.,* R. E. Druschel,* J. Halperin,* J. R. Walton	"Thermal Neutron Capture Cross Section and Resonance Integral for 10.7 Yr Krypton 85"	*Nucl. Sci. Eng.* **47,** 371 (1972)
Botts, J. L.	(See Tennery, V. J.)	
Brady, L. J.	"Preliminary Program, 15th Conference on Analytical Chemistry in Nuclear Technology, Oak Ridge, Tenn., Oct. 12–14, 1971"	*Anal. Chem.* **44**(11), 45A (1972)

AUTHOR(s)	TITLE	PUBLISHER
Bronstein, H. R.,* D. L. Manning	"Lanthanum Trifluoride as a Membrane in a Reference Electrode for Use in Certain Fluoride Melts"	*J. Electrochem. Soc.* **119**, 125 (1972)
Burtis, C. A.,* W. F. Johnson,* J. E. Attrill	"Automated Sample-Reagent Loader for Use in the GeMSAEC Fast Analyzer"	*Clin. Chem.* **18**, 433 (1972)
Butts, W. C.[1]	"Two-Column Gas Chromatography of Trimethylsilyl Derivatives of Biochemically Significant Compounds"	*Anal. Biochem.* **46**, 187 (1972)
Caton, J. E., D. D. Willis,* N. G. Anderson*	"Variable-Speed Drive for the Mechanical Stage of a Microscope Used as the Optical Component in a Microdensitometer"	*Anal. Biochem.* **46**, 232 (1972)
Christie, W. H., H. S. McKown	"Computerized Acquisition and Processing of Isotopic Mass Spectra"	*Chem. Instrum.* **3**, 99 (1971)
Christie, W. H., D. H. Smith,[2] H. S. McKown, G. R. Hertel	"A New High-Resolution Mass Spectrometer with Partial Second-Order Double Focusing"	*Internat. J. Mass Spectrometry and Ion Phys.* **8**, 311 (1972)
Christie, W. H.	(See Smith, D. H.)	
Coleman, R. L.,[3] W. D. Shults, M. T. Kelley, J. A. Dean*	"Environmental Applications of Parallel Photometric Analysis: The Determination of Sulfur Dioxide"	*Anal. Lett.* **5**, 169 (1972)
	"Turbidimetry via Parallel Photometric Analysis"	*Anal. Chem.* **44**, 1031 (1972)
Corbin, L. T.	(See Laing, W. R.)	
Dunn, H. W.	"Use of Computers for X-Ray Absorption Edge, X-Ray Fluorescence, Electron Probe, and X-Ray Diffraction Analyses at Oak Ridge National Laboratory	*Chem. Instrum.* **3**, 245 (1972)
Eby, R.	(See McCracken, J. E.)	
Eldridge, J. S.	(See O'Kelley, G. D.)	
Eldridge, J. S., G. D. O'Kelley,* K. J. Northcutt	"Abundances of Primordial and Cosmogenic Radionuclides in Apollo 14 Rocks and Fines"	*Lunar Science III*, p. 221, Lunar Science Institute, Jan. 10–13, 1972, Houston, Texas
Emery, J. F., S. A. Reynolds, E. I. Wyatt, G. I. Gleason*	"Half-Lives of Radionuclides-IV"	*Nucl. Sci. Eng.* **48**, 319–23 (1972)
Feldman, C.	Book Review of: *Atomic Absorption Spectrochemical Analysis* (2d ed.), B. V. L'Vov	*Appl. Opt.* **11**, 217 (1972)
Friedman, H. A.,* J. R. Stokely, R. D. Baybarz*	"Polarographic Evidence for the Divalent Oxidation State of Californium"	*Inorg. Nucl. Chem. Lett.* **8**, 433 (1972)
Fung, K. W.,* G. Mamantov,* J. P. Young	"Reaction of Aluminum with Molten Chloroaluminates"	*Inorg. Nucl. Chem. Lett.* **8**, 219 (1972)
Goldstein, G.	(See Wolford, J. C.)	
Guerin, M. R.	"Detection of Sulfur-Containing Compounds in the Gas Phase of Cigarette Smokes"	*Anal. Lett.* **4**, 751 (1971)
Handley, T. H.	(See Harmatz, B.)	

1. Present address: Department of Laboratory Medicine, University of Washington, Seattle 98105.
2. Present address: IAEA, Vienna, Austria
3. Present address: Harvard Medical Unit, Boston City Hospital, 818 Harrison Ave., Boston, Mass. 02118.

