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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT
Period Ending September 30, 1973

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$5.45; Microfiche \$1.45

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ORNL-4930
UC-4 – Chemistry

Contract No. W-7405-eng-26

ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
For Period Ending September 30, 1973

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JANUARY 1974

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
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U.S. ATOMIC ENERGY COMMISSION

Reports previously issued in this series are as follows:

ORNL-686	Period Ending March 31, 1950
ORNL-788	Period Ending June 30, 1950
ORNL-867	Period Ending October 10, 1950
ORNL-955	Period Ending January 10, 1951
ORNL-1088	Period Ending March 26, 1951
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ORNL-2218	Period Ending December 31, 1956
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ORNL-2866	Period Ending December 31, 1959
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ORNL-3243	Period Ending December 31, 1961
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ORNL-4466	Period Ending October 31, 1969
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Preface

This has been another eventful year for the Division and the Laboratory. At the start of this period, we were engaged in reconciling the Division roster with a trimmed budget. At the close of the period, we foresee much brighter and happier times ahead despite the inconveniences and discomforts that the energy shortage brings. For example, the Division's activities in work for other Government agencies continue to increase markedly, particularly with the National Cancer Institute and its Smoking and Health Program. The role that the Division is asked to play in this program is becoming well defined — a condition that affords stability and continuity with their concomitant advantages. Our involvement with the National Science Foundation—Ecology and Trace Contaminants Analyses (EATC) has also continued with some significant changes in programmatic content. These two programs constitute about 30% of our effort and have enabled us to establish an extremely broad capability for the analysis and characterization of organic compounds and other trace environmental contaminants. We are consequently much better equipped to assist the AEC in its new programs designed to alleviate the nation's energy problems.

The Division's major involvement with the AEC reactor programs has been reoriented to the High-

Temperature Gas-Cooled Reactor Program (HTGR). D. A. Costanzo was appointed to serve as the Coordinator for Analytical Chemistry for the HTGR Program to facilitate the early awareness and resolution of analytical problems. The Division continues to provide the analytical support required by the research divisions at ORNL. Accounts of all these activities are included in this report.

A new activity was launched in this period which is designed to enable the Union Carbide Nuclear Division to achieve more efficient and economical use of capital equipment items by combining the programmatic requirements of the production, operating, and research plants and laboratories that make use of such equipment. A major step was taken in the establishment of a gas analysis facility that will be equipped with the latest advancements in gas analysis technology. This facility will be located within our Mass Spectrometry Group. Other possible consolidations of programmatic requirements for specified analytical functions that are not customarily fully supported by a single plant are under study. We look forward to participating with the ORGDP and Y-12 analytical laboratories in this endeavor.



1. INSTRUMENTATION AND ADVANCED METHODOLOGY

To augment analytical capability for the determination of organometallic compounds in general, and organomercury compounds specifically, a new and unique analytical system was developed. The device consists of a high-resolving-power gas chromatograph coupled to a microwave discharge detector assembly. Compounds eluted from the column are instantly decomposed to simple atomic and molecular species upon entering the microwave plasma. The excited materials can be detected either photometrically or photographically with high sensitivity and selectivity. For a variety of organomercury compounds, the absolute detection limit is in the range of 2 to 5 pg. A Varian model 63 carbon rod analyzer was acquired for the determination of many elements by atomic absorption spectrometry. Preliminary work with this unit has been directed toward the assay of lead and cadmium in environmental samples. Ultratrace analysis of many elements is possible because of the high sensitivity (<0.1 pg) that can be obtained with the system. Work continues with the radio-frequency furnace instrument, particularly directed toward the analysis of "real" samples. Materials already investigated include fossil fuels, soils, and both animal and plant tissues. Homogeneity effects in solid and semisolid samples appear to be a major problem.

As part of the ORNL NSF/RANN project on Ecology and Analysis of Trace Contaminants, applications of the GeMSAEC fast analyzer are being investigated. A major effort has been directed toward the development of methods for the determination of pollutants in air and water. At present, two analyzers are in operation, both under computer control. Thus far, fast techniques for the determination of iodide, copper, selenium, zinc, iron, magnesium, and ozone have been developed.

During the past year, work on the specific ion electrode for uranium has come to fruition. Electrodes have been fabricated that exhibit linear response over the range of about 10^{-1} to 5×10^{-4} M uranyl chloride. A study of the stability of dilute mercury solutions and techniques to stabilize these solutions has been completed. This work has important implications for sampling methods used with environmental materials. A new technique to measure the distribution coefficient of mercury and dimethylmercury between various aqueous solutions and argon or air has been developed; results obtained are in excellent agreement with those obtained with slower and more tedious methods. A study of biochemical and biological indicators of environmental pollution has also been completed.

This group has also been involved with a variety of instrumentation problems. A study of the applications of pulse polarography has been initiated. Trace element determinations at <1 ppb appear practical. Computer programming and application activities have been extensive. Work was done for the GeMSAEC program, on electrochemical analysis systems (coulometry), and for the Mass Spectroscopy Group. A number of small instrumental systems have been designed and others updated for state-of-the-art performance.

2. BIO-ORGANIC ANALYSIS

The Bio-Organic Analyses Group continues its primary involvement in bioanalytical studies supporting Laboratory programs in human biochemistry and in organic analytical studies related to smoking and health. Bioanalytical studies have focused on the application of immunotechnology to analytical problems. Efforts related to tobacco smoke analysis have expanded considerably, and new responsibilities for the National Cancer Institute program have been added. The numbers and types of experimental products studied and scheduled for future study have increased, as have

responsibilities related to the inhalation bioassay development project. Major expansions of effort in bioanalytical studies related to the bioassay and in chemical studies of the exposure environment are beginning. A new project area, the chemical and physical characterization of smokes generated by inhalation bioassay machines, has been initiated; it is funded by the Council for Tobacco Research, U.S.A.

Studies of present sample-handling procedures demonstrate the need for examining alternative procedures for special applications. Modifications of the puff-averaging machine have allowed its application to the determination of reactive smoke components. Final data have been submitted to the National Cancer Institute on the quantities of approximately 25 components in the first series of 23 experimental cigarettes. Data on the isoprene deliveries of the cigarette as well as on the quantities of seven metals and five fatty acids in samples of condensate and particulate matter, respectively, were submitted to the NCI also.

Based on these data, isoprene and free fatty acids are now routinely determined on the primary experimental cigarettes. Final data have been submitted characterizing a series of cigarettes containing selective filters and several sets of special experimental products. A study of the second series of experimental cigarettes, involving approximately 25 components on each of 25 products, is approximately two-thirds complete.

New or substantially improved methods have been established for the semiroutine determination of carbon monoxide, carbon dioxide, hydrogen cyanide, benz(a)anthracene, benzo(a)pyrene, free fatty acids, nitric oxide, and sulfur gases. Studies of the sulfur components of smokes have reconciled the differences between literature results and ORNL results and have further confirmed our contention that the quantities and number of sulfur components present are greater than had been assumed. Studies of the nitrogen-selective electrolytic conductivity detector, in addition to providing superior methods for the determination of nitric oxide and gas-phase amines, suggest this to be a generally applicable tool of great promise for future studies. Continuing work with component profiling has produced data demonstrating the utility of this approach for dramatically expanding the number of kinds of components which can be surveyed for biological significance. Component profiling as well as standard analytical methods have been applied to studies of the "little cigar."

The Inhalation Bioassay Project has continued with the development and supply of specialty hardware and instrumentation. Several additional smoke exposure

systems, including two which double the normal animal capacity for each pump, are in regular use. A viable hamster containment tube is on hand, and a viable rat containment tube appears close to realization. A machine for preparing radiolabeled cigarettes and several machines designed elsewhere for exposing dogs to smokes have been fabricated for collaborating NCI contractors. Carbon-14-dotriacontane has been shown to be an effective smoke tracer for lung deposition studies and has been applied in approximately 20 dosimetry experiments. Measurements of breathing rate and tidal volume have been carried out in studies of the intralaryngeal cannula, in studies of the dependence of dosimetry on respiration, and in studies of changes in respiration as a function of smoke exposure time.

An initial survey of the chemical characteristics of smokes produced by inhalation exposure machines is under way. Studies in this area are supported by both the NCI and the Council for Tobacco Research, U.S.A. The distribution of particulates in the chamber as functions of position and time revealed that mixing can be improved for the ORNL machine. The gas phase is distributed more uniformly. With animals present, decreases in particulates and gas-phase components have been found to correlate well with deposition data and to be very helpful for the interpretation of biological observations. Studies of nitric oxide and gas-phase organics suggest that compositional changes during the exposure period are much smaller than expected.

Bioanalytical projects have focused on the study and application of immunochemical techniques. Immuno-subtractive chromatography, particularly when adopting newly developed automated systems, has proved useful for the isolation of specific proteins. Combining immunochemical techniques with high-resolution electrophoresis allows the visualization of minor components in complex mixtures of macromolecules. High-resolution electrophoresis alone has proved valuable for the characterization of mutated plant strains.

3. ENERGY PROGRAMS

The voltammetric method under development for in-line determination of U^{3+}/U^{4+} was used for the in situ analysis of simulated MSRE fuel during the salt preparation and also after the fuel was transferred to fuel pins for an in-pile experiment. This was a highly practical application in that it permitted the elimination of a number of steps in the procedure and materially reduced the time required for the operation. In-line voltammetric measurements were also performed in NaF-NaBF₄, the proposed coolant for molten-salt reactors,

in support of the operation of the Coolant Salt Technology Facility (CSTF). Reproducible waves for the reduction of 100 ppm of Fe(II) and 30 ppm of Cr(III) were recorded at gold electrodes inserted in the melt in a specially designed salt monitoring vessel that was fed by a side stream from the CSTF. Reduction waves were also observed for Ni(II), Fe(III), and an unknown species that was probably Mo(III).

Traces of an electroactive proton species in the coolant were observed as an increase in the pressure within an evacuated palladium electrode held cathodic to the melt. From such measurements, the half-life of this species in the CSTF was estimated to be about 10 hr. It was demonstrated by a standard addition of water that concentrations of this species in the ppb range could be measured. These observations, together with electroanalytic and spectrophotometric research, indicate that the active proton species is distinct from BF_3OH^- and highly mobile (diffusion coefficient $\sim 8 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$). Since it is in equilibrium with a condensable species, probably $\text{BF}_3 \cdot \text{H}_2\text{O}$, in the cover gas, it may serve as an agent for the containment of tritium. A large distribution coefficient, $(C_{\text{condensate}}/C_{\text{melt}}) = \sim 10^5$, was observed for tritium leached from the CSTF components.

Square-wave voltammetry was tested for the measurement of UF_4 in molten $\text{LiF}\text{-BeF}_2$. Because of the low resistance of the medium, the technique can be applied at higher frequencies than possible in aqueous media. The method offers increased sensitivity and resolution over linear sweep voltammetry. Tellurium, a fission product of nuclear reactors, was found to exist as Te_3^- in molten $\text{LiF}\text{-BeF}_2$. This ion was unstable with respect to disproportionation, oxidation to Te^0 , or reduction to Te^{2-} .

Based on the application of a theory by Vander Sluis and Nugent, it has been found possible to establish the coordination number of a trivalent rare-earth ion from the position of its first charge-transfer band. From a knowledge of the first $f-d$ absorption, similar but less reliable predictions are possible. There appears to be another, as yet unknown, parameter involved in the theory. From these considerations, it seems probable that Ce(III) is 8-coordinated in molten $\text{LiF}\text{-BeF}_2\text{-ZrF}_4$ or $\text{LiF}\text{-NaF}\text{-KF}$. Apparatus is being designed and fabricated to investigate the generation and characterization of unusual oxidation states of transuranium ions by spectral study in various molten salt systems. In a preliminary assessment of solvents, some spectral studies of Cu(II) and Ni(II) in molten $\text{NaOH}\text{-KOH}$ have been carried out.

4. NUCLEAR AND PHYSICS METHODS

The scanning electron microscope-x-ray fluorescence technique has been used to examine environmental samples of mud, ore, and ore tailings; the method has also proved useful in more fundamental studies, such as inclusions in mica. X-ray-induced x-ray fluorescence techniques are being developed using Si(Li) detectors and monochromatic x-ray sources. Electron spectroscopy for chemical analysis (ESCA) has been applied to studies involving adsorption of various elements and herbicides on clays. The program to measure trace elements through a coal-fired steam plant continued, with major emphasis on determining fallout outside the plant and volatiles in the stack gas. The long-time cooperative isotope program was terminated in March; several reports summarize its accomplishments including collecting nuclear data, checking quality control of isotope products, answering requests, and working with national organizations. MONSTR, a PDP-15 program for analyzing gamma-ray spectra from Ge(Li) detectors, has been used with excellent results in neutron activation analysis (NAA). Low-level radioactivity measurements were made on grasses and air filters for the AEC. A program has begun to develop better methods for determination of plutonium and other actinide elements in environmental samples; for Safeguard Inventory, improvements in gamma-ray spectrometry of ^{235}U are being studied. Hypothetical levels of tritium in products made from nuclearly stimulated gas were calculated. Work continued in evaluating fission product behavior in HTGR coolant circuits, and studies on fission product release from fuel microspheres were completed. Detector, timer, and sample shape were studied at the HFIR-NAA facility, ^{252}Cf activation was tested for two round-robin samples from AEC, and calculations made for the flux gradient at the ORELA photon activation analysis facility were checked experimentally. Radioactivity measurements for Apollo 17 included the NaI detector (for induced activities) carried on the flight and a number of lunar rocks and fines for solar-flare-induced activities as well as primordial radioelements. Results from similar measurements on Apollo 16 samples were also reported.

5. MASS AND EMISSION SPECTROMETRY

To aid in more efficient data reduction from the spark-source mass spectrometer, an interactive computer (PDP-8/E)-operated data acquisition and processing system to read photographic plates is under develop-

ment. Two types of programs are being used. The first uses an emulsion calibration program; it takes percent transmittance data for two isotopes and computes a relative intensity data table using the Churchill two-line method. The second type of program makes isotope dilution calculations for 11 different elements — Cd, Zn, Hg, Pb, Cu, W, Cr, Fe, Se, Zr, and U. Both of these basic programs written originally in FORTRAN were translated into FOCAL, thus reducing the work load on the IBM 1130 and eliminating the cumbersome and slow card-punching step.

The collaborative research in strontium-rubidium geochronology and weathering experiments with the University of Georgia has continued. Very precise $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are obtained using the two-stage 12-in. machine. The measurements of the absolute abundance of krypton on the earth's atmosphere were completed. A final result of 1.1074 ± 0.0083 ppm by volume is the value determined from ten measurements. Another significant development during the year was the development of a combined analytical system for measuring total nitrogen and its isotopic abundance in environmental samples. The system is composed of a reductive pyrolysis unit and a 6-in. mass spectrometer. The geochronology of speleothems (stalagmites) was the basis for some interesting research work done by a graduate student this past year. He found that by using the ^{234}U disequilibrium method, stalagmites up to 1,500,000 years old are potentially datable. Another problem, determining the gas composition in salt crystals, has been accomplished by in situ crushing of the salt in a simple device tied in with a 6-in. gas mass spectrometer. Much greater reliability of analysis is achieved over the previous method of dissolving, where possible, in degassed water.

In the Mass and Emission Spectrometry Group, analytical developmental studies on various matrices for ORNL-funded NSF/RANN projects, EPA, and the ORNL-Purdue cadmium project have continued. In addition to taking advantage of the multielemental coverage of spark-source mass spectrometry, isotope dilution techniques for Hg, Cd, Zn, Pb, Cu, Te, and Se have been evaluated and used on a variety of environmental problems. The APDC extraction procedure used prior to atomic absorption measurements of cadmium, lead, and zinc was modified to eliminate iron and other spectral interferences. A three-stage thermal emission mass spectrometer is being used for the quantitative measurement of lead and uranium in coal, fly ash, and heating oils and for lead in gasoline. Coal samples analyzed for cadmium by isotope dilution showed that cadmium concentrations generally increased with ash content.

Improvements were made in the procedure for analyzing trace metals in gasoline by SSMS; the method involves bromine oxidation and freeze drying. The isotopic abundance of lead was measured in a series of soil samples that are used as secondary standards for ion microprobe lead isotopic ratio measurements.

During the past year approximately 900 organic samples were analyzed on the single-stage mass spectrometer. The Body Fluids Analysis Program of the Chemical Technology Division furnished the major sample load with others coming from the Biology, Chemistry, Health Physics, and Environmental Sciences Divisions. In addition, support was given to other groups in the Division and to plant production personnel. The single-stage instrument has been interfaced to the IBM 1130 computer for acquiring and processing data. The high-resolution instrument was used in the analysis of 150 samples. The sublimation-sputter-ion pump has been replaced by a 1200-liter/sec diffusion pump to allow coupling of a gas chromatograph.

The cooperative study with W. Lijinsky, of the Biology Division, of the mass spectra of N-nitroso compounds resulted in some interesting and unexpected results to be reported in a forthcoming TM report. Another interesting short project in organic GC-MS was successfully completed during the year for the Viking mission to Mars.

The mass spectrometry service laboratory reported over 17,250 isotopic and gas analysis results this past year. These include both stable and radioactive elements for the Isotopes Division and alpha-active materials in support of TRU and LWBR programs. Uranium and plutonium were determined in the safeguards round-robin IDA-72 program. Isotopic measurements were made in this laboratory on over 50 elements. The cooperative arrangement continues with the Y-12 mass spectrometry laboratory whereby gas analysis service is provided.