AUTHOR(s) 1	TITLE	PUBLISHER
Harmatz, B.,* T. H. Handley	"Nuclear Spectroscopy of Neutron-Deficient La, Dy, and Er Activities"	*Nucl. Phys.* **A191**, 497 (1972)
Hertel, G. R.	(See Christie, W. H.)	
Heurtebise, M.,* W. J. Ross[4]	"Application of ^{80m}Br to the Semi-Automated Analysis of Bromine in Biological Fluids"	*J. Radioanal. Chem.* **8**, 5–12 (1971)
	"Radiochemical Separations with Halogenated Resins"	*Anal. Chem.* **44**, 596 (1972)
Horton, A. D.	"Gas Chromatographic Determination of Trimethyl Phosphate, Dimethylbutyl Phosphate, Methyldibutyl Phosphate and Tributyl Phosphate"	*J. Chromatogr. Sci.* **10**, 125 (1972)
Kelley, M. T.	"ORCAL – A Conversational Calculating Language for the ND-812 Computer"	*Chem. Instrum.* **3**, 345 (1972)
Kelley, M. T.	(See Coleman, R. L.)	
Laing, W. R., L. T. Corbin	"The Analysis of Advanced Reactor Fuels"	*Proc., Symp. Anal. Meth. in the Nuclear Fuel Cycle,* pp. 387–93 (December 1971)
Lyon, W. S.	Book Review of: *Principles of Activation Analysis,* Paul Kruger, John Wiley	*Anal. Chem.* 44(2), 111A (1972)
Lyon, W. S., E. Ricci, H. H. Ross	"Nucleonics"	*Anal. Chem.* **44**, 438R (1972)
Manning, D. L., G. Mamantov*	"Determination of the Diffusion Coefficient of Nickel(II) in Molten LiF-BeF_2-ZrF_4 by Linear Sweep Voltammetry and Chronopotentiometry"	*High Temp. Sci.* **3**, 533 (1971)
Manning, D. L.	(See Bronstein, H. R.)	
McCracken, J. E.,[5] J. C. Guyon,* W. D. Shults	"Coulometric Determination of Uranium and Iron-Uranium Mixtures with Feedback-Controlled Electrolysis Current"	*Anal. Chim. Acta* **57**, 151 (1971)
	"Coulometric Microdetermination of Neodymium Using Feedback-Controlled Electrolysis Current"	*Anal. Chem.* **44**, 305 (1972)
McCracken, J. E.,[5] J. R. Stokely, R. D. Baybarz,* C. E. Bemis,* R. Eby	"Determination of Half-Lives of ^{246}Cm and ^{248}Cm by Absolute Specific Activity Techniques"	*J. Inorg. Nucl. Chem.* **33**, 3251 (1971)
McCracken, J. E.,[5] J. C. Guyon,* W. D. Shults, H. C. Jones*	"Instrument for Coulometric Titrimetry with Feedback-Controlled Electrolysis Current"	*Chem. Instrum.* **3**, 311 (1972)
McKown, H. S.	(See Christie, W. H.)	
Moore, F. L.	"Solvent Extraction of Mercury from Brine Solutions with High-Molecular-Weight Amines"	*Environ. Sci. Technol.* **6**, 525 (1972)
	"Liquid-Liquid Extraction of Mercury with High-Molecular-Weight Amines from Iodide and Bromide Solutions"	*Separ. Sci.* **7**, 505 (1972)
Moss, M. L.	"Quartz Fiber Ultramicrobalance"	*J. Histochem. Cytochem.* **20**, 545 (1972)
Mrochek, J. E.,* W. T. Rainey	"Identification and Biochemical Significance of Substituted Furars in Human Urine"	*Clin. Chem.* **18**, 821 (1972)
Northcutt, K. J.	(See Eldridge, J. S.)	
	(See O'Kelley, G. D.)	