The spark-source and emission spectrometry laboratory reported over 54,600 results during the year to many divisions and projects at ORNL. Important projects participated in are the production of iridium metal sheet and the HTGR and BAPL reactor fuels programs. In all of these, the importance of impurity analyses in meeting specifications is a vital part of necessary quality assurance programs.

6. METHODS DEVELOPMENT AND SPECIAL PROJECTS

The group has continued its effort to establish and support analytical development programs within the service laboratories and to establish analytical capa-

bilities for the analysis of reactor materials and fuel and environmental and biological materials. Other research and development studies are aimed toward new practical methods for pollution abatement of toxic metals and the preparation of inorganic and organic materials not readily and/or commercially available.

The methods which were evaluated or developed for reactor fuel and materials analyses included the electrolytic disintegration of HTGR fuel compacts, damaged pyrolytic carbon-silicon carbide coated fuel particles, hydrogen release and open porosity of pyrolytic-carbon-coated fuel particles, particle size distribution of $^{233}\text{UO}_2$ powder by sedimentation, and dissolution of noble-metal alloys and refractory oxides.

Environmental field samples have been analyzed for carbon, nitrogen, and sulfur by reductive pyrolysis-gas chromatography and for mercury by cold-vapor atomic absorption spectrophotometry. Several methods were evaluated for the determination of total carbon (dissolved and particulate organic or inorganic) in aqueous field samples.

Inorganic materials which were prepared included RbClO_4 , ND_4ClO_4 , NaBF_3OD , FeCoS_4 , BaTbO_4 , TbF_4 , and $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 2.3\text{H}_2\text{O}$. Large quantities of some fused salts were prepared, such as LiNO_3 , KNO_3 , and CsNO_3 . Some programs carried out were the preparation of a series of standards of high-purity iron containing from 0.005 to 10.0 wt % cobalt, the growth of single crystals of solid solutions of FeS_2 with CoS_2 , the electrolytic saturation of palladium with hydrogen, the doping of Eu_2O_3 with various amounts of CaO , and the preparation of solid solutions of NH_4I in RbI .

Stable isotopes salvaged during the year were ^{57}Fe , ^{54}Fe , ^{154}Sn , and ^{61}Ni .

PART B. SERVICE ANALYSES

The General Hot Analyses Laboratory's work continued in support of the LWBR program to produce $^{233}\text{UO}_2$, and several specimens of paint coatings were tested for resistance to corrosion, radioactive contamination, and radiation damage. Consolidation of the General Hot Analyses Laboratory facilities was also completed during the past year.

The General Analyses Laboratory used automated colorimetry, gas chromatography, and atomic absorption to analyze large numbers of environmental samples for essential elements and trace metals. The atomic absorption method was used to analyze four types of iridium alloys, and refinements were made in several methods used to analyze HTGR samples.

The new Environmental Analyses Laboratory, located in Buildings 2024 and 2026, was established to coordinate the analytical requirements of the Environmental Sciences Division and to provide a "clean room" facility for special sample preparation.

Laboratory housekeeping has steadily improved since the Radiation Control and Safety Program's quarterly laboratory inspections began. Again this year we had 12 medical treatment cases but no unusual accidents.

The Quality Control Program started four new controls by atomic absorption and one by infrared absorption; an increase was reported in the overall quality level and the number of control samples.



Part A. Analytical Research and Development

1. Instrumentation and Advanced Methodology

H. H. Ross, Head

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D. L. Manning
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ANALYTICAL SYSTEMS DEVELOPMENT

Gas chromatography. A gas chromatograph—microwave emission spectrometric detector (GC-MES) analytical system has been built and successfully applied to a variety of analytical and physical problems. The system is composed of a gas chromatograph combined with a highly sensitive and selective microwave-excited plasma-emission detector. The separated materials coming off the GC column enter into the high-energy plasma, where they are instantly decomposed to simple molec-

ular species and free atoms. The characteristic molecular and atomic emission spectrum is monitored by a monochromator-PMT system. We have also incorporated a photographic detection capability in the monochromator that can cover a selected 50-nm spectral region; this feature is quite important for determining the optimum operating conditions for nonroutine samples.

Our efforts, thus far, have mainly concentrated on the application of the system to the practical analysis of trace organomercury compounds, in particular CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$, in environmentally based samples. The absolute detection limit of the system for these compounds is 2 to 5 pg, and the relative sensitivity is 0.02 to 1.0 ppb. Using this technique, we have developed new methods for the analysis of CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$ in water, sediment, and fish samples. A new type of GC column utilizing pyrolytic graphite spheres as the support was also developed that allows the direct determination of CH_3HgCl in water without extraction. Studies involving the determination of CH_3HgCl in fish have been carried out in cooperation with the Environmental Sciences Division. The work required an accurate and simultaneous determination of both total mercury and CH_3HgCl at base-line and at various contamination levels. One study has already been completed, and a paper has been submitted for publication to *Science of the Total Environment*. These investigations clearly demonstrated the superiority of the MES over the widely used electron capture (EC) detector in the following ways:

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1. ORAU summer student research trainee.
 2. ORAU graduate participant.
 3. Consultant.

1. Sensitivity for mercurials is at least one order of magnitude better.

2. In contrast to EC, the detectability of the MES is almost independent of the molecular nature of the species; that is, equal sensitivity for both CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$ is obtained.
3. The detector can be used with virtually any solvent system.
4. No time-consuming cleanup procedures of the solvent are required before injection into the GC.
5. Samples can be injected at a faster rate, that is, 30 to 40 samples/hr compared with 1 to 2 samples/hr with EC.

These features of the MES are a direct result of the high degree of selectivity of the detector. The sensitivity for elements whose most prominent spectral lines lie near or at the vacuum uv spectral range (arsenic, antimony, selenium) is somewhat reduced, but this is partially compensated for by the simultaneously improved selectivity.

In addition to the above environmental studies, we have completed a series of physical chemistry studies in cooperation with R. Mesmer, Chemical Technology Division, as part of the ORNL/NSF(RANN) Program. The studies included the following:

1. determination of the vapor pressure of CH_3HgCl and its dependence on temperature and pH,
2. distribution coefficients of $(\text{CH}_3)_2\text{Hg}$ and CH_3HgCl between water and air phases,
3. the rate of decomposition of CH_3HgCl by halogens.

This last study has important implications for the analytical methodology of CH_3HgCl and also suggests an effective mechanism for the destruction of CH_3HgCl in water. This work is being prepared for publication.

Presently, we are investigating the applicability of the GC-MES system to other trace contaminants. The determination of various arsenic acids involves their reduction to corresponding arsines. The arsine mixtures are then separated on the GC column and quantitatively detected by monitoring the light emitted at the 288-nm arsenic line. The method is still in the development stage, but the observed arsenic detection limit of 20 to 50 pg and the efficient separation by GC are encouraging.

Simultaneously, we have also started a new project to study the determination of trace selenium. Selenium is extracted from digested samples after reaction with 4-nitro-*o*-phenylenediamine or 2,3-diaminonaphthalene. The preliminary results are promising and demonstrate the potential capability of the system to detect selenium in water at the 0.1-ppb level. Further work is

required and is primarily concerned with the sample preparation technique.

A flame spectrometric detector system (FSD) has also been developed for gas chromatography applications. The system utilizes a premix nitrous oxide-acetylene burner to reduce noise caused by flame turbulence and a monochromator for observation of the excited spectra of the eluted elements. The FSD is operated in tandem with a flame ionization detector (FID) to permit a convenient comparison of the chromatograms obtained with the two detectors. The FSD generally provides lower sensitivity than conventional detectors (detection limits varied from 3 μg for arsenic to 20 ng for beryllium vs typical limits of 5 ng for the FID and sulfur-specific detectors); however, its specificity provides unambiguous identification of the peak containing the desired elements and frequently permits the use of simpler sample preparation procedures and less vigorous chromatographic separations. Thus it is often possible to achieve a higher concentration in the gas chromatographic eluate.

The FSD was utilized to develop a method for the determination of cacodylic acid, a popular defoliant, via chromatography of its volatile complex with allylthiourea. This complex is readily formed in aqueous solution. Procedures for the elimination of possible interferences were developed.

An investigation of the chromatography of the $\text{Be}(\text{tfa})_2$ chelate (tfa = trifluoroacetylacetonate) revealed that the chelate partially decomposed on the column, causing poor reproducibility of this measurement. The decomposition is largely eliminated by the use of a Teflon column with a Teflon support. Investigation of the chromatography of vanadium tfa chelates revealed that the volatile species was $\text{V}(\text{tfa})_3$ rather than the reported $\text{VO}(\text{tfa})_2$. A procedure was developed in which $\text{VO}(\text{tfa})_2$ is extracted into organic solvents and then reduced to $\text{V}(\text{tfa})_3$ with metallic zinc for chromatographic measurement. The gas chromatographic determination of $\text{Cr}(\text{tfa})_3$, chromium hexafluoroacetylacetonate, three arene tricarbonyl chromium complexes, $\text{Al}(\text{tfa})_3$, and $\text{Cu}(\text{tfa})_3$ was also demonstrated.

Atomic emission and absorption. During the past year the Division acquired a Varian model 63 carbon rod analyzer. This device offers superior sensitivity for many elements by flameless atomic absorption spectrometry, and it requires only microliter volumes of samples. Drying and atomization are achieved by (programmable) resistance heating of a small carbon tube furnace which is mounted directly within the optical light path. We are evaluating this instrument for

ultratrace analysis of many sample types from our environmental programs. Concurrently, we have evaluated an improved extraction technique that utilizes 2-heptanone rather than hexane as the organic solvent in APDC extractions. This improvement provides both increased extraction coefficients and decreased background levels (blanks) for many elements. Work to date has emphasized the determination of lead and cadmium, for which we observe absolute detection limits of 0.1 pg and 5 pg respectively. We find that considerable "technique" is required to obtain satisfactory reproducibility with this device, partly because the test portion is small (1 to 5 μ l) and partly because solutes in the test portion can interfere with the atomization or measurement process. Indications are that these problems can be overcome by the use of the APDC-heptanone extraction procedure prior to the flameless AA measurement. By this technique, for example, we obtained a value of 0.27 ppm cadmium for the NBS standard reference material, bovine liver (SRM 1577); the NBS value is 0.28 ppm. As part of the study, we are investigating procedures that involve direct injection of organic extractant as well as procedures that require an aqueous stripping step.

The overall objective of this work is to devise an extraction/measurement technique for ultratrace analysis of many elements of current environmental interest.

Our radio-frequency furnace (RFF) system has proved to be a valuable tool for trace analysis of the four elements tested (Cd, Zn, Pb, and Cu), in both the atomic absorption and atomic emission modes. Emphasis was placed upon the ability to analyze "real" samples. Samples analyzed included fossil fuels such as coal and light oil, geological samples such as soil, and animal and plant tissue such as orchard leaves and bovine liver. Results obtained were compared either with certified values or with results obtained by an independent method. On this basis, the average relative standard deviation of all samples analyzed in this study was less than 3%, and accuracy ranged from 0 to 20%.

A major effort was spent on a comparison of sample pretreatment procedures, including direct analysis, wet ashing, tissue solubilization in Soluene 100, and dry ashing. Direct analysis has been, in general, the least useful because of the lack of control over homogeneity in solid or semisolid samples. Wet ashing appears to be the most generally applicable pretreatment method for this instrument.

Much time was also spent in characterizing the physical parameters of the instrument. It is concluded that the absolute sensitivity of the instrument in either the AA or AE mode cannot match that of the carbon

rod atomizers, primarily because of the large volume of the RFF analysis chamber. However, the RFF seems much superior in its lack of interference from sample matrices. In addition, it is one of the few flameless techniques which can be used in both AA and AE spectroscopic modes. Finally, once the samples are prepared, the short instrument-analysis time is a significant advantage.

APPLICATIONS OF THE GeMSAEC FAST ANALYZER

As part of the ORNL/NSF(RANN) project on Ecology and Analysis of Trace Contaminants, we are investigating applications of the GeMSAEC fast analyzer to analyses of interest in evaluating environmental quality. We are currently emphasizing methods for the determination of air pollutants and for analysis of natural, treated, and waste waters, because these kinds of samples usually require little or no pretreatment and the rapid analysis capabilities of the analyzer can be used to best advantage. Virtually all photometric methods are adaptable to the GeMSAEC analyzer and hence are available to us for the solution of analytical problems. We are presently concentrating on spectrophotometry, because it is the most widely used photometric technique (many methods which can be adapted are already available), and on kinetic methods (fixed time, variable time, initial rate) because of the analyzer's unique capabilities in rapidly collecting and processing data. A major task, now almost completed, has been the development of appropriate software to implement each of these analytical techniques.

Two analyzers are now in operation. GeMSAEC I, the analyzer constructed by the Analytical Chemistry Division, is equipped with a monochromator and interfaced to the computer having 4K of core memory and disk. GeMSAEC II, acquired from the MAN Program, uses optical filters rather than a monochromator and is interfaced to the computer with 8K of core memory and magnetic tape reader. The characteristics important to photometric analysis have been evaluated for both of these systems, and a summary of these tests is shown in Table 1.1. In general, the precision of GeMSAEC I, although limited by considerable electrical noise, is still better than most ordinary spectrophotometers. GeMSAEC II is virtually noise-free but suffers from a stray light problem because of the relatively broad spectral bandwidth of the available optical filters that limits its linear absorbance range.

A few instrumental modifications have been made in the past year. A bucking circuit to suppress the dark

Table 1.1. Photometric characteristics of GeMSAEC fast analyzer systems

	GeMSAEC I	GeMSAEC II
Maximum photometric precision ^a	0.2%	0.04%
Optimum transmittance range ^b	10–40% <i>T</i>	5–60% <i>T</i>
Average optical path length	0.973 cm	0.950 cm
Optical path length differences ^c	0.21%	0.07%
Linear absorbance range	0.1–1.2 ^d	0.1–0.6

^aRelative standard deviation of repetitive measurements on individual cuvetts, for groups of 16 measurements.

^bFor maximum precision.

^cRelative standard deviation of average optical path length.

^dRange tested.

current was installed on both analyzers. We also plan to incorporate additional signal amplification capability because we have had difficulty in obtaining sufficient signal when strongly absorbing solutions were measured. Since we intend to use GeMSAEC II mainly for chemiluminescence measurements, we have replaced the tungsten lamp light source with a light-emitting diode (LED) having approximately the same intensity as chemiluminescence signals. The LED provides a stable light signal for instrument setup and evaluation, software development, and daily checks on instrument operation.

To exploit GeMSAEC II, it was necessary to make several changes in computer programs. Since the Tennecomp tape unit used for disk backup on the 4K PDP-8/I on GeMSAEC I was transferred to provide the program interchange function on GeMSAEC II, a new version of FOCAL (FOCG2) was written on the premise that the 4K computer would be dedicated completely to GeMSAEC operation. The system was simplified so that it could be loaded more simply by its own built-in bootstrap instead of depending on a disk monitor. In FOCG2, it has been found possible to introduce a faster FLOG function without seriously reducing core data storage capacity. The dedicated mode of operation has also increased the disk storage for programs from 23 to 40 and has significantly increased disk storage for single-precision and floating-point data.

Starting from FOCG2, a FOCAL version for GeMSAEC II (FOCGT) was written using the Tennecomp unit for program storage. More recently, the 8K PDP-8/I computer with two disks has been connected to GeMSAEC II (using a modification of FOCG2), thus releasing the 8K-Tennecomp unit for use in collecting ESCA spectra.

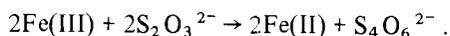
The following analytical methods have been developed:

Iodide. Iodide is determined in water by an initial-rate kinetic method based on its catalytic effect on the rate of reduction of Ce(IV) by As(III) in acid medium. Under the conditions employed, the reaction is first order with respect to both Ce(IV) and I⁻ concentrations and is independent of As(III) concentration. Since Ce(IV) is the only light-absorbing species at 407 nm,

$$\log A_t/A_0 = -k[I^-]t,$$

where A_0 is the absorbance at time 0 and A_t is the absorbance at any other time t , and the slope of a plot of $\log A_t/A_0$ vs time is proportional to iodide concentration. The computer was programmed to take ten absorbance readings at 5-sec intervals, starting at 10 sec after rotor startup, to calculate the log of the absorbance ratio, to determine the best straight line by the method of least squares, and to print out the slope. From 20 to 100 ppb of iodide was determined with a relative standard deviation of 5 to 15%. Compared with standard methods,^{4,5} the GeMSAEC method uses a much smaller sample and has a shorter analysis time, only 1 min.

Copper. For the estimation of copper, we adapted a method⁶ in which copper acts as a catalyst in the reduction of Fe(III) by $S_2O_3^{2-}$:



Thiocyanate is also added to the solution as an indicator for Fe(III) and to slow the reaction to a reasonable time scale. A variable-time kinetic method was used, with the time required for the absorbance of ferric thiocyanate at 455 nm to decrease from its initial value to a preset lower value (0.1 in this case). Concentration of the copper catalyst is proportional to the reciprocal of this time. To implement the variable-time method, a computer program was prepared which takes up to 100 absorbance readings at fixed time intervals, storing them in disk memory. After data collection is complete the stored data are recalled, and

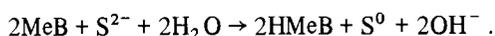
4. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 13th ed., Washington, D.C., 1971, p. 185.

5. American Society for Testing and Materials, *Annual Book of ASTM Standards. Part 23. Water: Atmospheric Analysis*, Philadelphia, 1972, p. 212.

6. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Pergamon Press, Oxford, 1966, p. 120.

the time at which the absorbance reaches the preset value is calculated by linear interpolation between the absorbances bracketing that value. Up to five standards are run in the same rotor as the samples, and a calibration curve (concentration vs reciprocal time) is calculated by either a linear or parabolic fit. Concentrations in the samples are then printed out. For copper analysis, 45 absorbance measurements were taken at 2-sec intervals after an initial 20-sec delay. From 0.1 to 1 ppm of copper was determined with a relative standard deviation of less than 5%. Analysis time is about 2 min.

Selenium. Selenium was determined in natural waters by a variable-time kinetic method based on catalysis of the reduction of methylene blue by sulfide ion:⁷



Absorbance measurements at 560 nm were started 20 sec after rotor startup and taken at 1-sec intervals for a total of 90 sec; the time required to bleach the methylene blue to an absorbance of 0.1 is then calculated. This method is applicable for the estimation of 0.1 to 0.5 μg of selenium with a relative standard deviation of 2 to 10%. Interfering elements in natural water were removed by a cation exchange separation or masked with EDTA. A paper describing this work is being prepared.⁸

Zinc. Zinc was determined spectrophotometrically by reaction with 4-(2-pyridylazo)resorcinol (PAR).⁹ The reaction product, $\text{Zn}(\text{PAR})_2$, is water soluble, has an unusually high molar absorptivity of 8.3×10^4 at 493 nm, and forms rapidly in carbonate buffer at pH 9.7. Using citrate as a complexing agent, only nickel, cobalt, and copper interfere seriously. Standards are run in the same rotor as the samples and are used to construct a calibration curve. The concentration of each of the samples is calculated and printed out along with the relative standard deviation. From 0.2 to 1 ppm of zinc in natural and treated waters was determined with a relative standard deviation of less than 3%. Although the zinc content of the natural waters tested was very low (less than 0.05 ppm), as much as 1 ppm was found

in treated potable water, presumably due to corrosion of galvanized plumbing. A paper describing this work has been submitted for publication.¹⁰

Iron. For the determination of soluble iron in natural waters, the well-known thiocyanate spectrophotometric method¹¹ was selected because of its high sensitivity and freedom from interferences. Although only Fe(III) is measured by this method, Fe(II) can be determined by difference after oxidation with KMnO_4 . Copper is the only serious interference. Absorbance measurements were made at 480 nm after a color development time of 5 min. From 0.1 to 3 ppm of iron was determined with a relative standard deviation of less than 3%. Several natural water samples collected locally were analyzed and had a total soluble iron content of less than 0.1 ppm. Spikes added to these samples were recovered quantitatively.

Magnesium. After a study of the photometric methods available for the determination of magnesium, we selected a turbidimetric method in which magnesium is precipitated as the phosphate.¹² This method was found to be relatively free from interferences and more nearly linear in the 5 to 70 ppm magnesium range than methods involving the formation of colored lakes. Magnesium is precipitated by a saturated HPO_4^{2-} solution, containing cyanide as a masking agent, at pH 10.8. After a 5-min delay to allow formation of the precipitate, the solution was stirred vigorously by air bubbling for 15 sec and the absorbance measured at 480 nm. The computer program prepared for spectrophotometric measurements was also used here for turbidity. Surface and treated waters containing from 5 to 20 ppm of magnesium were analyzed with a relative standard deviation of about 5%.

Ozone. Analysis of ozone, an important air pollutant, was accomplished by a modification of a method suggested by Sachdev et al.¹³ The air sample is first reacted with eugenol (4-allyl-2-methoxyphenol), a liquid 1-olefin, in a small gas impinger. Ozone attacks the double bond releasing formaldehyde, which is swept into a trap containing a dichlorosulfitomercurate(II) ion solution and then analyzed by a modification of the

7. P. W. West and T. V. Ramakrishna, "A Catalytic Method for Determining Traces of Selenium," *Anal. Chem.* 40, 966 (1968).

8. J. L. Bowling, J. A. Dean, and Gerald Goldstein, "Determination of Selenium in Natural Waters Using the Centrifugal Photometric Analyzer," to be submitted to *Analytical Letters*.

9. M. Kitano and J. Ueda, "Spectrophotometric Determination of Zinc with 4-(2-Pyridylazo) Resorcinol," *Nippon Kagaku Zasshi* 91, 983 (1970).

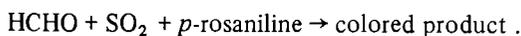
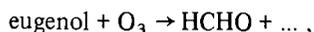
10. Gerald Goldstein, W. L. Maddox, and M. T. Kelley, "Spectrophotometric Analysis with the GeMSAEC Fast Analyzer. Determination of Zinc Using 4-(2-Pyridylazo) Resorcinol (PAR)," submitted to *Analytical Chemistry*.

11. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3d ed., Interscience, New York, 1959, p. 524.

12. *Ibid.*, p. 625.

13. S. L. Sachdev, J. P. Lodge, Jr., and P. W. West, "Specific Method for the Determination of Ozone in the Atmosphere," *Anal. Chem. Acta* 58, 141 (1972).

West-Gaeke method for sulfur dioxide, previously adapted to the GeMSAEC analyzer:¹⁴



To avoid the necessity of waiting for full color development, a fixed-time kinetic method is used. This method has the advantage of being selective for ozone rather than for total oxidants. Sensitivity is of the same order as the standard KI method. At the 1-ppm level, we have obtained a relative standard deviation of 1 to 2%. A paper describing this method has been prepared.¹⁵

SPECIAL ANALYTICAL STUDIES

Ion-selective uranium electrode. We have continued our studies on ion-selective electrodes for uranium. The electrodes are prepared by incorporating the uranyl salt of di-(2-ethylhexyl)phosphoric acid¹⁶ ($\text{UO}_2\text{D2EHPA}$) in a polyvinyl chloride (PVC) matrix. Significant extension of the useful lifetimes of the membranes was made by combining the $\text{UO}_2\text{D2EHPA}$ exchanger with a suitable solvent such as diamyl amylphosphonate or di-(2-ethylhexyl) ethylphosphonate. These have a stabilizing effect on the $\text{UO}_2\text{D2EHPA}$ exchanger and extend the usefulness of the membranes to several weeks. Semilog calibration plots are linear from about 10^{-1} to 5×10^{-4} M uranyl chloride. Other promising specific ion electrode systems for uranium were found to be PVC membranes made from uranyl salts of mono-*n*-butylphosphoric acid or di-(2-ethyl-4-methylpentyl)phosphoric acid in combination with the solvents diamyl amylphosphonate or di-(2-ethylhexyl) ethylphosphonate. Interference studies for the favorable membranes revealed that of the common cations only copper(II) and iron(III) constituted serious interferences; however, the anions sulfate, nitrate, and perchlorate likewise interfere and should be absent or less than about 10^{-4} M. A more detailed report on this work is being prepared for publication.

Mercury studies. It is well known that dilute mercury solutions — ppm concentrations and below — tend to decrease in concentration with time. The losses are generally attributed to volatilization and/or adsorption on the container walls, and they can be severe. For example, we found that a 100-ppb mercury solution in 1% HNO_3 lost half of the mercury in 53 days, and a 10-ppb mercury solution lost half of the mercury in only five days. Means for preserving dilute mercury solutions are needed for the collection and storage of water samples as well as for the preparation of standard solutions. Accordingly, we have studied the stability of dilute mercury solutions in several media and in several container types. A paper describing these studies has been accepted for publication.¹⁷

Five types of solution, all prepared with distilled and demineralized water, were investigated. These included (1) untreated water, (2) HNO_3 solutions, (3) solutions containing H_2SO_4 and KMnO_4 , (4) HNO_3 solutions containing $\text{Cr}_2\text{O}_7^{2-}$, and (5) quasi-neutral solutions containing $\text{Cr}_2\text{O}_7^{2-}$. The first three are commonly referenced in the literature. The other two were tested because our experience had indicated that Cr(VI) had a stabilizing effect upon dilute mercury solutions. Tests were conducted with both glass and polyethylene containers, using mercury concentrations that ranged from 0.1 to 10 ng/ml. In every medium except $\text{HNO}_3\text{-Cr}_2\text{O}_7$, substantial losses of mercury occurred within ten days. With 5% (v/v) HNO_3 and 0.01% $\text{Cr}_2\text{O}_7^{2-}$, however, no detectable losses occurred at either the 0.1-, 1.0-, or 10.0-ng/ml mercury concentrations over a test period of five months. Both the acid and the oxidant are necessary to ensure stability. The efficacy of this mixture is probably due to its ability to prevent hydrolysis of dissolved mercury and to prevent its reduction to oxidation states lower than +2.

In the movement of mercury (or other chemical species) through the environment, it is often necessary to know the distribution coefficient of the species between two phases (e.g., water/air). This distribution is usually measured by determining the concentration of the species in both phases or by measuring the concentration in one phase and calculating it in the other by difference. However, these methods may be unreliable or inconvenient under certain conditions. One phase may be difficult to sample or to analyze for the species of interest. The concentration of the species in the phase not analyzed may be difficult to calculate by difference due to chemical equilibria existing in the

14. R. L. Coleman, W. D. Shults, M. T. Kelley, and J. A. Dean, "Environmental Applications of Parallel Photometric Analysis. The Determination of Sulfur Dioxide," *Anal. Lett.* 5, 169 (1972).

15. J. L. Bowling, J. A. Dean, and W. D. Shults, "Determination of Atmospheric Ozone Using the Centrifugal Photometric Analyzer," submitted to *Analytical Letters*.

16. H. H. Ross et al., "Analytical Activities in the Transuranium Research Laboratory," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 4.

17. C. Feldman, "The Preservation of Dilute Mercury Solutions," *Anal. Chem.*, in press.

system, or the total quantity of the species in the system may not be known. We have recently completed the development and testing of a technique that enables us to determine the distribution coefficient of a material by analyzing only a single phase of the system; this technique is based on the method of successive equilibrations. We have shown that:

$$K_{I/II} = (V_{II}/V_I)(R_{n/n+1} - 1),$$

where K is the distribution coefficient, V is volume, Roman numerals represent the phases, and $R_{n/n+1}$ is the ratio of the concentration of the species in the phase analyzed after the n th equilibration to its concentration in that phase after the $(n + 1)$ th equilibration. If equilibrium has been reached, $R_{n/n+1}$ is independent of n . Either the phase analyzed or the other phase may be chosen to be discarded after each equilibration.

Using this technique, we have measured the distribution coefficients of Hg^0 and $(\text{CH}_3)_2\text{Hg}$ between various aqueous solutions and argon or air. The results obtained are in excellent agreement with those determined by other conventional techniques and are presented in detail in a paper submitted for publication in *Analytical Chemistry* entitled "Determination of Gas/Liquid (or Other) Distribution Coefficients by Analysis of One Phase Only."

Other work. A study of biochemical and biological indicators of environmental pollution was made for the Environmental Indices Group of the ORNL-NSF Environmental Program. Biochemical indicators were discussed orally, and a paper was published.¹⁸ An annotated bibliography of biological indicators was also prepared,¹⁹ covering the literature through 1971 and containing over 500 entries. The bibliography is organized by the level of biological complexity of the indicator starting at the molecular level and continuing through to communities, and also by pollutant. Entries were selected on the basis of their apparent value in implementing actual monitoring programs.

A Princeton Applied Research pulse polarograph has been evaluated for multielement analytical applications in both the polarographic and anodic stripping modes of operation. Since we are interested primarily in high-sensitivity applications, most of our work has been

aimed at evaluations using the differential pulse anodic-stripping technique with a wax-impregnated graphite electrode. Efforts were made to determine copper, lead, cadmium, and zinc simultaneously at the ppb level in water samples.

Our studies indicate that the instrumental sensitivity is adequate for determination at the low (<1) ppb level. The practical sensitivity limit, however, is set by the level of impurities present in the electrolyte and containment vessels. Under our best condition, background levels of 0.5 to 2.0 ppb of the elements were obtained. Therefore, determination of a few ppb of the elements can be made with minimal effect from impurities.

A severe problem in the analysis of zinc and copper using stripping techniques is the formation of intermetallic compounds between these elements. Formation of these compounds yields low results for zinc and severely limits the application of stripping techniques for the simultaneous determination of zinc and copper. Lead and cadmium intermetallic compounds also appear to be formed, but the effect on analysis is not nearly so severe. Studies on the Zn-Cu intermetallic compound show that a 1:1 compound is formed, and the compound is stripped from the electrode at potentials near the copper stripping wave.

COMPUTER PROGRAMMING AND APPLICATIONS

Numerical integration procedures such as Simpson's rule require equal intervals between the data points. We have developed a Lagrangian polynomial interpolation algorithm for handling curves formed by unequally spaced data points. This algorithm is written in the BASIC language for operation on the DEC system 10 computer and in the FOCAL language for operation on our PDP-8/I and PDP-8/E computers.

The PDP-8/E computer system for operation of our Perkin-Elmer 403 atomic absorption spectrophotometer has been put into routine operation and has been used in the analysis of hundreds of samples, often for up to 16 hr/day. Modified circuit and programming functions will now permit computer control of the LKB sample changer, which can be used for the analysis of up to 200 samples in approximately 20 min. However, except for cases where several elements are run on the same sample dilution, the time required to fill the special sample containers is not justified. Several minor modifications to the FOCAL program for this computer permit the use of its cubic fit routine for calculating other analyses conducted in the Environmental Sciences laboratory.

18. Gerald Goldstein, "Biochemical Indicators of Environmental Pollution," p. 109 in *Indicators of Environmental Quality*, ed. by W. A. Thomas, Plenum Press, New York, 1972.

19. W. A. Thomas, Gerald Goldstein, and W. H. Wilcox, *Biological Indicators of Environmental Quality*, Ann Arbor Science, Ann Arbor, Mich., 1973.

Further features have been added to the ORCAL interpretive language for the ND-812 computer which have increased its usefulness both to users at ORNL and elsewhere. These features include routines for a high-speed paper tape reader and punch; the storage and retrieval of programs via a cassette tape unit, which permits the storage and retrieval of single-precision, double-precision, or floating-point data in fields 2 and 3; and the operation of a real-time clock. Versions of ORCAL containing these features, with corrections for a few minor "bugs," have been submitted to the Nuclear Data Users Society Library of programs.

The DEC system 10 (PDP-10) time-sharing computer has continued to find application, especially in the processing of the voluminous tables of data from the Tobacco Smoke Analysis Program. One of its most useful features has been the generation of correlation plots between various parameters measured both at ORNL and at other sites using the INTRIGUE plotting package on the DEC-10. By using cigarette code numbers to indicate the location of points on the plots and also putting in a least-squares straight line fitted to the data, it is possible to show general trends and to identify deviations from the trend in the same plot. Programs for the DEC-10 have also been written to plot ESCA data and particle size plots (from the Coulter counter), functions which were displaced from the 4K PDP-8/I used on GeMSAEC I. The plots produced from the DEC-10 are suitable for reproduction and require less operator time as well.

We have developed a computer technique for direct transfer of a DEC system 10 disk file to 10- by 15-in. Multilith mats for reproduction. The DEC system 10 program DECPRT.SRC is modified and stored in our disk area. We use TECO, the DEC 10's text editor and corrector, to edit the file for error correction and for proper spacing and paging, and then use the system program RUNOVR to queue the edited file for printing on mats by the IBM 360 line printer.

We have added to the hardware and software of our 8K PDP-8/I computer assigned to electrochemical applications by installing a Sykes Compu/Corder 100 cassette digital recorder. The cassette recorder gives us much needed bulk storage for operation of the OS/8 operating system.

Our work in computer-electrochemical applications was continued with a study of numerical integration techniques for coulometry. For this work we designed a data acquisition algorithm that takes 128 analog-to-digital converter (ADC) readings in exactly 1/60 sec, looping 32 times to give a summation of 4096 measurements acquired in a 1-sec period. An average of

these 4096 measurements is computed and stored in field 1 of the core memory as a 12-bit, single-precision number. A coulometric titration lasting 20 min generates 1200 data points representing 4.0 million ADC measurements. Numerical integration of the area under the current vs time curve is accomplished with a function that calls the field 1-stored data into the floating-point accumulator. Because the time interval between data points is 1 sec, simple summation of the value of the current at each data point produces a number equivalent to the area. Simpson's rule was also applied to these same data to calculate an area. The above data acquisition algorithm is only 53% efficient. We have increased the efficiency of the data-taking step to 97% by elimination of all programmed delays. This results in a time interval of 0.55 sec. At the same time, we designed a machine language program to handle, store, and retrieve double-precision data.

We examined the technique of "predictive" coulometry to ascertain if an end result can be predicted from initial measurements of current. The equation for current as a function of time is:

$$i(t) = i_0 \exp(-kt),$$

where i_0 is the initial current and k is an experimentally determined constant. A least squares fit of the straight line

$$\ln i(t) = -kt + \ln i_0$$

permits evaluation of k and i_0 , with the ratio i_0/k giving the number of coulombs involved in electrochemical transfer. The chemical system used in this work was coulometric titration of U(VI) \rightarrow U(IV) in 1 *N* sulfuric acid. The instrument used was the ORNL model Q-4010 controlled-potential coulometric titrator. For the uranium titration, concentrations accurate to 0.4 to 0.8% could be predicted from the first 2 to 4 min of a run.