4. Work performed while on leave of absence to the Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela.
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AUTHOR(s)	TITLE	PUBLISHER
O'Kelley, G. D.,* J. S. Eldridge, E. Schonfeld,* K. J. Northcutt	"Primordial Radioelements and Cosmogenic Radionuclides in Lunar Samples from Apollo 15"	*Science* **175**, 440 (1972)
	"Concentrations of Primordial Radioelements and Cosmogenic Radionuclides in Apollo 15 Samples by Nondestructive Gamma-Ray Spectrometry"	*Lunar Science,* Lunar Science Institute, Jan. 10–13, 1972, p. 587
Pearce, T. H.,* L. M. Jones,* R. L. Walker	"Strontium Isotope Composition of Analcite-Bearing Volcanics"	*Trans. Amer. Geophys. Union* **52**(11), 926 (1971)
Quincy, R. B.	(See Sturm, B. J.)	
Rainey, W. T.	(See Mrochek, J. E.)	
Reynolds, S. A.	"Radioisotope Characterization, Quality Control, and Standards"	*Isotopes Development Programs Research and Development: 1971,* TID-4067, pp. 46–47 (1972)
	(See Emery, J. F.)	
Ricci, E.	"Chemical Stability of Biological Samples Subjected to Proton-Reaction Analysis"	*J. Radioanal. Chem.* **9**, 273 (1971)
	"Determination of Carbon-12, Carbon-13 Isotopic Abundances and Nitrogen/Carbon in Biological Substances by Proton-Reaction Analysis"	*Anal. Chem.* **43**, 1866 (1971)
	(See Lyon, W. S.)	
Rickard, R. R., E. I. Wyatt	"Separation of Te and Se and Their Fission Products by Precipitation with 1,10 Phenanthroline"	*Anal. Chem.* **44**, 877 (1972)
Ross, H. H.	(See Lyon, W. S.)	
Ross, W. J.	(See Heurtebise, M.)	
Shults, W. D., J. Beauchamp*	"Statistically Based Air Quality Indices"	*Proc. 138th AAAS Nat. Meeting,* Philadelphia, Pa., Dec. 28, 1972
Shults, W. D.	(See Coleman, R. L.)	
	(See McCracken, J. E.)	
Smith, D. H.[2]	"Mass Spectrometric Investigation of Surface Ionization. X. Desorption of Uranium Ions and Neutrals from Carburized Rhenium"	*J. Chem. Phys.* **55**, 4152 (1971)
Smith, D. H.,[2] W. H. Christie	"FORTRAN Programs to Design Mass Spectrometers with Complete Second-Order Focusing"	*Chem. Instrum.* **3**, 165 (1971)
Smith, D. H.	(See Christie, W. H.)	
Stokely, J. R., R. D. Baybarz,* J. R. Peterson*	"The Formal Potential of the Bk(IV)-Bk(III) Couple in Several Media"	*J. Inorg. Nucl. Chem.* **34**, 392–93 (1972)
Stokely, J. R.	(See Baybarz, R. D.)	
	(See Friedman, H. A.)	
	(See McCracken, J. E.)	
Sturm, B. J.,* R. B. Quincy, C. T. Butler*	"Preparation of High Purity Magnesium Oxide Powder of High Bulk Density"	*Bull. Amer. Ceram. Soc.* **51**, 529 (1972)
Talmi, Y., G. H. Morrison*	"Induction Furnace Method in Atomic Spectrometry"	*Anal. Chem.* **44**, 1455 (1972)
	"Use of Induction Furnace Source for Spectrometric Determination of Iodine"	
Tennery, V. J.,* J. L. Botts	"The Chemical Characterization of Uranium Nitride"	*Nucl. Technol.* **13**, 264 (1972)

AUTHOR(s)	TITLE	PUBLISHER
Walker, R. L.	(See Pearce, J. H.)	
Walton, J. R.	(See Bemis, C. E.)	
Whiting, F. L.[6]	"Spectral Studies of O_2^-, NO_2^-, CrO_4^{-2} in Molten LiF-NaF-KF and O_2^- in Liquid Ammonia"	*J. Inorg. Nucl. Chem.* **34**, 2475 (1972)
Wolford, J. C.,[7] J. A. Dean,* G. Goldstein	"Separation of Oxypurines by Ligand-Exchange Chromatography and Determination of Caffeine in Beverages and Pharmaceuticals"	*J. Chromatogr.* **62**, 148 (1971)
Wyatt, E. I.	(See Emery, J. F.)	
	(See Rickard, R. R.)	
Young, J. P.	(See Bamberger, C. E.)	
	(See Fung, K. W.)	
	(See Whiting, F. L.)	
Zittel, H. E.	"Effect of Gamma Radiation on Colorimetric Determination of Iron"	*Anal. Chim. Acta* **58**, 323 (1971)

6. Present address: E. I. duPont de Nemours and Co., Kirston, N.C.
7. Present address: East Tennessee Baptist Hospital, Knoxville, Tenn.

Theses

AUTHOR(s)	TITLE	PUBLISHER
Ealy, J. A.	*A Study of the Extraction and Determination of Some Organo-Mercury(II) Compounds*	University of Tennessee Knoxville, December 1971
Matthews, D. R.	*The Gas Chromatographic Determination of Trace Anions in Aqueous Media*	University of Tennessee Knoxville, Jan 20, 1971

Reports

AUTHOR(s)	TITLE	REPORT NO. AND DATE
Corbin, L. T.	*Statistical Quality Control Report, Analytical Chemistry Division, April Through June 1972*	July 17, 1972
Guerin, M. R.	*Tobacco Smoke Analysis Program Progress Report for the Period September 1, 1970, to July 1, 1971*	ORNL-4435 (October 1971)
Houtzel, A.,* F. F. Dyer	*A Study of Fission Products in the Molten Salt Reactor Experiment by Gamma Spectrometry*	ORNL-TM-3151 (August 1972)
Kelly, M. J.,* C. J. Barton,* A. S. Meyer, E. W. Chew,* C. R. Bowman*	*Theoretical Evaluation of Consumer Products from Project Gasbuggy: Final Report. Tritium Behavior in a Natural Gas Processing Plant*	ORNL-4775 (July 1972)
Kelley, M. T.	*ORCAL – A Conversational Calculating Language for the ND-812 Computer*	ORNL-TM-3697 (February 1972)
	Statistical Quality Control Report, Analytical Chemistry Division – October Through December 1971	Jan. 21, 1972
	January Through March 1972	April 18, 1972
	July Through September 1971	October 20, 1971
Lyon, W. S.	*Report on Foreign Travel*	May 22, 1972 (unpublished)

AUTHOR(s)	TITLE	REPORT NO. AND DATE
Mueller, T. R., D. J. Fisher	*Check-Out and Test Procedures and Performance Specifications for Automatic, Controlled-Current Coulometric Karl Fischer Titrator*	ORNL Q-5137 ST (Dec. 21, 1971)
Meyer, A. S.	*Methods for the Analysis of MSRP Samples and Process Stream*	July 1972 (unpublished)
Reynolds, S. A.	"Radioisotope Characterization, Quality Control and Standards," pp. 46–47 in *Isotopes Development Programs Research and Development: 1971*	TID-4067 (February 1972)
Shults, W. D.	*Analytical Chemistry Division Research and Development Monthly Summary –*	
	May 1972	June 1, 1972
	June 1972	July 3, 1972
	July 1972	August 1, 1972
	August 1972	Sept. 1, 1972
	September 1972	Sept. 30, 1972 (unpublished)
Thomas, W. A., L. R. Babcock, Jr., W. D. Shults	*Oak Ridge Air Quality Index*	ORNL-NSF-EP-8 1971
White, J. C.	*Analytical Chemistry Division Research and Development Monthly Summary –*	
	October 1971	Oct. 29, 1971
	November 1971	Dec. 3, 1971
	December 1971	Jan 6, 1972
	January 1972	Feb. 2, 1972
	February 1972	March 1, 1972
	March 1972	April 4, 1972
	April 1972	April 28, 1972 (unpublished)

ORAL PRESENTATIONS

The number and titles of presentations at local, national, and international conferences reflect the acceptance of the Division's research in areas of long-recognized competence as well as in such new fields as geo- and bioanalytical chemistry. Much of this work has been performed by people who have recently and successfully moved into a new field of expertise and through the application of instruments and facilities developed by the Division in only the last year or two.

Sixteenth Conference on Analytical Chemistry in Nuclear Technology

This conference returned to Gatlinburg this year and for three days (October 24–26) took inventory of the analytical programs of 12 laboratories that are AEC contractors. Each of the 12 sessions was devoted to a description of the facilities and work as presented by members of the installation. The following laboratories participated:

University of California–Los Alamos Scientific Laboratory

Atlantic Richfield Hanford Company

Westinghouse Hanford Company, Hanford Engineering Development Laboratory

Argonne National Laboratory

Iowa State University, Ames Laboratory, USAEC

Associated Universities, Inc., Brookhaven National Laboratory

University of California, Lawrence Livermore Laboratory

Dow Chemical Company, Rocky Flats Division

Union Carbide Corporation Nuclear Division, Y-12 Plant

Union Carbide Corporation Nuclear Division, Oak Ridge Gaseous Diffusion Plant

USAEC New Brunswick Laboratory

Oak Ridge National Laboratory

Members of the Conference Committee were: L. J. Brady, Chairman; H. R. Beatty, Treasurer and Exhibits Coordinator; L. T. Corbin; W. D. Shults; and J. C. White.

Analytical Specialists Meeting

This year Oak Ridge National Laboratory was the site of the annual two-day meeting of analytical chemists from the many divisions of the Union Carbide Corporation. Our Division was host for four sessions that were held March 20 and 21, and several members of the Division participated as specialists. The program of this conference is included to show the variety of interests within the corporate analytical programs.