ANALYTICAL INSTRUMENTATION DESIGN AND MODIFICATION

Cyclic voltammeter. At the request of Hugh Isaacs, Metals and Ceramics Division, we have designed a new cyclic voltammeter. The instrument was fabricated by the Instrumentation and Controls Division and checked out and calibrated by Isaacs and T. R. Mueller. The instrument will be used in studies on stress corrosion of stainless steels. Primary instrument requirements include a linear cyclic potential ramp with a slope of

about 1 V/day (0.002 mV/min) for some of the studies and faster potential sweep rates for others. Isaacs also requested a logarithmic converter function so that log current vs potential could be recorded. Since some of his test specimens cannot be isolated from earth ground, the instrument ground can be "floated" with respect to ground, or an ac ground can be established. In this new design, we have simplified interpretation of panel control functions by the operator by including more logic within the instrument than was feasible in earlier designs (models Q-2792 and Q-2943). Some salient features of the instrument are:

1. Chopper-stabilized, low-current-drift current-to-voltage converter. This permits accurate measurements of cell current between 30 nA and 300 mA, with a maximum error set by resistor tolerances, in this case $\pm 0.5\%$ overall. At 2 nA the measurement error is only 5%.
2. Current-summing potentiostat. External command signals are easily scaled to the desired command voltage at the cell.
3. Low drift in "hold" mode.
4. Cycle counter permits cutoff of sweep at the end of $\frac{1}{2}$, 1, 2, or 4 cycles.
5. Nine sweep rates from 0.002 to 1 V/min. There is also a variable range, resettable to one part in a thousand.
6. Plug-in circuit cards arranged according to circuit function. This permits one to tailor performance to the required specifications or to add or delete functions as desired.

No actual performance data are available since the instrument has just been completed.

Fluorometric instrumentation. The determination of uranium in the range 10^{-9} to 10^{-6} g by fluorometry in fused NaF dates back to work reported in 1926. Numerous modifications of the matrix salt to eliminate specific interferences and a number of instruments for excitation and detection of the uranium fluorescence have been described since that time. There is one commercially available instrument, but sample manipulation with it is cumbersome. The apparatus and methods used in our Division are described in the Master Analytical Manual as methods 1 003080, 1 219240, and 9 00719240. Our instrument, ORNL model Q-1165, was designed over 20 years ago. Continued use of the method and increasing difficulty and expense in obtaining replacement parts seemed to

indicate that it was time to update the instrument. We decided to retain the convenient sample-handling part of the instrument but to replace the electronics package and excitation source lamps. Replacing the lamps required only minor mechanical modification and reduced the excitation power input from 200 W to only 8 W. By eliminating the bulky power transformers and ballasts, we were able to place all electronic components into a single small cabinet. The instrument is very easy to use since operation of the electronic portion is virtually automatic. Once a sample has been selected, the instrument automatically programs the most sensitive usable measurement range and positions the decimal point in a digital readout that displays nanograms of uranium directly.

Other projects. To study the noise characteristics of various luminous sources, particularly flames used in atomic emission and absorption studies, we designed a new photometric amplifier (model IX-C) utilizing field-effect transistor input operational amplifiers. These amplifiers supply the high input impedance required to obtain an accurate measure of photomultiplier current and provide a low output impedance to drive other signal processors or recorders. The model IX-C has a fixed gain for the input amplifier, which can be set to values between 1 V/nA and 1 V/100 μ A. The input amplifier is followed by low-pass filter stages with variable gain and roll-off characteristics. Response is flat with frequency to 20 kHz with minimum filtering. The system with its dc power supply is mounted in a portable cabinet and is being used in flame-noise studies.

Harry Bronstein, Chemistry Division, inquired about a voltmeter for his work on graphite-bead-column electrode studies. His special requirements in an instrument were good potential control, slow linear scan as a function of time, cell current capability in hundreds of milliamperes, and a stable current integrator. Our ORNL model Q2943A cyclic voltmeter satisfied all of these requirements except that existing sweep rates were too high. Since we incorporated a low-drift chopper-stabilized amplifier in the sweep generator design, it appeared possible to modify the instrument for the desired slower sweep rates. After the required changes were made, sweep rates between 50 μ V and 500 V/sec could be obtained.

We designed a system for A. L. Bacarella, Chemistry Division, utilizing discrete field-effect transistors, that was needed to provide currents in the range 1 to 100 μ A. A junction field-effect transistor operated in the saturation region was used as a constant-current device. Two-terminal constant-current devices that are designed

to be incorporated in hybrid circuitry are available commercially. However, these devices only cover the range of currents between $40\ \mu\text{A}$ and $6\ \text{mA}$. In our design, system supply voltage could be varied from 4 to 30 V, and the load could be varied simultaneously from 0 to $10\ \text{k}\Omega$ without significantly changing the output

current ($<0.1\%$). The particular advantage of this type of supply for electrochemical work is that a low-voltage source can be utilized to obtain an inexpensive current source. A desirable feature is the small package into which such a supply can be fitted; a case the size of a cigarette package is ample.

2. Bio-Organic Analysis

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TOBACCO SMOKE CHEMISTRY

The primary purpose of the Tobacco Smoke Chemistry Project is to provide chemical data for interpretation and prediction of the biological activity of cigarette smoke. Our data are sent to the National Cancer Institute (NCI) for correlation with results of bioassays from the same experimental products. Mouse skin carcinogenicity, determined by an independent NCI contractor, is the main biological response considered. A secondary purpose is to study the effect of the gas phase of cigarette smoke on respiratory tract clearance mechanisms.

In addition to our semiroutine quantitative analyses of cigarette smoke condensate, gas phase, and particulate matter, we also evaluate current analytical methods and develop new ones. The final judgment on such methods is provided by interlaboratory collaborative studies, primarily with participating tobacco companies.

Our responsibilities in the chemical aspects of the NCI tobacco program have been enlarged to include (1)

studies of sample selection protocols, (2) schedules for the condensate preparations, and (3) development of analytical methods for the more complete characterization of smoke. In addition we are to collaborate on studies of analytical procedures and surveys of miscellaneous components related to biological activity. Such research efforts now proceed continuously.

Much of the work summarized here is presented in considerable detail in our annual progress report.¹

Sample generation and preparation. The six-port Filamatic pump smoking machine has operated reliably and appears ideally suited for the generation of total particulate matter (TPM) samples and of combined TPM-gas phase samples for hydrogen cyanide determination. The six-port puff-averaging ("hexapuffer") machine (Fig. 2.1) was modified to improve reproducibility; the puff is now taken by direct connection to the vacuum pump rather than to an evacuated vessel. The modified system provides small, very fresh samples. A further modification, substituting Teflon for metal in the sample flow line, permits determinations of highly reactive components. Other apparatus used for sample generation or analysis are shown in Fig. 2.1.

By adopting a number of smoking criteria, we can now ensure highly reliable smoke generation. Machine performance is tested periodically by smoking a standard reference cigarette. Cigarettes are selected by pressure drop and weight; a final test of machine performance involves a periodic puff profile measurement by which minor variations in timing and valve performance are easily seen. Comparisons with collaborators' data and in-house data up to 18 months old indicate that all smoke generation systems are operating properly.

In a collaborative study of condensate preparation and sampling methodologies, we found that the pro-

1. M. R. Guerin and P. Nettesheim, *Tobacco Smoke Research Program Progress Report*, ORNL-4879, pp. 1-51 (April 1973).

cedure used by the contractor supplying condensate was adequate for biological testing but could contribute significantly to poorly reproducible chemical results. A new sampling procedure begun last year has improved lot-to-lot variability only slightly. Thus it would appear that the variability introduced by smoke generation is greater than that introduced by sample handling. Raising the number of condensates for analysis from two to four should minimize difficulties with lot-to-lot variability.

We have begun to study how condensate generation and handling procedures influence chemical results. The Borgwaldt automatic condensate-production smoking machine generates condensates on-site. Variables include the effect of drying, relative utility of acetone and methanol, and the relationship between TPM and condensate. Samples generated at ORNL, samples gen-

erated by an NCI contractor for chemical analyses and for biological testing, and accumulated composite samples are being compared; high correlations between contractor and ORNL samples may allow significantly improved scheduling and results.

Control chemical analyses. Studies of gas phase and particulate matter samples from here and condensates from the NCI contractor who prepares samples for biological testing are continuing. Table 2.1 summarizes the smoke parameters.

Studies of the first series of primary experimental cigarettes (23 variables), a series of experimental filtered cigarettes (12 variables), and a high nicotine-low nicotine pair are complete, and final data have been reported to the NCI. We have also determined selected components delivered by cigarettes treated with ammonium sulfamate, made of flue-cured and air-cured

PHOTO 0472-73

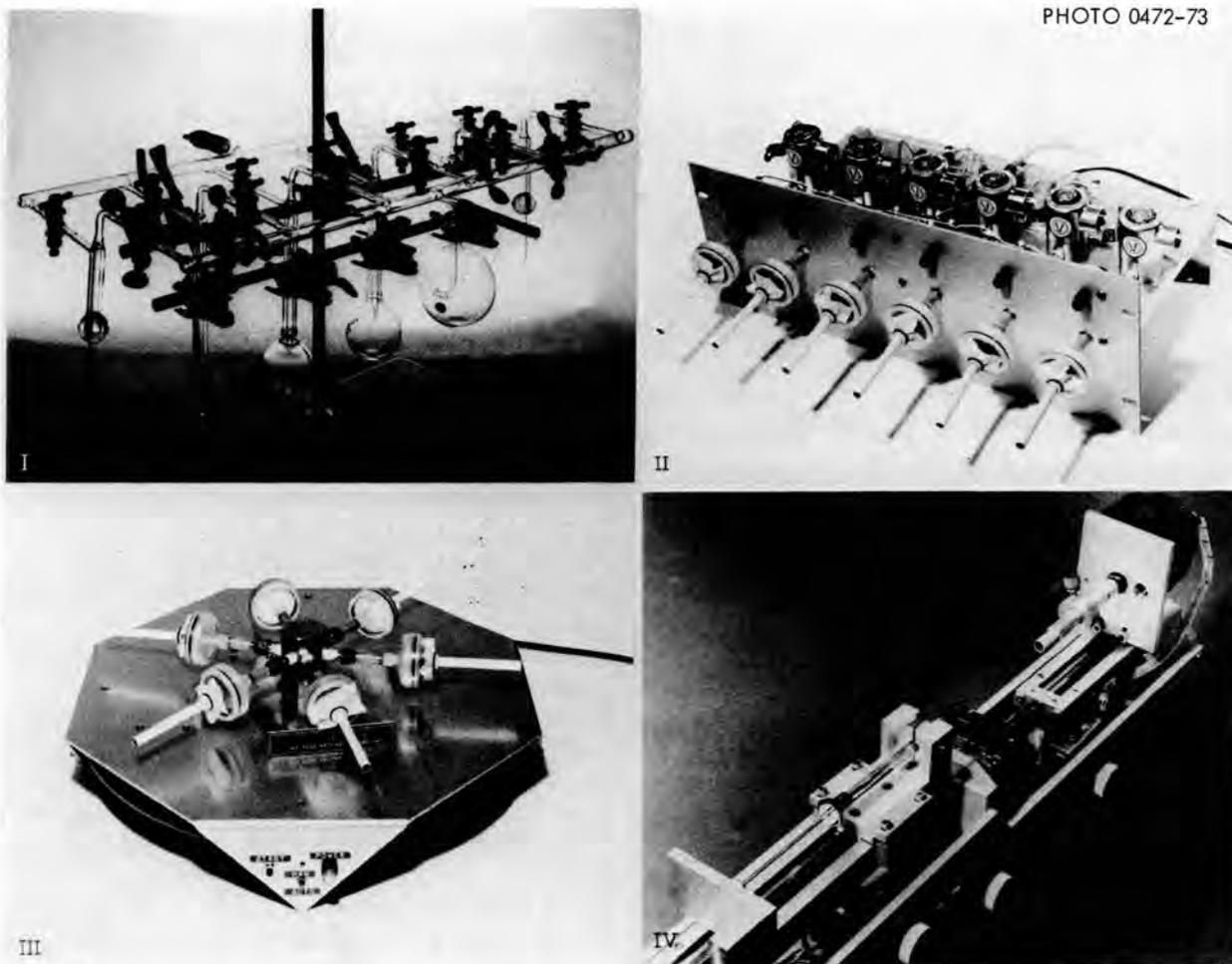


Fig. 2.1. Chemical apparatus: (I) evaporative concentration, (II) sequential smoker, (III) puff-averaging smoker, (IV) cigarette injector.

Table 2.1. Chemical components considered in control analysis activity (9/72-9/73)

Particulate matter	Gas phase	Condensate
TPM	Isoprene	Water
Water	Acetaldehyde	Acetone
Nicotine alkaloids	Acrolein	Nicotine alkaloids
Tar	Formaldehyde	Nicotine
Hydrogen cyanide	Hydrogen cyanide	Phenolics
Phenolics ^a	Carbon monoxide	Phenol
Palmitic acid ^a	Carbon dioxide	Cresols
Stearic acid ^a	Nitrogen oxides	Weak acids
Unsaturated acids ^a	Hydrogen sulfide ^a	Very weak acids
Weak acids ^a	Carbonyl sulfide ^a	Phenanthrene
Very weak acids ^a	Sulfur dioxide ^a	Benz(<i>a</i>)anthracene
Glycerol ^a	Carbon disulfide ^a	Benzo(<i>a</i>)pyrene
		Palmitic acid
		Stearic acid
		Unsaturated acids
		Indole
		Skatole
		Trace metals (Ni, Cd, Zn, Hg, Cr, Pb) ^a
		Glycerol

^aSelected samples only.

tobacco prepared by a new homogenized curing process, and marihuana. About two-thirds of the analyses scheduled for the second series of experimental cigarettes (25 variables) are completed. Miscellaneous special products including artificial smoking materials are under study. During the period May 1, 1972, to May 1, 1973, 2597 analyses and approximately 10,000 determinations (port and aliquots) were performed.

Several changes have been made in the basic protocol of the control assay facility. Phenanthrene is no longer determined; free fatty acids, isoprene, indole, and skatole are routinely measured. Sulfur compounds in gas phase; pH, amines, acids, and metals in condensate; and "phenolics" in TPM will be determined on selected samples. Samples from here and elsewhere will be analyzed, so there will be both more samples and more components to run.

The data from completed studies have been used to define the reliability of our analytical procedures. We have tabulated the average coefficient of variation, relative standard error, and confidence interval for each procedure. Lot-to-lot correlation coefficients and differences expressed as percents of the average further define the variability to be expected in normal operations. We find that analyses of gas phase and particulate matter are generally accompanied by coefficients of variation of $\pm 5\%$ or better; ± 5 to 10% is common for condensate analyses. Lot-to-lot correlation coefficients

range from 1.0 to 0.4, depending on the component analyzed.

We have completed two informal collaborative studies which further define the reliability of our results. We find, to date, good correlations between our results and collaborators' results for TPM, water, nicotine alkaloids, tar, TPM-phenolics, acetaldehyde, acrolein, hydrogen cyanide, oxides of nitrogen, carbon monoxide, carbon dioxide, benz(*a*)anthracene, and benzo(*a*)pyrene. Shortcomings in our methods for the determination of polynuclear aromatic hydrocarbons, oxides of nitrogen, and hydrogen cyanide, identified as a result of these studies, have been reduced or eliminated. Further studies are planned to test the reliability of our results and to further improve interlaboratory agreement.

Laboratory computer facilities are being applied to data handling problems. Programs designed by M. T. Kelley allow port-by-port and aliquot-by-aliquot data to be treated to provide average results and analytical statistics for results expressed in five different units. Run-to-run data are combined to provide final results and statistics, and the data are formatted for final submission to the NCI. Provisions are included for computing correlation coefficients and displaying the run-to-run or parameter-to-parameter agreement as a plot with the points given as cigarette code numbers. We are in the process of generalizing the program in preparation for reporting the final results on the second series of cigarettes.

New analytical methods. We have continued to improve and expand the capabilities of the control analysis group by adopting and developing new analytical methods. A particular interest is to establish alternative methods for those found to produce questionable results. Other objectives are to improve the efficiency of each determination and to add new components to the routine analytical schedule. Each new procedure is evaluated by informal collaborative studies, by comparison with data generated on reference cigarettes, and/or by comparisons with data generated on a series of cigarettes, using an independent method. An increasing interest in special products, always available in limited quantities, has required that we modify procedures normally applied to condensate samples for application to TPM samples. The desire to correlate TPM data with condensate data further requires that we evaluate existing and new methods for applicability to both types of samples.

Condensate and TPM. Colorimetric phenols, titrimetric weak acids, and titrimetric very weak acids can be determined in TPM samples with only minor procedural modifications. The modified procedures

were applied to the pilot filter series, and we were in good agreement with collaborators' data. Free fatty acids can be determined in both TPM and condensate. Preliminary results suggest that we can confidently determine indole and skatole in both sample types as well.

C₁₆-C₁₈ free fatty acids. Studies of the procedure developed here for the rapid quantitative determination of palmitic acid; combined oleic, linoleic, and linolenic acids; and stearic acid have been completed. The fatty acids were determined in TPM generated by the first series of primary experimental cigarettes. We found a sufficiently good correlation with biological data to warrant including the procedure in the regular assay schedule for the second experimental series. The procedure typically provides a coefficient of variation better than $\pm 5\%$, reduces the analysis time by a factor of 4 when compared with methods previously available, requires no chemical separation steps, and is equally applicable to TPM and condensate. A note has been submitted to *Analytical Chemistry* describing the method.