Monday Morning, March 20

"Gas Chromatography of Corrosive Substances," John G. Million

"Gas Chromatography – Column Selection and Detector Correction Factors," L. A. Prince

"Electrophoresis as an Analytical Tool," J. E. Caton (ORNL)

Discussion Groups: Activation Analysis, X-Ray Fluorescence, and I-R Data Retrieval

Monday Afternoon, March 20

"Fourier Transform NRM," Earl Whipple

"Spark Source Mass Spectrometry," J. A. Carter (ORNL)

"Computerized Bookkeeping System," P. D. Coulter

"Low-Level N-S-Halogen Analyses by Coulometry," G. Hellerman

Discussion Groups: Analytical Costs, Computerized Bookkeeping; Liquid Chromatography; Special Topics

Tuesday Morning, March 21

"Electron Spectroscopy as an Analytical Technique," L. D. Hulett (ORNL)

"Pollution Analyses," P. D. Coulter

"Emission Spectroscopy, Flame Emission, Atomic Absorption," L. A. Prince

"Spectrographic Electrodes," Dale Hiler

Discussion Groups: Pollution Analyses, Upgrading Control Laboratories, Special Topics

Tuesday Afternoon, March 21

Discussion Groups: Other Computer Applications, Special Topics

At Meetings of Professional Societies, Conferences, and the Like

AUTHOR(s)	TITLE	PRESENTED AT
Bate, L. C.	"Neutron Activation Analysis in Criminology"	Symposium on Scientific Techniques for Law Enforcement, Southwestern University, Memphis, Tenn., Dec. 7, 1971
	"Determination of Minor Elements in Soil Profiles by Neutron Activation Analysis"	Second International Conference on Forensic Activation Analysis, Glasgow, Scotland, Sept. 22–23, 1972

AUTHOR(s)	TITLE	PRESENTED AT
Botts, J. L.	"Chemical Characterization of Uranium Nitride"	American Ceramic Society, Philadelphia, Pa., Sept. 25–27, 1972
Caton, J. E.	"Electrophoresis"	Medical Technology Class, St. Mary's Hospital, Knoxville, Tenn., Jan. 18, 1972
	"The Potential of Analytical Polyacrylamide Gel Electrophoresis"	Departments of Plant Pathology and Biochemistry, Clemson University, Clemson, S.C., Feb. 1, 1972
	"Electrophoresis as an Analytical Tool"	Analytical Specialties Meeting, Union Carbide Corporation, Oak Ridge, Tenn., Mar. 20, 1972
	"The Potential of Analytical Polyacrylamide Gel Electrophoresis"	ORAU Traveling Lecture, Department of Chemistry, University of Miami, Coral Gables, Fla., Apr. 24, 1972
	"Gel Electrophoresis and the Analysis of Macromolecules"	ORAU Traveling Lecture, Department of Chemistry, Florida Atlantic University, Boca Raton, Apr. 25, 1972
	"Polyacrylamide Gel Electrophoresis"	ORAU Traveling Lecture, Department of Chemistry, University of Puerto Rico, Rio Piedras, Apr. 27, 1972
Eldridge, J. S.	"Calibration and Use of a Large Low-Background Gamma-Ray Spectrometer for Lunar and Geochemical Samples"	Tenth Meeting of the Society for Applied Spectroscopy, St. Louis, Mo., Oct. 18–22, 1971
	"Lunar Sample Analysis"	Seminar, Democritos Nuclear Center, Athens, Greece, Sept. 6, 1972
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"	First International Summer School on Radionuclide Metrology, Herceg, Novi, Yugoslavia, Aug. 21–Sept. 1, 1972
Goldstein, G.	"Biochemical Indicators of Environmental Pollution"	American Association for the Advancement of Science Annual Meeting, Philadelphia, Pa., Dec. 26–31, 1971
	"Development of Specifications for Labeled Nucleotides and Related Compounds"	164th American Chemical Society National Meeting, New York, N.Y., Aug. 27–Sept. 1, 1972
Guyon, J. C.,* W. D. Shults, J. E. McCracken*	"Coulometric Titrimetry with Feedback-Controlled Electrolysis Current"	IUPAC International Congress on Analytical Chemistry, Kyoto, Japan, April 3–7, 1972
Horton, A. D., M. R. Guerin, G. Olerich	"Sulfur-Containing Compounds in the Gas Phase of Cigarette Smoke"	25th Tobacco Chemists Research Conference, Louisville, Ky., Oct. 6–8, 1971
Horton, A. D., W. D. Shults, A. S. Meyer	"Determination of Nitrogen, Sulfur, Phosphorus, and Carbon in Solid Ecological Materials via Hydrogenation and Element-Selective Detection"	15th Conference on Analytical Chemistry in Nuclear Technology, Oak Ridge, Tenn., Oct. 12–14, 1971
Hulett, L. D.	"Application of ESCA to Environmental Problems"	2nd Trace Metals Symposium, University of Illinois, Urbana, Nov. 18–19, 1971
	"Electron Spectroscopy as an Analytical Tool"	Seminar, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada, April 18, 1972
Hulett, L. D., A. L. Bacarella*	"Analysis of the Surfaces of Solids by Photoelectron Spectroscopy"	15th Conference on Analytical Chemistry in Nuclear Technology, Oak Ridge, Tenn., Oct. 12–14, 1971
Laing, W. R., L. T. Corbin	"The Analysis of Advanced Reactor Fuels"	Symposium on Analytical Methods in the Nuclear Fuel Cycle, Vienna, Austria, Nov. 29–Dec. 3, 1971
Kelley, M. T.	"Recent Features of Instrumentation for Chemical Analyses at ORNL"	Symposium, Horiba, Ltd., Kyoto, Japan, April 6, 1972
	"The ORNL Parallel-Analysis System – Features and Performance Characteristics"	IUPAC International Congress on Analytical Chemistry, Kyoto, Japan, April 3–7, 1972