Indole and skatole. We have developed a procedure for the determination of indole and skatole in condensate and have completed their determination in one complete series of condensates. Approximately 1 g of dry condensate is partitioned between hexane and methanol-water, the hexane extract is chromatographed on Florisil, and the collected fraction is analyzed by gas chromatography. Carbon-14-indole is used to follow the separations and for computing recoveries. Recoveries typically range from 70 to 85%, and a coefficient of variation of $\pm 5\%$ or lower is generally observed upon analysis of four samples. The indole content of the second series condensates ranges from 400 to 1600 $\mu\text{g g}^{-1}$, while skatole ranges from 300 to 700 $\mu\text{g g}^{-1}$. Condensates from the tobacco substitutes contained 100 $\mu\text{g g}^{-1}$ or less of indole and no detectable skatole. The indole-skatole ratio was found to remain constant at various stages in the analysis and to be the same in TPM and condensate. These observations are important, because the indole-skatole ratio has been proposed as a measure of condensate aging. We are continuing studies of the method through its routine application to condensates and completing its modification for analyses of TPM.

Carbazole. It may also be necessary to determine carbazole. We find that carbazole is present in the indole-skatole fraction and that it is retained considerably longer by the gas chromatographic column. Carbazole is present at approximately 1/10 to 1/20 the level of indole. Attempts to use concentrated indole

fractions to determine carbazole have been unsuccessful. Alternative procedures are being considered.

Polycyclic aromatic hydrocarbons. Studies of the procedure for determining polycyclic aromatic hydrocarbons have continued. The deletion of phenanthrene from the routine schedule, an increase in the number of samples to be analyzed, and results of a comparative study with an industry laboratory required that steps be taken to improve efficiency and reliability. We found that one additional DMSO extraction and modifications of sample handling and transfer procedures significantly improved recoveries and resulted in better precision and better interlaboratory agreement. In-house preparation of our own acetylated papers for chromatography and purification of some heavily used solvents have significantly reduced costs. Further improvements particularly in the gas chromatographic determination of benz(a)anthracene are now being sought.

Hydrogen cyanide. We have adopted a new method for the determination of hydrogen cyanide deliveries. Early results were found to be substantially lower than had been expected, and we found an occasional completely unpredictable occurrence of irreproducible results. Difficulties with reproducibility were found to be associated with batch-to-batch differences in the Ascarite used for trapping the hydrogen cyanide. As expected, the reason for the low results was that a large percentage of the hydrogen cyanide was trapped by the filter employed to prepare gas phase samples. Our new procedure involves the analysis of both the filter and gas phase for hydrogen cyanide. Silica gel is now used to trap gas phase hydrogen cyanide, and the chloramine-T-pyrazolone reaction is used to form the colored complex. As a further test of the utility of earlier generated results, we examined the correlation between the results obtained using the new procedure and those obtained using the original procedure and found good agreement. Consequently, initial results can be used for correlation with biological data.

Carbon monoxide and carbon dioxide. A new procedure for the determination of carbon monoxide and carbon dioxide in the gas phase of smoke was developed. The full gas-phase delivery is still collected in a Saran bag, but the content of the bag is now analyzed on a single column packed with nickel-form ion exchange resin rather than on two columns as before. The single-column data were found to be in excellent agreement with earlier results generated here and with collaborators' data. Analysis time is reduced by a factor of 2. We have summarized details of both procedures in a paper accepted for publication by the *Journal of Official Analytical Chemists*.

New methods for the determination of sulfur components in smoke and nitrogenous components including nitric oxide were developed, and the utility of component profiling was further defined. These topics are discussed separately in the following sections.

Sulfur components in cigarette smoke. The first phase of our research on the quantitative determination of COS, H₂S, CS₂, and SO₂ in the gas phase of cigarette smoke is now completed. A Tracor Special Silica column, a flame photometric detector, and an improved version of the puff-averaging smoking machine² constituted the final analytical system. Using this system, we obtained an average of 30 μg COS, 85 μg H₂S, 1.5 μg CS₂, and 3.4 μg SO₂ per cigarette for popular 85-mm nonfiltered or for 85-mm cellulose-acetate-filtered cigarettes. Cellulose acetate filters do not affect sulfur delivery. However, granulated charcoal filters were found to remove about 65% of the H₂S and CS₂, 10% of the COS, and 20% of the SO₂.

Our data on H₂S relative to COS are significantly different from those reported earlier.³ We have found that the difference is due, primarily, to major losses of H₂S and only minor losses of COS in the presence of metals. The use of Teflon in the improved smoking device has shown markedly increased deliveries of H₂S and only slight increases in COS deliveries. Aging the gas phase drastically affects the delivery of H₂S — a 70% decrease is observed in 1 min. In the same time interval, we observe a corresponding increase in the higher boiling components — primarily organic sulfides. Twenty-four such components were observed with the chromatographic system. Aging the gas phase in the presence of stainless steel reduces the H₂S delivery even more and increases some of the higher boiling components by as much as 300%. The reactivity observed for H₂S suggests that even the slight contact with metal surfaces still present in our sampling system may be sufficient to produce artifacts. Studies are planned to evaluate this problem. Correlations with biological activity will then be sought.

Nitrogen components of cigarette smoke. Difficulties in the quantitative determination of nitric oxide and gas phase bases, coupled with increasing interest in nitrogenous smoke components, prompted a consideration of element-selective gas chromatography as a preferred

analytical tool. The Coulson electrolytic conductivity detector is selective for nitrogen components if a basic trap is used for removal of acidic components in the sample. Nitrogen compounds are converted to ammonia by a hydrogen-active nickel catalyst, and the increase in electrical conductivity when the ammonia dissolves in highly purified water is a measure of the amount of the compound in the sample.

We have used the detector to obtain gas chromatographic profiles of nitrogenous components in the gas phase of cigarette smoke. Compounds observed include nitric oxide, hydrogen cyanide, thiocyanogen, and assorted organic nitrates, nitrites, amines, and nitriles. We find 15 to 20 components in this class by use of a Pennwalt 223 gas chromatographic amine column temperature-programmed to 200°C. Some have been tentatively identified by cochromatography as nitric oxide, hydrogen cyanide, *n*-butylamine, *n*-amylamine, acetonitrile, acrylonitrile, and pyridine. We used a Porapak "P" column to isolate nitric oxide from all interfering components and have successfully developed a method for the determination of nitric oxide in the gas phase of smoke. We compared our data on a series of experimental filter cigarettes with data submitted by a collaborator who used on-line spectroscopic analysis. Our results agree with that of the collaborator: absolute values were within ±10%, and the correlation coefficient of the two sets was 0.93. This method is expected to replace the current colorimetric method, which gives consistently low values for nitric oxide.

Nitrogen component profiles were obtained for two cigarettes containing synthetic smoking material. Two components were observed from one cigarette that did not appear at all in the other. Attempts are under way to isolate these components by preparative gas chromatography for further examination by analytical gas chromatography and by mass spectrometry.

Chromatographic component profiling. The great effort associated with biological testing and with accurate quantitative chemical analyses of smoke samples is the single major obstacle to progress toward identifying characteristics of a less hazardous cigarette. It is impractical to survey a significant fraction of the many individual constituents. The problem is further complicated because relatively few components which appear promising enough to warrant intensive study have been identified. Those components which have been studied, even the most promising, seldom appear to account for a sizable portion of the overall biological response.

We believe that chromatographic component profiling affords an effective approach to dramatically expand

2. M. R. Guerin et al., "Tobacco Smoke Inhalation Bioassay Methodology," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 17.

3. P. J. Groenen and L. J. Van Gemert, "Flame Photometric Detection of Volatile Sulphur Compounds in Smoke from Various Types of Cigarettes," *J. Chromatogr.* **57**, 239-46 (1971).

the number and kinds of smoke constituents practically surveyed for biological significance. It is well known that chromatographic methodology already exists to allow visualizing as many as 200 components in a single analysis. We now have data which demonstrate the possibility of carrying out correlations between biological data and chromatographic peak responses directly. It is therefore possible to survey the biological significance of any component visualized chromatographically. Once a promising correlation is identified, the peak can be identified and the known constituent subjected to rigorous quantitative analytical and/or biological analysis. Profiling thus provides a means to extend the number of constituents considered and to provide "leads" as to new compounds of biological significance.

We have completed studies of TPM profiling that demonstrate the feasibility of using chromatographic peak areas for correlation studies. Five cigarette types varying significantly in deliveries of nicotine, phenol, and palmitic acid were subjected to our TPM profiling procedure.¹ The reproducibility of the peak areas for these components was as good as, and in some cases better than, the precision of their individual determinations. Very high correlations between analytical results and relative peak areas over the series of tested cigarettes were found. Good correlation between biological data and chromatographic profile data could be obtained. Importantly, each of the other 40 peaks observed in these profiles can also be correlated with bioassay results. Since these correlations can be carried out without knowing the identity of the peaks, we refer to this procedure as a "blind assay."

Profiles of TPM are of added general utility because they constitute a "picture" of the overall composition of "tar." We find these profiles particularly valuable for studies where the composition of tar or of the particulate phase of smoke is important. The technique has been applied to studies of the effect of time on particulate composition, the effect of varying puff parameters on tar composition, and the effect of differences between cigarettes and "little cigars." A specific example of the utility of the technique, illustrated in Fig. 2.2, is our finding that smoke delivered by tobacco cigarettes adulterated with as little as 10 wt % marihuana is readily distinguished from normal cigarette smoke. Further, the results of our study of correlations between absolute quantitative data and relative peak sizes strongly suggest that it may be possible to simultaneously determine many of the constituents now requiring independent methods. It may be possible to simultaneously determine nicotine,

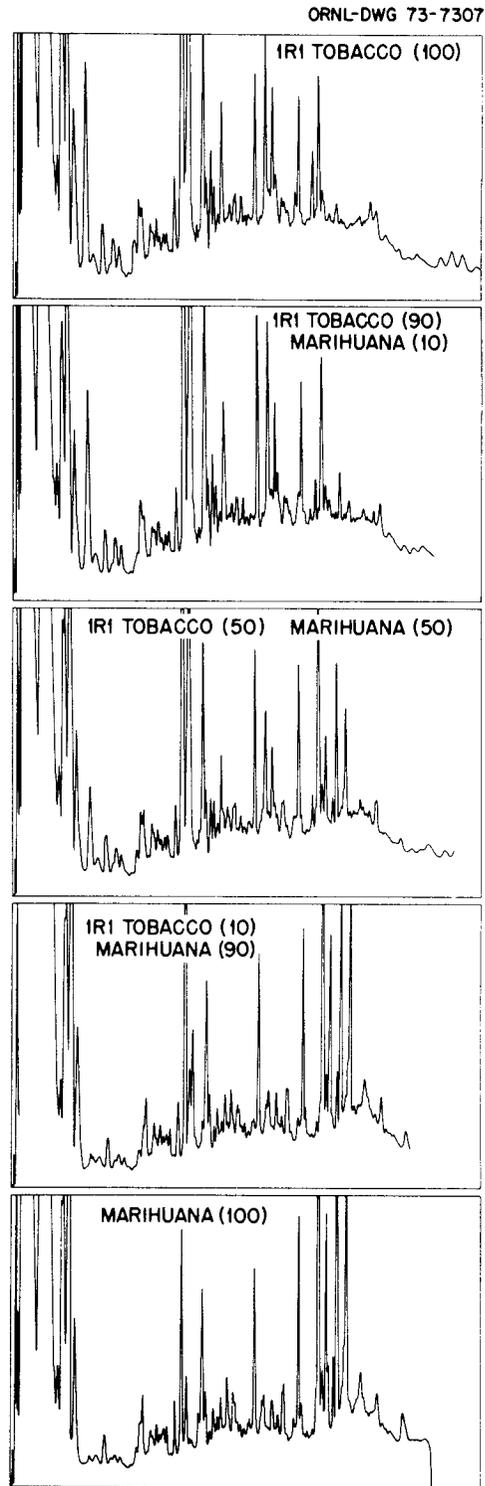


Fig. 2.2. Total particulate matter profiles for marihuana-tobacco cigarettes.

phenol, *o*-cresol, *m*-cresol, *p*-cresol, palmitic acid, oleic plus linolenic plus linoleic acid, stearic acid, glycerol, indole, and catechol.

Our studies of TPM profiling to date have emphasized the use of standard packed columns in an attempt to make routine screening possible. In view of the great utility of the method, we are now emphasizing increased resolution. The quantity of information which can be extracted from the profiles would appear to justify the longer analysis times and sophisticated instrumentation. Initial studies have demonstrated that significantly improved resolution is easily achieved. We have carried out pilot experiments which indicate that nitrogen-selective detection will further extend the utility of the technique.

The procedure in use for the routine determination of acetaldehyde, acrolein, and isoprene is actually a profiling procedure. This gas phase profile, as well as the sulfur and nitrogen profiling procedures discussed earlier, can also be used for studies of biological activity. A paper is in preparation which describes the utility of TPM and gas phase profiling.

INHALATION BIOASSAY METHODOLOGY

We have continued an active collaborative study with members of the Biology Division directed at developing a viable inhalation bioassay to test the carcinogenicity of cigarette smoke. Our primary areas of responsibility include the design and fabrication of exposure instrumentation and the development and application of chemical methods to direct and interpret biological efforts. Personnel assigned to this Division have contributed further by acquiring expertise in biological aspects of the work and carrying out studies under the direction of Biology Division personnel.

Progress in this report period includes completing the evaluation of intralaryngeal cannulation, establishing optimum smoke-air cycles for maximum daily dose to normal hamsters, demonstrating the practicality of maintaining permanent tracheal openings, and developing a technique by which some condensate can be tested on respiratory tract epithelia. En route to these accomplishments, we have developed a successful containment system for hamsters and a smoke exposure system which doubles our previous hamster capability. A viable method for determining lung deposition in smoke-exposed animals was also developed. In addition, respiratory parameter data that better define dosimetry and acceptable exposure protocols have been determined. In an initial survey of the chemical characteristics of smoke offered the animals for inhalation, we

found that intermittent exposure devices may be not only "acceptable" but better than some of the more complex continuous exposure devices for chronic studies.

Progress summarized below includes only those studies which were directed and/or carried out primarily by Analytical Chemistry Division personnel. The work summarized, as well as much of that excluded as primarily "biological," includes significant contributions from personnel in both divisions. A more complete summary of progress in these areas is presented in the Tobacco Smoke Research Program Progress Report.¹

Hardware and instrumentation. The design and development of hardware in direct support to biological experimentation in our bioassay program and for other NCI contractors have continued. Figure 2.3 shows some of the hardware developed in the program. In addition to the three smoking machines mentioned in the previous annual report, we have constructed two "double-puffer" machines which service two inhalation-chamber assemblies with a single Filamatic pump. We have also fabricated a fourth single-chamber machine which is used primarily in smoke-chamber chemistry experiments. A special Filamatic-based smoking machine was designed and built which expels a stream of undiluted smoke at selected rates. This machine was designed to evaluate the possibility of directing smoke into tracheas grafted into the backs of hamsters.

We have assisted the biological team in the design and fabrication of pelletizers which make small reproducible cylindrical pellets of gelatin or beeswax containing a carcinogen. Carcinogen-containing pellets are to be inserted into the grafted tracheas. In another study a device, developed by H. Schreiber and P. Nettesheim of the Biology Division, that secures exfoliating cells from the tracheas of hamsters or rats for cytology is being redesigned. In keeping with our role as a supporting laboratory for other tobacco-related NCI contractors, we designed and manufactured a new cigarette injector for primary use by the American Health Foundation. The injector is particularly useful for accurately preparing radiolabeled cigarettes.

We were requested by the NCI to do some design revision and to fabricate a test group of six smoking machines for dogs based on a prototype furnished by S. P. Battista of the Arthur D. Little Company. Several contributions to the design were made during the construction, and other changes were suggested based on experience gained while evaluating our initial product. The machines were forwarded to the Veterans Hospital at East Orange, N.J., for evaluation there by

Dr. Oscar Auerbach's team. An extensive study of the chemical characteristics of this machine concept was also completed.

We have found that containment devices designed for hamsters cannot be used for rats. In particular, it appears that rats will not learn to tolerate a collar. To circumvent this and still keep the animals' noses in the smoke chamber, we have designed a tube that has a long inside cone in which a recess is cut to provide relief for the eyes. This design looks promising. Additional studies of hamster containment revealed that an oval hole in the vertical collar is to be preferred to a round one. A hamster that habitually struggles in collars with a round hole becomes quiet in a collar with a hole elongated from top to bottom.

We had observed earlier that the pressure drop attending a puff in a smoking machine provides a

sensitive indication of minor irregularities in the performance of the smoking mechanism. Puff profiling (recording the pressure drop as a function of time) is easily done with the DR-8 research recorder, which is located at Y-12 and unfortunately is not portable. Consequently, a small, sensitive pressure transducer and its associated carrier-demodulator were acquired and put into service at X-10 to periodically examine all of the smoking machines.

Several new commercial instruments have been acquired for utilization in the chamber chemistry and inhalation bioassay programs: a Perkin Elmer model 900 gas chromatograph (GC) for high-resolution analysis of the particulate phase in inhalation chambers (this will be interfaced with our PDP 8/E computer); a Carle model 8000 GC for O₂, CO₂, CO, and H₂; and a Carle model 9500 GC with a flame ionization detector for

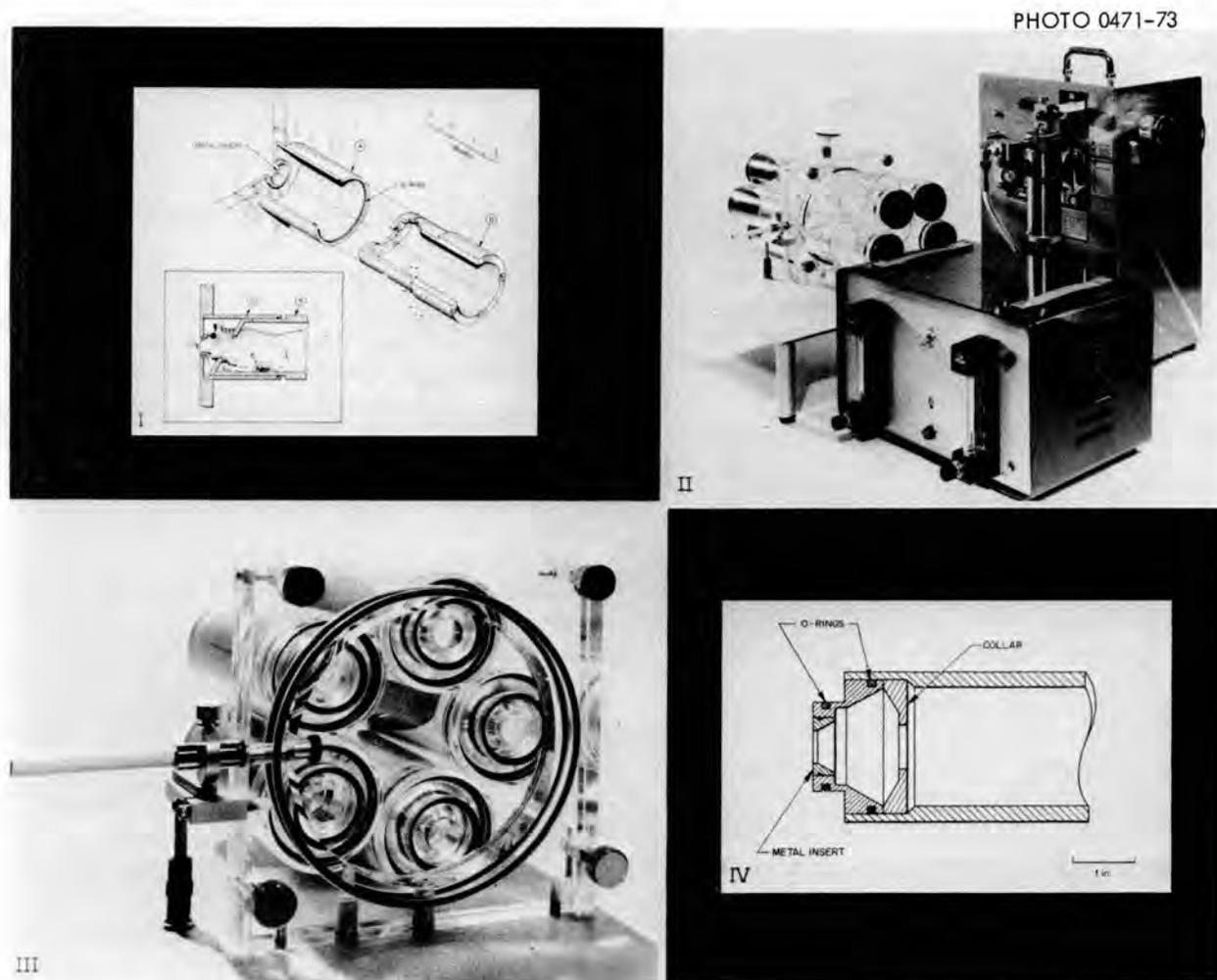


Fig. 2.3. Apparatus used in exposures of rodents to tobacco smoke.

assessment of uniformity in the smoke-chamber atmosphere. A Tracor model 150 GC is due shortly. Its application will be to in-chamber high-resolution gas phase analysis.

Slant-collar tubes and side plates of our design were fabricated elsewhere for evaluation with the Council for Tobacco Research Walton reverse smoking machine. Measurements of hamster respiratory characteristics on this assembly have been completed, and deposition studies are under way.

Lung deposition methodology. We have continued studies on the deposition of smoke particulate matter in hamsters. In the past year, 17 more deposition studies using radiolabeled smoke have been carried out. Several of these experiments continued the series involving the use of an intralaryngeal cannula as a nasal bypass device.³ Results bore out earlier conclusions that the use of the cannula increased lung deposition by a factor of 2 and whole-body deposition by a factor of 1.5 over that in freely breathing hamsters.

Respiratory parameters are being measured as an integral part of selected lung deposition experiments. Initial results suggest that average smoke respiration is about four times greater for the cannulated animals. The cannulated animals generally maintain a normal breathing pattern throughout the test but with a 30% increase in breathing rate. The test period included a sham smoking period and the smoke from one unlabeled cigarette as well as that of the test cigarette. The nose-breathing hamsters showed a more or less consistent apneic (breath holding after inspiration) breathing pattern after the first few puffs of the unlabeled cigarette. In addition, breathing rate dropped to about 40% of normal during smoke periods of the test cigarette. There was no significant difference in minute volume compared with the twofold difference in lung deposition. This suggests that the breathing pattern of the hamster is as important in lung deposition as the respiratory volume. Correlation of lung deposition with minute volume was relatively good for both sets of hamsters, but correlation with respiratory rate was very poor.

The cannula is useful as a means of avoiding the various physiological and physical impediments to lung deposition in hamsters. These impediments include nasal passage absorption, clearance from the lungs, and turbulent air effects. An example of the usefulness of the cannula for acute deposition studies was a set of tests run to compare deposition under controlled breathing conditions. The animals were paralyzed with curare and then given artificial respiration at two different tidal volumes and respiratory rates. Minute

volumes were the same. The animals that were respired slowly and deeply had a lung deposition of about 2.5-fold more than the ones respired at twice the rate and half the tidal volume. When this was attempted with noncannulated hamsters, we found the results extremely erratic and useless.

Another set of experiments allowed a measurement of particulate matter deposition under various smoking regimes. With the ORNL smoking machine set for 20, 30, and 40 sec of smoke per cycle, we found TPM depositions of about 0.010, 0.035, and 0.070 mg per lung per minute respectively. When the Hamburg II continuous smoking machine was studied, we found the deposition for a platter of 30 cigarettes was about the same as for one cigarette at the 30-sec smoke time on the ORNL machine.

We carried out a similar series of tests with 20-, 30-, and 40-sec smoke periods on the ORNL machine with the respiratory characteristics being measured through a sham smoking period, one unlabeled cigarette, and then the test cigarette. Results differed from those above. Depositions of 0.086, 0.068, and 0.121 mg TPM per lung per minute were found for the three smoking periods. The hamsters were from a different group, and a different smoke adaptation procedure was used which may account for the difference. Minute volumes were about 30, 23, and 52 ml respectively.

Two experiments were performed with dual-labeled cigarettes to evaluate the feasibility of using the second label, decachlorobiphenyl (DCBP),⁴ rather than the ¹⁴C-labeled dotriacontane for future deposition studies on dogs. Results were somewhat ambiguous, probably because of the complications involved in the analysis. For the determination of DCBP, the tissues were blended and extracted with hexane, and the DCBP then determined by gas chromatography.

Respiratory parameters. A program was initiated to characterize the respiration of hamsters under smoking conditions and to measure changes in respiratory capacity during long-term smoking studies. These parameters are used as the basis of comparison among groups of animals under various conditions. Monitoring procedures are similar to those described by Amdur and Mead⁵ using an Electronics for Medicine, Inc., DR-8 electronic recorder.

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

5. M. O. Amdur and J. Mead, "Mechanics of Respiration in Unanesthetized Guinea Pigs," *Amer. J. Physiol.* 192, 364 (1958).

Our first respiratory study involved a group of hamsters which had been on a smoking program for three months. We measured the respiration of five of these animals over a course of ten cigarettes, using the ORNL smoking machine set for a cycle of 30 sec of smoke and 30 sec of air. The average minute volume was found to be about 10% less than the normal minute volume measured immediately before the smoking began that day. There was a strong tendency for the animals to hold their breaths during the smoke portion of the fifth cigarette. After a rest period, the second five cigarettes were administered, and we observed similar results. For this particular group of hamsters, at this point in their smoking test, the average intake of smoke was about 1400 ml for the ten cigarettes.

Other hamsters are being monitored during a long-term smoking study to determine their respiratory characteristics as a function of exposure. Of the 30 Sprague-Dawley strain that we measured before smoking began, the average minute volume was found to be 66.5 ml, tidal volume was 0.84 ml, and the rate was 82 respirations per minute. These values compare well with those of 60.9 ml, 0.83 ml, and 74 per minute, respectively, found by Guyton.⁶ An examination of 15 of the 87.20 strain of hamsters revealed an average minute volume of 55.0 ml, tidal volume of 1.03 ml, and rate of 54 respirations per minute. The normal respiratory characteristics were measured again after the animals had been on a smoking program of 12 cigarettes per day for two months. The Sprague-Dawley smokers had lost an average of 25% of their minute volume capacity, compared with a loss of 15% for the container controls and a gain of 5% for the no-treatment controls. Change of breathing capacity correlated roughly with change of weight. The 87.20 group of smokers lost less than 10% of their minute volume capacity, compared with no change for the container controls.

We have compared the respiratory characteristics of a group of five hamsters using three styles of body containment tubes. Essentially no difference was found in either tidal volume or respiratory rate when the hamsters were placed in the two types of body tubes used on the ORNL smoking machine.² When the animals were placed in the Walton tube, there was no change in tidal volume, but the respiratory rate almost doubled. This style of tube not only cramps the upper torso of the animal but also prevents his nose from projecting into the smoke chamber.

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

Chamber chemistry. The actual concentration of smoke offered to experimental animals, the distribution of the smoke in the chamber, and the composition of the offered smoke have traditionally received very little attention in bioassay development and application. In our opinion it is extremely important to define concentrations and distribution to allow interlaboratory comparisons. We feel it is even more important to establish that the composition of the smoke offered the experimental animals is relevant to that produced by analytical smoking and, particularly, human smoking practice. Initial experimentation for the Council for Tobacco Research and for the NCI has allowed preliminary conclusions in these areas.

We find that the concentrations of particulate matter, measured as nicotine, and of gas phase, measured as carbon monoxide and carbon dioxide, are in excellent agreement with analytical smoking data when the ORNL machine is used. The uniformity of the smoke in the chamber is also acceptable biologically if long-term chronic studies are in mind. Changes in nicotine and carbon monoxide concentration in the chamber may be particularly useful for interpreting toxicity and establishing preferred exposure protocols. Particularly important, we find that the composition of the organic volatiles fraction of smoke remains remarkably constant during the typical stand periods needed to expose the animals. These and other observations are discussed more fully in our latest progress report¹ and in the following section of this report.

SMOKE GENERATION—BIOLOGICAL EXPOSURE SYSTEMS

Smoking devices have been used here recently and at other laboratories for some time to expose experimental animals to tobacco smoke for development or application of inhalation bioassay techniques. Little information is available on the chemical composition, concentration, or aerosol properties of smoke offered to animals in these devices. Such information is needed to assess the relevance of smoke generated by different devices to smoke generated by humans, to define the concentration of smoke offered to animals during exposures, and to identify and study the interaction of smoke components with smoke itself, machine components, or experimental animals. Presently, we are studying or plan to study smoke in the exposure chambers of four types of smoking machines. Initial efforts have dealt mainly with two intermittent exposure devices, the ORNL and Walton horizontal smoking machines. Limited work has been done on the

Hamburg II smoking machine, and future studies are planned for the Lorillard machine. Initial activities have been exploratory in nature, and we have relied heavily on existing methodology. In general, for each of the machines, we are attempting to answer basic questions related to the relevance of smoke offered to animals in the machine as well as to obtain chemical information to assist in the interpretation and planning of biological experiments.

A greatly expanded effort in this area — evidenced by the initiation of a detailed study for the Council for Tobacco Research, U.S.A. — prompts us to summarize progress separately from the two established tobacco projects. Studies of the ORNL machine discussed below were carried out primarily as part of the Inhalation Bioassay Methodology Project. Some studies of the ORNL system and all studies of the Walton machine were carried out with combined NCI and Council support.

Smoke particulates in the ORNL exposure chamber. Smoke in the exposure chamber is made up of two major components: a particulate phase consisting of water, nicotine, and "tar," and a gas phase composed of inorganic gases and volatile organic compounds. We have investigated the spatial and time distribution of the particulate phase during the smoke cycle to determine how well smoke is mixed in the exposure chamber, the delivery of smoke from the cigarette to the chamber, and at what rate smoke is eliminated from the chamber during the air purge. In addition, estimates of smoke exposure, animal uptake, and retention of particulates were examined.

Methodology was developed for sampling the particulate phase at five sampling positions at 5- or 10-sec intervals during the smoke cycle. Nicotine was used as an indicator of the particulate concentration. Nicotine, a major component of this phase, occurs mainly with the particulates and, it is suspected, is distributed uniformly in the particulate phase.

Without animals on the machine, we find large particulate concentration gradients in the chamber. During the exposure period, the particulates settle to the bottom of the chamber so that by the end of the exposure the particulate concentration there is nearly two times greater than the average concentration. With a full load of hamsters under exposure conditions, the particulates are distributed more uniformly in the chamber, apparently because the animals' breathing serves to mix the smoke. Only a 20% difference in particulate concentration (top to bottom) is observed with animals. Because of this concentration difference, consideration is being given to placing a stirrer in the chamber to improve mixing.

The average concentration of particulates over the entire chamber is useful for assessing delivery and losses of smoke. The average concentration is computed from the concentration obtained at five sampling ports for selected times in the smoke cycle. Without animals present, we find the average concentration agrees well (within 10%) with the concentration calculated from cigarette delivery. This agreement indicates that the machine generates and delivers the smoke properly and that there are minimal losses of smoke to the chamber walls. Average concentrations have also been used for evaluation of purging conditions. These data show that, under our standard purge condition (air flow of 5 liters min^{-1}), the particulate concentration drops asymptotically. About 15 sec is required to reduce the concentration to 10% of its initial value. Appreciable exposure occurs during the purge period, and the magnitude of this exposure has been determined under different exposure conditions.

With hamsters on the machine, we observe a steady decrease in the average particulate concentration during exposure which we attribute to uptake and retention of particulates by the animals. The decrease is brought about because the chamber volume is small (350 ml) compared with the total minute volume of the hamsters (800 ml). A 1% decrease in the particulate concentration per second with ten animals is observed; this gives a total uptake and retention of 3% per animal during a 30-sec exposure. Experiments with dead animals show that smoke is not lost to the fur of the animals or to the animal containment tubes. Therefore, we think the decrease in the particulate level is due to internal deposition. This technique, with confirmation and refinement, may be a useful adjunct to tracer deposition methodology for obtaining total internal deposition in animals.

Carbon monoxide and dioxide in the ORNL exposure chamber. Carbon monoxide and carbon dioxide are two major components of the gas phase of smoke important in exposures with intermittent smoking devices. Carbon dioxide affects animal respiration, and carbon monoxide is partially responsible for the acute toxicity of smoke. We have developed and applied methodology for determination of those gases in the ORNL smoking machine.

Carbon monoxide analysis of the chamber during exposure of hamsters shows that the animals remove an appreciable amount of the gas during an exposure. In 30 sec the animals reduced the carbon monoxide concentration from 0.38 to 0.17%. The small chamber volume and high retention of the gas by the animals cause the reduction. Overall, the animals receive a smaller total dose of carbon monoxide than would be

expected from the calculated delivery of the cigarette or from exposure to fresh smoke. It is likely that the lower acute toxicity of smoke in intermittent smoking devices as compared with continuous devices (fresh smoke) is due to the reduced carbon monoxide concentration.

In contrast to carbon monoxide, the carbon dioxide concentration increases in the chamber during animal exposures. This buildup is due to the addition of carbon dioxide to the chamber by animal exhalation. The carbon dioxide concentration increases to 3 to 4% during a 30-sec exposure and to 8 to 10% after 90 sec. It does not appear that the carbon dioxide reaches a toxic level in normal exposures, but it is suspected that the animal's respiration is affected. Further studies are planned to define the behavior of respiratory gases in the inhalation chamber.

Nitric oxide concentration. Nitric oxide is an important component of the gas phase of cigarette smoke. It reacts with oxygen to give nitrogen dioxide, which can further react with the secondary amines in smoke to give nitrosamines. Some nitrosamines are known to be chemical carcinogens. Therefore, there is a possibility of formation of carcinogens as smoke ages in intermittent smoking devices. We have undertaken a pilot study to examine this possibility for the ORNL smoking machine.

A gas chromatographic method developed for analysis of nitric oxide in the chemical analysis part of this program was adapted to provide nitric oxide data on smoke in the smoking machine. This method was used to monitor the decrease in nitric oxide as a function of time. It was observed that nitric oxide disappears very slowly from the inhalation chamber by reaction with oxygen, indicating that very little, if any, nitrogen dioxide is found during the exposure period. Therefore, it is unlikely that appreciable quantities of nitrosamines are generated during normal animal exposures.

Experiments with hamsters on the machine show that the animals remove large quantities of nitric oxide from the chamber during exposures. The concentration of nitric oxide drops by a factor of 2 during a 30-sec exposure. Apparently, the uptake and retention of nitric oxide by the animals are high. Reduction of the nitric oxide concentration by the animals is at least an order of magnitude faster than loss through reactions with oxygen; thus formation of appreciable quantities of nitrosamines in the exposure appears unlikely.

Organic gas phase components. A study was made to assess the possibility of changes in the composition of organic gas phase components in the smoking machine

as the smoke ages or as the animal breathes the smoke. Our routine gas chromatographic method for isoprene, acetaldehyde, and acrolein was modified for this work. Using this method, the profile of approximately 30 gas phase components can be visualized, although the identity of all these components is not known. We are primarily interested at this time in determining relative peak sizes which can be correlated with the age of the smoke or animal interaction with smoke.