AUTHOR(s)	TITLE	PRESENTED AT
	"Application of Centrifuge Photometric Analysis to Environmental Problems"	Southeastern Regional ACS Meeting, Nashville, Tenn., Nov. 4–6, 1971
Kubota, H.	"Status of Nuclear Analytical Chemistry in the United States"	Seminar, Analytical Chemistry Division, Japanese Atomic Energy Research Institute, Tokai, Japan, April 11, 1972
	"Impression of Research Establishments in Japan"	Seminar, Isotope Development Center, J.A.E.R.I., Oarai, Japan, April 12, 1972
Kubota, H., M. R. Guerin, C. A. Pritchard	"Polar Apiezons for the Gas Chromatographic Determination of Phenanthrene and Benz(a)anthracene in Smoke Condensates"	25th Tobacco Chemists Research Conference, Louisville, Ky., Oct. 6–8, 1971
Lyon, W. S.	"Recent Work at ORNL in the Application of Neutron Activation Analysis"	Seminar, Democritos Nuclear Center, Athens, Greece, April 24, 1972
	Chairman of Session "Medicine, *in-vivo* Studies"	IAEA Symposium on Nuclear Activation Techniques in the Life Sciences, Ljubljanna, Yugoslavia, April 10–14, 1972
	Chairman of Session "Forensic Activation Analysis"	2nd International Conference on Forensic Activation Analysis, Glasgow, Scotland, Sept. 27–29, 1972
Lyon, W. S., L. C. Bate, J. F. Emery	"Environmental Pollution: Use of Neutron Activation Analysis to Determine the Fate of Trace Elements from Fossil Fuel Combustion in the Ecological Cycle"	IAEA Symposium on Nuclear Activation Techniques in the Life Sciences, Ljubljanna, Yugoslavia, April 10–14, 1972
Lyon, W. S., E. Ricci, L. C. Bate, F. F. Dyer	"Reliability in Scientific Evidence Based on Multi-Trace Forensic NAA"	2nd International Conference on Forensic Activation Analysis, Glasgow, Scotland, Sept. 27–29, 1972
Maddox, W. L., R. B. Quincy, H. H. Ross, G. Olerich, M. R. Guerin	"Carbon-14 and Neutron-Irradiated Cigarettes for Animal Lung Deposition Experiments"	25th Tobacco Chemists Research Conference, Louisville, Ky., Oct. 6–8, 1971
Mamantov, G.,* D. L. Manning	"Electrochemistry in Molten Fluorides"	UCHEM Meeting on Molten Salts, Sheffield, England, Sept. 11–15, 1972
Matthews, D. R., W. D. Shults, M. R. Guerin	"The Extraction-Derivatization-GC Determination of Trace Phosphate in Aqueous Media"	15th Conference on Analytical Chemistry in Nuclear Technology, Oak Ridge, Tenn., Oct. 12–14, 1971
Moss, M. L.	"Microchemical Pathology"	Seminar, East Tennessee Children's Hospital, Knoxville, Tenn., Jan. 4, 1972
	"Recent Research in Muscular Dystrophy"	Television Interview, "Jerry Lewis Telethon," Knoxville, Tenn., Sept. 6, 1972
Mueller, T. R., D. J. Fisher, W. D. Shults	"An Electrochemical Ambient Air Monitor for Chloride and Chlorine"	Symposium on Advances in Electrochemical Science, Rocky Mountain Regional ACS Meeting, Colorado State University, Ft. Collins, June 30–July 1, 1972
O'Kelley, G. D.,* J. S. Eldridge, K. J. Northcutt, E. Schonfeld*	"Some Consequences of Solar Proton Activation of Lunar Surface Materials"	Lunar Science Institute Conference on Modern and Ancient Energetic Particles from the Sun, Houston, Texas, Oct. 13–15, 1971
Rainey, W. T., W. C. Butts, M. R. Guerin, F. Snyder*	"Combined Gas Chromatography-Mass Spectrometry for the Identification of Compounds of Biological Interest"	15th Conference on Analytical Chemistry in Nuclear Technology, Oak Ridge, Tenn., Oct. 12–14, 1971
Reynolds, S. A.	"Material and Information Needs of Standards Users"	Atomic Industrial Forum Meeting on Radioactivity Standards, Washington, D.C., June 5, 1972