Initial work consisted in obtaining the organic gas phase profiles of smoke in the chamber in the absence of animals. Results in this study indicate that the smoke components visualized are extremely stable; no significant changes in composition were observed over a 50-sec exposure period. Even when the period was extended to 15 min, the relative composition had changed little, although there was a lower concentration of all components. With animals in the chamber, we still do not observe large changes in composition; there is no evidence for highly selective removal of components from the gas phase by the animals.

Further investigations are planned in this area to develop high-resolution profile analysis of the particulate phase as well as the gas phase. This work is needed because of the importance of the organic composition to the relevance of smoke in artificial inhalation devices.

Machine monitoring. Methodology was developed and applied for monitoring the performance of the ORNL and Hamburg II smoking machines used for inhalation studies in the Biology Division. This methodology involved determination of the total particulate matter input to the machines and the average nicotine concentration in the inhalation chamber during animal exposures. All ORNL machines in use were shown to give the same smoke concentration, and the concentration of smoke in the Hamburg II machine was determined for comparison of the two types of machines.

Smoke distribution in the Walton horizontal-chamber machine. A study is under way to determine the spatial and time distribution of smoke in the exposure chamber of this machine. We are interested in the uniformity of smoke in the chamber, delivery of smoke to the chamber from the cigarette, and losses of smoke to the vent line and chamber walls. Since the gas and particulate phases of smoke could behave differently, monitors for both phases are being used — carbon monoxide and dioxide for the gas phase and nicotine for the particulate phase. Much of the methodology for this work was developed previously and is being applied with minor modifications. Information obtained in this study will permit preliminary assessment of machine

operation. Future work is planned to develop better methodology for obtaining data on smoke distribution in the chamber.

Future studies for the Council for Tobacco Research.

Work for the Council for Tobacco Research is in the planning and procurement stage at present. Over the next year, we plan to develop methodology for obtaining high-resolution gas chromatographic profiles of gas phase, particulates, and semivolatile components of smoke in the exposure chamber. Aerosol properties of smoke will be investigated. Analytical techniques and instrumentation will be developed for continuous monitoring of smoke and smoke components in the machines. Preliminary experiments with animals will be undertaken to determine the effect of animals on the smoke concentration and composition in the chambers. Methods for determination of respiratory gases and carbon monoxide will be applied to the machines. Better methodology for sampling exposure chambers will be examined to permit application of new or different analytical techniques to chamber analysis.

BIOANALYTICAL PROJECTS

We have continued studies of high-resolution electrophoresis and immunosubtractive chromatography as part of the Molecular Anatomy (MAN) Program. Further development and new applications of immunotechnology are being emphasized.

Immunosubtractive chromatography. Conventional methods for the purification of mixtures of proteins whose physicochemical differences are subtle generally result in incomplete and unsatisfactory separations of such mixtures. However, immunosubtractive chromatography utilizes the biological specificity of such macromolecules. This biological specificity involves localized regions in one macromolecule that are highly specialized toward recognition of some localized region of a second macromolecule. The interaction of this pair of macromolecules is very specific, and there is little interference from other macromolecular species. Thus, immunosubtractive chromatography involves a stationary phase which consists of an inert support to which one of the interacting species has been bonded covalently. This covalently bonded macromolecule, or ligand, must be immobilized in such a way that its ability to recognize and interact with the other specific macromolecule is not impaired. Therefore in successful immunosubtractive chromatography a sample mixture containing the macromolecule or macromolecules for which the column is specific is washed onto the column in the buffer used to equilibrate the column. The

column adsorbs those macromolecules which the immobilized ligands on the column recognize. The remainder of the sample mixture is eluted from the column by the equilibrating buffer. The specifically adsorbed portion of the sample is then eluted from the column by changing conditions (pH, ionic strength), which break up the complex formed by the immobilized ligand and the macromolecules for which it is specific.

One of the most important features of immunosubtractive chromatography is that a small amount of a specific macromolecule can be utilized many times. Thus, even if one has only a small amount of a specific macromolecular ligand, it can be utilized in an immunosubtractive chromatography procedure to prepare many times its equivalent of the macromolecules for which it is specific. It is generally true that specific immunosorbents are available in very limited amounts, so only small columns can be prepared. To prepare useful quantities of materials from such columns then requires many passes over such a column and much personal attention. To reduce the need for such attention, we developed an automated system. This system, called "Cyclums," sequentially equilibrates the column with buffer, loads the column with a specified amount of sample, washes the unadsorbed sample from the column with the equilibrating buffer, and collects this unadsorbed material. The cycle continues with the column being washed with a second eluting solution which dissociates the adsorbed macromolecules from the column packing and collects this eluted material in a second container. Subsequently, a new cycle is started by the equilibration of the column with the initial buffer solution. We designed the Cyclum to operate continuously with operator time required only to refill sample and eluting solution reservoirs and to empty collection reservoirs. Continuous runs for periods of one week have been made.

A good example of the use of the Cyclums is the preparation of samples of human serum devoid of a single human serum protein.⁷ Here antibodies to a specific human serum protein were immobilized on an inert support and used as an immunosubtractive chromatography system on the Cyclums. In the case of the human serum protein, hemopexin, only enough antibody to react with the hemopexin in about 300 μ l

7. J. E. Attrill, J. E. Caton, D. W. Holladay, and N. G. Anderson, "Affinity Chromatography of Human Serum Using Antisera Against 'All But One' Human Serum Proteins," *ANAL* 32, 165th ACS National Meeting, Dallas, Texas, April 8-13, 1973.

of human serum was available. However, a column prepared from this antibody was used to subtract the hemopexin from over 30 ml of human serum. We passed the human serum over the column five times, with each pass requiring about 30 cycles. The total time for the five passes was about two weeks. However, the actual operator time was probably less than 2 hr.

Several other investigations are based on the use of immunosubtractive chromatography. These include a study to ascertain whether or not one can isolate from the serum of tumor-bearing rats specific distinguishing components that are not present in the serum of normal rats. Another investigation concerns the immobilization of the antibody fraction from the serum drawn from pregnant women at term. This study is designed to ascertain if the antibodies in pregnant women can be used to isolate any specific components in human placental extract or in serum drawn from human cancer patients.

Polyacrylamide gel electrophoresis. We have employed the specificity of antibodies in analytical electrophoresis.⁸ Here a band or bands may be subtracted with specific antibodies prior to electrophoresis. By subtracting or diminishing a band with a specific

antibody, one has essentially identified that band in the resulting electrophoretic pattern when it is compared with a control. Thus such a technique retains the identification advantages of immunodiffusion or immunoelectrophoresis without sacrificing any of the much higher degree of resolution obtained by polyacrylamide gel electrophoresis.

Kathy Lowry, ORAU Undergraduate Research Trainee from New College, Sarasota, Florida, carried out another study involving mainly polyacrylamide gel electrophoresis. Ms. Lowry was advised in her work by D. E. Farod (Biology Division) and J. E. Caton. An abstract of her work follows.

Of 8 solvents compared, a tris-glycinate buffer (pH 8.6) containing 2-mercaptoethanol extracted the most protein for electrophoretic analysis of the flours of soybean varieties Lee, Pickett, and Harosoy and three radiation-induced morphological mutants of Harosoy. Sonication extracted more protein than agitation. The only effect of type of solvent and of sonication versus agitation was in the amount of protein dissolved. Electrophoresis of seed proteins on gradient polyacrylamide slab gels detected previously unreported differences between Lee and Pickett varieties and revealed that two of the mutants have a pattern similar to one another, but different from the other mutant. The latter has a pattern similar to the parent Harosoy variety. Treatment of the extracts with sodium dodecylsulfate and 2-mercaptoethanol before electrophoresis on gels containing sodium dodecylsulfate distinguished differences in major proteins or protein subunits of the two mutants that have similar patterns on gradient gels. This revealed that the remaining mutant and the three varieties share the same proteins, differing only in the amount of a given protein.

8. J. E. Caton, D. W. Holladay, and N. G. Anderson, "Immunosubtraction Electrophoresis on Gradient Polyacrylamide Gels," *ANAL* 31, 165th ACS National Meeting, Dallas, Texas, April 8-13, 1973.

3. Energy Programs

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ANALYTICAL DEVELOPMENTS FOR THE MOLTEN-SALT REACTOR PROGRAM

Determination of trivalent uranium in molten fluoride fuel. The equipment for the automated in-line determination of U^{3+}/U^{4+} ratios in molten-salt reactor fuels⁵ was utilized to measure the degree of reduction of the synthetic fuel charged to fuel pins (metal capsules fabricated from proposed structural alloys) for an in-pile experiment, TeGen-1.

This experiment was the first of a series designed to investigate the effects of fission products, particularly tellurium, on the intergranular corrosion of alloys for molten-salt reactor fuel containment. In order to simulate the conditions of reactor operations, in which the fuel would be maintained in a reducing condition, it was necessary to adjust the U^{3+}/U^{4+} ratio in the charge to a level sufficient to maintain a reducing fuel (approximately 1% in U^{3+}) despite the oxidation resulting from the fission process. Moreover, it was

calculated that oxide in the inner surface of the capsules might be sufficient to consume a substantial fraction of the U^{3+} , and therefore, a preequilibration "soaking" period of the pin with the fuel was required to assure a known concentration of U^{3+} in the capsules. One proposal was to drain the pins after the equilibration period and recharge them with reduced fuel. This operation would require cooling the system and breaking and reconnecting numerous fittings, a procedure which might jeopardize the experiment. It would also consume time from an exceedingly tight schedule. Accordingly J. H. Shaffer, Reactor Chemistry Division, designed the following procedure to permit analyses of the equilibrated fuel and requested that we adapt our analytical techniques to it.

The fuel would be mixed in a reaction vessel and partially reduced by hydrogen sparging. After analysis the U^{3+}/U^{4+} ratio would be adjusted to the desired range by successive treatments with beryllium metal. A portion of the fuel would then be transferred to a prefill vessel that is connected to the fuel pin assemblies and again analyzed. The pins (three sets of four pins, each set fabricated from a different alloy) would be filled and soaked for four days. Following this equilibration, the excess fuel from each set of pins, $\sim 4 \text{ cm}^3$, would be sequentially blown back into a small cavity at the bottom of the prefill vessel and again analyzed. If the ratios remained within the desired reducing range, the filling operation would be terminated and the costly refilling operation eliminated.

We designed and installed electrode systems to fulfill these unusually exacting requirements. Because of the hazards from the ^{233}U in the fuel, it was necessary to perform the operations in a dry box in an alpha containment facility. To protect our equipment from the remote possibility of contamination, we located our electronic components, voltammeter and PDP-8/I computer, in an adjacent room. Thus the operation fulfilled many of the criteria of our proposed future usage for

1. Bio-Organic Analysis Group.
2. Instrumentation and Advanced Methodology Group.
3. Co-op student.
4. Consultant, Professor of Chemistry, University of Tennessee, Knoxville.
5. J. M. Dale and A. S. Meyer, "In-Line Chemical Analysis of Molten Fluoride Salt Streams," *MSR Program Semiannu. Progr. Rep. Aug. 31, 1971*, ORNL-4728, p. 69.

in-line analysis, including remote operation and the rapid acquisition of data without the hazardous operation of sample withdrawal.

The results of the analyses are summarized in Table 3.1. The agreement between the first three values reflects both the precision of our analyses and the care in the performance of the operation by the Reactor Chemistry Division personnel. The ratios found in the samples from the fuel pin follow a trend which would be expected if the fuel were partially oxidized during the transfer then re-reduced during equilibration in proportion to the activity of chromium in these different alloys. In view of the limited amount of data, this correspondence may well be fortuitous.

It is of interest to note that the first ratio in the table, 1.88%, was substantially higher than expected. On the basis of the rate of evolution of HF at the termination of the hydrogenation step and thoroughly established free energy values for the reaction of U^{4+} with hydrogen, a ratio of $<0.7\%$ was expected. An investigation to resolve this discrepancy revealed that the thermocouple used to measure the melt temperature was malfunctioning. The ratio recalculated at the corrected temperature was in reasonable agreement with the analytical results. Had beryllium reduction been performed on the basis of the initially calculated ratios, the upper concentration limit of 2% would most surely have been exceeded and the results of the experiment compromised. This operation thus serves as an example of the practical value of the in-line analytical methods that were being developed for reactor salt streams.

Analysis of MSRP coolant salt. Because a major engineering test loop, the Coolant Salt Technology Facility (CSTF), was put into operation during this period to study the application of NaF-NaBF₄ eutectic, we concentrated a large portion of our research and development activities on the study of this material.

The CSTF is a pumped loop in which about 500 kg of the fluoroborate eutectic is circulated about once every 10 sec. A. I. Krakoviak designed a salt monitoring vessel (SMV) to provide access to the salt for experiments proposed by members of the Reactor Chemistry and Analytical Chemistry Divisions.

The SMV is fed by a side stream which enters the bottom of the vessel through a throttling valve that permits control of flow from 0.2 to 2 gpm at maximum loop pumping speed. The eutectic flows upward through a funnel-shaped vessel and overflows to produce a relatively stable surface. The top of the SMV is penetrated by six risers each fitted with 1.5-in. ball valves. Two of these risers are fitted with Pyrex windows and angled so that their axes intersect the axis of one of the vertical risers at the surface of the melt and thus provide for the illumination and observation of the melt. For the initial operations, three of these vertical risers, including the one equipped for observation, were assigned to analytical measurements. We were thus provided with an unusual opportunity to more carefully study the proposed in-line electro-analytical methods. Experience at the MSRE had demonstrated that the composition of large quantities of salt can be more readily controlled than that of research melts.

On the basis of our research investigations we expected to perform voltammetric measurements of certain corrosion products and electroactive protonated species and to measure the melt potential vs a lanthanum fluoride membrane electrode that uses the Fe-FeF₂ couple as a reference. Prior to startup of the loop, we made voltammetric measurements on the material used to charge the CSTF in a quiescent melt to determine whether it presented any unusual features.

At 500°C, the melt exhibited the anticipated reduction waves for iron and a rather large proton wave (despite low BF₃OH⁻ analysis and careful pumping) but no chromium wave. Subsequent analyses of samples from the CSTF indicated that the total chromium content of the salt was 30 ppm or less initially. On heating to 600°C, the cathodic limit of the melt decreased several hundred millivolts, so that it was not possible to observe the reduction of 200 ppm of added Cr(III) at platinum. Previously, at 500°C, a Cr(III) → Cr(0) reduction wave had been observed at ~ -1.0 V near the cathodic limit of the melt.⁶ An even greater decrease in the cathodic limit was seen at the palladium

Table 3.1. MSR-ORR capsule TeGen-1 fuel analysis

Operation	U^{3+}/U_t %
Preparation container	
After fuel hydrogenation	1.88
Fuel frozen-remelted	1.76
Prefill container	
After transfer from prep container	1.83
After pin equilibration	
Stainless steel 304-H	1.75
Inconel 601	1.61
Hastelloy N	1.50

6. A. S. Meyer et al., "Voltammetry of Chromium(III) in Molten NaBF₄-NaF (92-8 Mole %)," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 25.

electrode. We attribute this change in the limit to the alloying of the boron reduction product with the electrode material.

We screened a number of alternative electrode materials and found that iridium, pyrolytic graphite, and copper yield resolved Cr(III) waves at 600°C that are comparable with those obtained at platinum at 500°C. On a gold electrode, however, the chromium wave appeared about 100 mV earlier, giving better resolution from the limit, apparently as a result of alloying of the deposited chromium. Silver offered no advantages, and rhenium and tantalum were too active for use in NaBF₄ melts.

On the basis of these studies, we selected electrode systems which included the evacuable palladium electrode for the measurement of the protonated species and pyrolytic graphite (PG), copper, iridium, and gold electrodes for the measurement of corrosion products. Some of these electrodes were installed in a shield tube which is inserted in one of the vertical risers. The shield is a 1-in. tube of thin-walled Inconel which penetrates the melt to below the level of the electrodes. It can be purged with He-BF₃ cover gas and then connected to the melt blanket gas to provide fresh melt surfaces and an essentially quiescent melt around the electrodes. The remaining electrodes were installed without shields beneath the viewing ports so that the effects of surface films on the measurements could be evaluated.

From these preliminary measurements, we expected to observe milliamperic reduction waves in the SMV of the protonated species at the palladium electrode and of Fe(III) → Fe(II) at about 0 V, Fe(II) → Fe(0) about -0.4 V, and Cr(III) → Cr(0) at -0.7 to -0.8 V at the gold, PG, iridium, and copper electrodes.

Actually our first measurements revealed a large, previously unobserved, wave of about 100 mA near 0 V. The wave and its attendant stripping wave were quite persistent and were obtained on all electrodes. After several hours of scanning, it began to decrease with each successive scan as shown in Fig. 3.1. We have attributed this wave to a deposit of nickel on the surface of the electrode, and indeed a plating of metallic nickel was later observed on electrodes removed from the SMV. When the electrode is set at the initial anodic potential, a film of sparingly soluble NiF₂ is formed to block further current. On scanning cathodically the film is reduced rapidly to give the sharp peak observed, slightly negative of zero volts. On the return scan the NiF₂ blocking layer is re-formed when the potential becomes anodic. It is of interest to note that the nickel film forms even on an electrically isolated electrode, apparently by mass transfer to the electrodes, which are

slightly cooled by conduction of heat up the support rod. At present this nickel wave does not appear to offer any practical analytical applications and is primarily a nuisance. We have found that it can be substantially eliminated by holding the electrodes at anodic potentials ($\geq +0.3$ V) when not in use.