AUTHOR(s)	TITLE	PRESENTED AT
	"ORNL Activities Relating to Methodology, Standard Materials, and Standard Data on Radioisotopes"	Meeting, American Nuclear Society Committee 16, Las Vegas, Nev., June 19, 1972
Ricci, E.	Chairman of Session "Activation Analysis"	1972 Annual Meeting of the American Nuclear Society, Las Vegas, Nev., June 18–20, 1972
Shults, W. D.	Chairman of Panel Discussion "Standardization and Validation of Analytical Methods"	2nd Annual Trace Metals Symposium, University of Illinois, Urbana, Nov. 18–19, 1971
	"Electrochemical Monitoring of Air Contaminants"	Seminar, Memphis State University, Memphis, Tenn., Mar. 17, 1972
Shults, W. D., W. A. Thomas,* J. R. Duncan,* L. R. Babcock, Jr.*	"Characteristics and Performance of Air Pollution Indexing Systems"	Air Pollution Control Association Meeting, Miami, Fla., June 18–22, 1972
Strain, J. E.	"Detection and Identification of Explosives"	Seminar, Aberdeen Proving Ground, Aberdeen, Md., Sept. 2, 1972
Talmi, Y.	"Analytical Potentialities of the Induction Furnace Method in Atomic Spectroscopy"	163rd American Chemical Society Meeting, Boston, Mass., April 13, 1972
		Seminar, Perkin-Elmer Corp., Norwalk, Conn., Nov. 18, 1971
Walker, R. L.	"Rhenium Analysis by Surface Ionization-Isotopic Dilution Method"	American Society for Mass Spectrometry, Committee VII Workshop, Dallas, Texas, June 8, 1972
White, J. C.	"Activation Analysis Program with the HFIR"	International Symposium on Radiochemical Aspects of Trace Analysis, Kyoto, Japan, Apr. 4–7, 1972

Seminars

The continual movement of the Laboratory into new areas of research has given need and impetus for good communications. The Division is attempting to do its part by enlarging its program of informal discussions within its staff as well as maintaining close contact with the various research divisions. Continual education is considered to be necessary so that the members of the Division will be aware of future problems as well as the existence of new or more effective methods of analysis.

ORNL Seminars

AUTHOR(s)	TITLE	PRESENTED AT
Cooper, J. H., Lamb, C. E.	"Capabilities of the Analytical Chemistry Division's Service Laboratories"	ORNL Metals and Ceramics Division Seminar, July 12, 1972
Fisher, D. J.	"Instrumentation Research in Analytical Chemistry"	Chemistry Division-Division of Research, Nov. 17, 1971
Goldstein, G.	"The Facilities of the Analytical Chemistry Division"	ORNL Biology Division Seminar, June 20, 1972
Guerin, M. R.	"Practical Capabilities of Gas Chromatography"	Oak Ridge Associated Universities, Jan. 20, 1972
	"Smoking and Health Program"	ORNL Research Committee, June 7, 1972
Gutenkunst, V. J., Eckles, R. G.[1]	"Summary of Work as ORAU Trainees"	ORNL Analytical Chemistry Division Seminar, Aug. 10, 1972
Horton, A. D.	"Element-Selective Detectors"	Oak Ridge Associated Universities, Jan. 20, 1972
Hulett, L. D.	"Capabilities of Electron and Physics Methods Group of the Analytical Chemistry Division"	ORNL Reactor Chemistry Division Seminar, Jan. 10, 1972
Hurt, H.[2]	"Alcoholism in Industry"	ORNL Analytical Chemistry Division Seminar, Sept. 19, 1972

AUTHOR(s)	TITLE	PRESENTED AT
Kelley, M. T.	"Small Computer Applications"	Chemistry Division-Division of Research, Nov. 17, 1971
Kelley, M. T., R. W. Stelzner	"Mini Computers in Analytical Chemistry"	ORNL Analytical Chemistry Division Seminar, Oct. 19, 1971
Laing, W. R.	"Precision and Accuracy of Pipetting Devices"	ORNL Biology Division Seminar, Sept. 15, 1972
Laing, W. R., Costanzo, D. A.	"Analytical Capacity of the Analytical Chemistry Division's Service Laboratories"	ORNL Chemical Technology Division Seminar, March 29, 1972
		ORNL Reactor Division Seminar, Feb. 11, 1972
		ORNL Metals and Ceramics Division Seminar
Lijinsky, W.[3]	"Analytical Methods in Chemical Carcinogenesis"	ORNL Analytical Chemistry Division Seminar, Dec. 14, 1971
Pomerance, H. S.[4]	"Reeling in the Information"	ORNL Analytical Chemistry Division Seminar, Sept. 7, 1972
Rainey, W. T.	"Modern Techniques in Mass Spectrometry"	ORNL Analytical Chemistry Division Seminar, Nov. 16, 1971
Ricci, E.	"Nuclear Methods in Chemical Analysis"	Chemistry Division-Division of Research, Nov. 17, 1971
	"Measurement of Environmental Base Lines and Reference Levels by Ultra-High Sensitive Activation Analysis"	ORNL-NSF Review Meeting, March 9, 1972
	"Photo Activation: ORELA's Analytical Twist"	ORNL Analytical Chemistry Division Seminar, May 16, 1972
Talmi, Y.	"Microanalysis of Solids by Atomic Absorption and Emission Spectroscopy Using RF Furnace Environmental Applications"	ORNL Analytical Chemistry Division Seminar, Nov. 11, 1971
	"Potentialities of an RF Induction Furnace as an Excitation Source for Atomic Absorption and Emission Spectroscopy"	ORNL Analytical Chemistry Division Seminar, Apr. 18, 1972
Walton, R. B.[5]	"Nondestructive Analytical Techniques for Material in the Nuclear Fuel Cycle"	ORNL Analytical Chemistry Division Seminar, Jan. 18, 1972
White, J. C.	"Future Research Program Planning"	Chemistry Division-Division of Research, Nov. 17, 1971
Young, J. P.	"Electrochemical-Spectral Studies of Molten Fluoride Salts"	Reactor Chemistry Division Seminar, Oct. 22, 1971

1. ORAU trainees.
2. ORNL Health Division.
3. ORNL Biology Division.
4. ORNL Information Division.
5. Los Alamos Scientific Laboratory.

Service Laboratory Seminars

AUTHOR(s)	TITLE	DATE
Burtis, C. A.[1]	"Bioanalytical Applications of Fast Analyzers"	January 20, 1972
Ealy, J. A.	"Extraction and Gas Chromatographic Determination of Methyl-, Ethyl-, and Methoxyethylmercury(II) Halides by G.L.C."	February 24, 1972
Guerin, M. R.	"Tobacco Smoke Analysis Program, Projects, and Problems"	October 21, 1971
Henderson, G. S.[2]	"Programs and Analytical Requirements of the Environmental Sciences Division"	May 11, 1972

AUTHOR(s)	TITLE	DATE
Matthews, D. R.	"Extraction-Derivatization-GC-Determination of Trace Phosphate in Aqueous Media"	February 24, 1972
Meyer, A. S.	"Analytical Program of the Molten-Salt Reactor Project"	November 12, 1971
Shults, W. D.	"Analytical's Role in the ORNL/NSF Programs"	June 22, 1972

1. ORNL Molecular Anatomy Program.
2. ORNL Environmental Sciences Division.

Patents

AUTHOR	TITLE	PATENT NO.	DATE ISSUED
Moore, F. L.	"Isolation and Purification of Americium from Other 5f and 4f Elements by Extraction Chromatography"	3,615,268	Oct. 21, 1971
	"Separation and Recovery of Americium from Curium and Other Elements"	3,687,641	Aug. 29, 1972

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

Reviewer or referee	Number of articles reviewed or refereed for indicated periodicals																				
	Anal. Biochem.	*Anal. Chem.*	*Anal. Chim. Acta*	*Anal. Lett.*	*ANSI Methods*	*ASTM Methods*	*Chem. Instrum.*	*Environ. Sci. Technol.*	*High Temp. Sci.*	*Isotop. Radiat. Technol.*	*J. Elect. Spect.*	*J. Nat. Cancer Inst.*	*J. Inorg. Nucl. Chem.*	*J. Phys. Chem.*	*J. Radioanal. Chem.*	*Nucl. Technol.*	*Radioanal. Lett.*	*Radiochem. Radioanal. Lett.*	*Science*	*Proposals*	Total
Caton, J. E.				1																	1
Christie, W. H.		6																			6
Costanzo, D. A.		2															2				4
Feldman, C.																				1	1
Fisher, D. J.		1					2														3
Gentry, K. W.		1																			1
Goldstein, G.	1			2																	3
Guerin, M. R.												2									2
Hulett, L. D.											2									2	4
Lyon, W. S.		4						1							3			5			13
Manning, D. L.		3							1					2							6
Moore, F. L.		2						1													3
Mueller, T. R.							1														1
Reynolds, S. A.					1	8				1			1			1			1		13
Ricci, E.		3																			3
Rubin, I. B.	1																				1
Shults, W. D.		3	1																	1	5
Stelzner, R. W.		2					1														3
Young, J. P.		2																			2
Zittel, H. E.		1														2					3
Total	2	30	1	3	1	8	4	2	1	1	2	2	1	2	3	3	2	5	1	4	78

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SEPTEMBER 30, 1972

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