By using this technique and by using faster scan rates (0.5 V sec⁻¹) to minimize the effects of flow variations, we were able to obtain corrosion product voltammograms of the quality shown in Fig. 3.2, which is an actual recording of a series of voltage scans. It is not yet possible to accurately interpret these scans in terms of concentrations, because the position of the base line at this scan rate is not accurately established. Tentatively, values of 100 ppm of iron and 15 to 30 ppm of chromium have been estimated. These concentrations are somewhat lower than those measured by wet chemical analyses of samples withdrawn from the loop (about 150 ppm of Fe and 40 ppm of Cr). This is to be expected, because the voltammetric method measures only soluble ionic species while the chemical analyses include insoluble species such as free metals. The small peak between the Fe(III) and Fe(II) reduction waves has not been observed previously. Mamantov has suggested that its potential - ~-0.2 V - might well correspond to the reduction of Mo(III) to the metal.⁷ About 25 ppm of Mo was reported by chemical analysis.

The precision of the measurement was quite satisfactory when parameters were held constant. Although during the early stages of operation many experimental changes were made, sufficient measurements were made at the gold electrode at 0.5 V sec⁻¹ scan rate to permit an estimate of the precision of the voltammetric measurements. For 25 measurements over a six-week operating period, the wave heights for the Cr(III) and Fe(II) waves were reproducible to better than ±15%. These values were calculated by including statistically rejectable values and without attempting to correct for possible systematic variations in the actual concentration in the loop charge and would be expected to improve with additional data and more careful evaluation. The precision of measurement of the Fe(III) wave, which is subject to interference from the residual nickel wave and the smaller Mo(III) wave, is on the order of ±20%. It is therefore indicated that the voltammetric method, although requiring much additional experimental work, should offer a practical method for the in-line monitoring of corrosion products in reactor coolant streams.

7. G. Mamantov, personal communication, 1972.

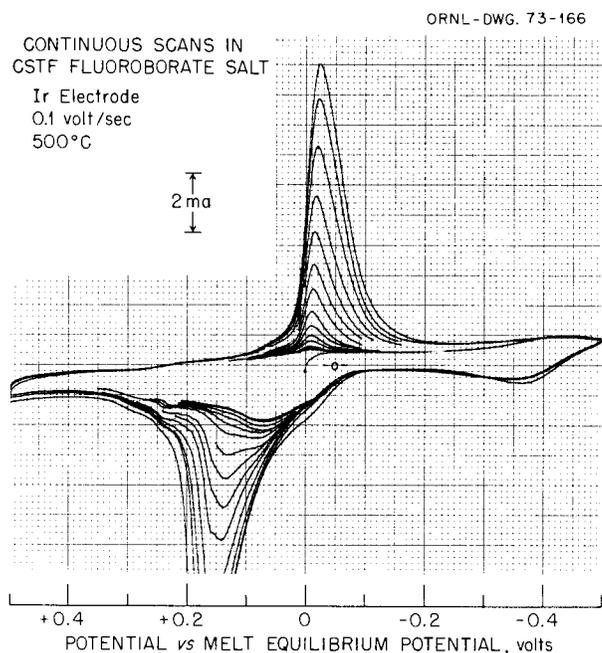


Figure 3.1. Decrease in $\text{NiF}_2\text{-Ni}^0$ wave during scanning.

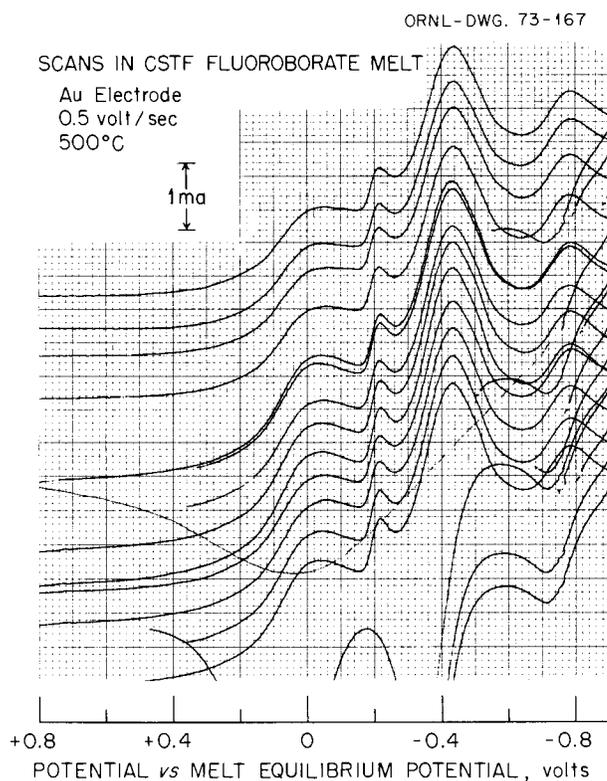
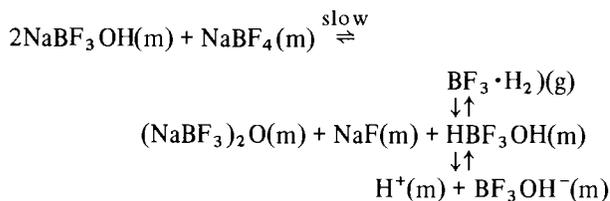


Figure 3.2. Voltammograms of corrosion products in CSTF.

Electroanalytical⁸ and spectrophotometric⁹ research have led us to believe the electroactive protonic species in fluoroborate melts is present in very small concentration and is highly mobile, in contrast to infrared-active BF_3OH^- , which appears to be relatively stable and perhaps covalent. Moreover the electroactive species is in rapid equilibrium with a volatile species which apparently corresponds to the condensate found in downstream sections of the off-gas systems of engineering test loops. Based on evidence from various sources, we have suggested that the phenomena observed are best explained by postulated equations of the following types:



We can make no claims for the actual composition of the compounds on the right of the above equation, and attempts to establish the stoichiometry and equilibrium constants by variational methods in small research melts were inconclusive because of the adventitious introduction of traces of protons during additions to modify gross melt composition. The large salt volumes in the CSTF offered promise for more precise studies of these protonated species.

During the initial operations of the CSTF, the nickel wave obscured any voltammetric measurements of the electroactive protonic species. Its presence was indicated by a pressure rise within the hollow palladium electrode when held at a potential cathodic to the wave (~ -0.5 V). The rate of pressure rise decreased rapidly to approach our limits of detection with a thermocouple vacuum gage during the first week's operation. After the loop was drained for a maintenance shutdown, some uncirculated salt was brought up from the drain tank, and a significant pressure rise was again noted. The rate of pressure rise over a two-day period is plotted as the upper curve in Fig. 3.3. The data are in good agreement with a first-order reaction of 10 hr half-life. After the protons had substantially been removed from the melt, 1 cm^3 of water was injected via

8. A. S. Meyer et al., "Voltammetric Studies of Protonic Species in Molten $\text{NaBF}_4\text{-NaF}$ (92.8 Mole %)," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 23.

9. A. S. Meyer et al., "Infrared Spectral Studies of Molten and Solid $\text{NaBF}_4\text{-NaF}$," *Anal. Chem. Div. Annu. Progr. Rept. Sept. 30, 1972*, ORNL-4838, p. 24.

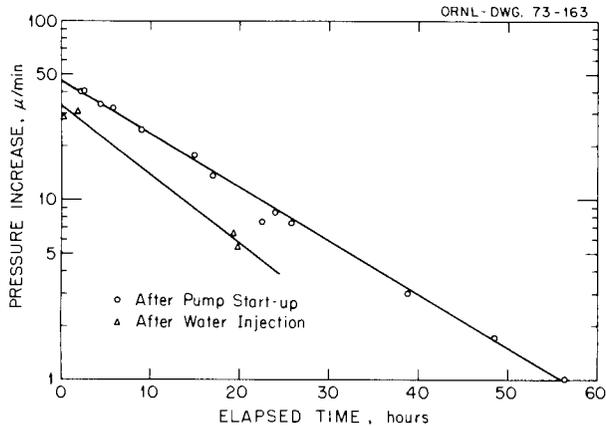


Figure 3.3. Decay of active protons in CSTF fluoroborate melt.

a stream of helium into the pump bowl. The data plotted in the lower curve show a similar rate of decay.

If all the hydrogen in the water had been converted to active protons, a concentration of 200 ppb would have been obtained. Since infrared measurements⁹ have demonstrated that some of the water absorbed on NaBF_4 is converted to BF_3OH^- on melting and some of the injected water may not have been absorbed, it appears likely that the initial rate of pressure rise corresponds to a concentration of no more than 100 ppb of protons. Combining these values with wave heights and pressure rise rates observed at similar electrodes in a research melt, we have calculated a diffusion coefficient of $8 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at 500°C . This confirmed our earlier conclusions that the active protonated species, probably a loosely solvated proton, must be more mobile than other ions in fluoroborate melts, whose diffusion coefficients are typically $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$.

The above experiments tended to support our hypothesis as to the nature of proton reactions in molten fluoroborate. We therefore suggested that the active proton species might be exploited to control the tritium emission which could be released to the environment from MSBRs by diffusion through heat exchangers and steam generators. Earlier suggestions that the tritium could be held up via exchange with BF_3OH^- appear to be of dubious value, as we have been unable to demonstrate significant exchange between BF_3OH^- and diffused deuterium.¹⁰ Exchange with the active protons would appear to be much more likely and would

offer an avenue for stripping the tritium through the off-gas system via either condensation or collection in a proton-depleted salt.

Dunlap Scott, Reactor Division, suggested that if our proposal were valid, residual tritium diffusing from the MSRE components from which the CSTF was fabricated would have collected in the condensate. The values reported in Table 3.2 clearly demonstrate a high concentration factor, $\sim 10^5$, in the collected condensate. These data are indeed promising but are not sufficient to establish the mechanism of the tritium transport or its overall effectiveness. We have no reliable information as to the quantities of tritium that could have diffused into the melt, the efficiency of trapping of the condensate and its chemical nature, or the nature of tritium bonding to the black film on the surface of the fluoroborate samples. We have performed analyses on the limited quantities of condensate available and on synthetic condensate generated by the reaction of BF_3 with water. Typical results are shown in Table 3.3.

Attempts to perform material and ionic balances on our results and to utilize NMR and IR spectra of such material indicate that they are a mixture rather than simple compounds. The synthetic mixture corresponds reasonably well to a mixture of $\text{BF}_3 \cdot \text{H}_2\text{O}$ with HF and H_3BO_3 . The condensate from the CSTF contains much less free fluoride and has a lower density than the synthetic products. It is possible that its composition had been modified during the extended sweeping periods and by reaction with the glass traps used for collection. The density of pure $\text{BF}_3 \cdot \text{H}_2\text{O}$ is reported to be 1.82.

These promising experiments were discontinued because of the termination of funding for the Molten-Salt Reactor Program; however, the fluoroborate eutectic may offer potential as a high-temperature heat exchanger medium for other nuclear energy sources which may encounter tritium containment problems, e.g.,

Table 3.2. Tritium content of NaF-NaBF_4 coolant loop exposed to tritium

Sample	Range of tritium values (nCi g^{-1})
Off-gas condensate	0.8×10^6 to 3.0×10^6
Salt	4 to 10
Black film concentrate	$>200^a$

^aIt was impossible to obtain a sample of black film without including some salt substrate. This value is certainly a minimum value; the tritium content of the black film only may be an order of magnitude higher.

10. J. P. Young, J. B. Bates, and G. E. Boyd, "Studies of Protons in Molten NaBF_4 ," *MSR Program Semiannu. Progr. Rep. Aug. 31, 1972*, ORNL-4832, p. 52.

Table 3.3. Analyses of BF₃ condensates

	Melt condensate	BF ₃ -liquid H ₂ O	BF ₃ -H ₂ O vapor
Density, g cm ⁻³	1.52	1.72	1.72
H ⁺ , millimoles g ⁻¹	12.0	12.1	12.9
Free F ⁻ , millimoles g ⁻¹	0.22	7.7	7.1
Bound F ⁻ , millimoles g ⁻¹	22.6	19.5	20.1
Total B, millimoles g ⁻¹	9.3	11.9	12.0
B as H ₃ BO ₃ , millimoles g ⁻¹	<i>a</i>	<i>a</i>	4.6

^aNot determined.

controlled thermonuclear reactors and other breeder reactor concepts. We have assisted Reactor Division personnel in the preparation of proposals for additional experiments which involve the controlled diffusion of deuterium into the CSTF. Such experiments should answer fundamental and practical questions as to the effectiveness of NaBF₄ as a tritium containment medium. The CSTF is presently in standby condition, and certain items needed to provide improved sensitivities in the measurement of active protons are available.

Studies on the electroreduction of uranium(IV) in molten LiF-BeF₂-ZrF₄ by square-wave voltammetry. We applied square-wave voltammetry to a study of the reduction of U(IV) in molten LiF-BeF₂-ZrF₄. The low resistance of molten salt solutions, which results in a low *RC* time constant for small-area electrodes, should render them attractive for square-wave voltammetric techniques. Other attractive features of square-wave voltammetry are the ability to measure Faradaic current in the virtual absence of charging current and the increased sensitivity afforded over conventional voltammetry. To our knowledge, however, there has been only one application of square-wave polarography to the study of solute species in molten salts.¹¹

At 500°C under our conditions, the equation for the peak current of a square-wave voltammogram is given as

$$i_{\max} = 3.496 \times 10^5 N^2 A D^{1/2} C F^{1/2} \Delta E, \quad (1)$$

where i_{\max} = peak current (A), N = number of electrons, A = electrode area (cm²), D = diffusion coefficient (cm² sec⁻¹), C = concentration of diffusing species (moles cm⁻³), F = square-wave frequency (Hz), and ΔE = magnitude of the square-wave step (V).

11. A. D. Graves, G. J. Mills, and D. Inman, *Advances in Electrochemistry and Electrochemical Engineering*, vol. 4, ed. P. Delahay, Interscience, 1066, p. 117-83.

A melt was prepared which contained 0.09 *M* U(IV), the concentration of interest in the MSRE fuel salt. We recorded current-voltage curves at small platinum and iridium electrodes by superimposing a square-wave voltage on the controlled potential ramp of a controlled-potential-controlled-current cyclic voltammeter. Oscillographic recordings were made of both cathodic and anodic branches of the cell current simultaneously. We observed that i_{\max} varied with frequency and amplitude of the square wave, as predicted from Eq. (1). The frequency and amplitude were varied from 100 to 1600 Hz and 0.01 to 0.05 V respectively. Linear voltage scan rates which were utilized varied from about 0.02 to 0.1 V sec⁻¹. From these observations, square-wave voltammetry appears well suited for the study of reversible electrode processes in molten salts. The apparent rapid decay of double-layer charging renders it feasible to utilize higher square-wave frequencies than normally used for aqueous systems.

A report describing this work was submitted for publication in *Electrochimica Acta*.

Chemistry of tellurium in molten fluoride salts. Further spectral studies of tellurium and several of its anionic compounds in molten fluoride salts were carried out. Tellurium occurs in nuclear reactors as a result of uranium fissioning. Only recently has tellurium been considered as a possible cause of intergranular corrosion of structural metals and alloys. These studies were undertaken to gain information about the reaction of tellurium in salts related to the Molten-Salt Reactor Program. The results of our study are summarized in a paper submitted for publication.¹² Initial studies of tellurium compounds in molten LiF-NaF-KF were

12. C. E. Bamberger, J. P. Young, and R. G. Ross, "The Chemistry of Tellurium in Molten Li₂BeF₄," *J. Inorg. Nucl. Chem.*, to be published.

described earlier.¹³ When a telluride was reacted with molten LiF-BeF₂, a different absorption spectrum was observed than that seen in LiF-NaF-KF. The colored tellurium species in the alkali fluoride melt was not identified, but in molten LiF-BeF₂ it seems likely that the colored species, absorption maximum at 478 nm, is Te₃⁻. The species can be formed by reaction of Te²⁻ and Te⁰ or can be added directly as LiTe₃. (This compound was kindly provided to us by P. T. Cunningham, Chemical Engineering Division, Argonne National Laboratory.) This species is destroyed on reducing Te₃⁻ to Te²⁻ or oxidizing it to Te⁰. In a thermal gradient the colored Te₃⁻ was decomposed by disproportionation to volatile Te⁰ and Te²⁻ ion. Tellurium metal does not dissolve in molten LiF-BeF₂, and Te²⁻ is colorless as a dissolved species. The colored Te₃⁻ species can be made by the addition of tellurium or other mild oxidants to Te²⁻ or by the reduction of Te⁰ with silicon metal.

No further study of the colored tellurium species in LiF-NaF-KF was made. Based on a comparison of the spectrum with that seen for Te²⁻ in chloride melts,¹⁴ the species seemed to be Te²⁻; however, when it was established that Te²⁻ was colorless in molten LiF-BeF₂, it seems unlikely that it is colored in the alkali fluoride solvent. In any case the spectrum of the species in the alkali fluoride is not the same nor is it as sensitive to the chemical environment as the Te₃⁻ species in LiF-BeF₂.

SPECTROPHOTOMETRIC RESEARCH

Spectral studies of the rare earths. The recent theoretical treatment of Vander Sluis and Nugent¹⁵ has made it possible to better understand the allowed electronic transition spectra of rare-earth ions. There is in the literature a relatively small amount of noncorrelated data relating to these absorptions, both *f-d* and electron-transfer types. Many times, however, these bands are described as the region of optical cutoff, or some other term, and are of no real interest to the investigator. We are participating in a systematic study of the allowed spectra of both trivalent lanthanides and

actinides, and we are making use of published data of others to test the applicability of the Vander Sluis and Nugent theory to describe coordination of a given rare-earth ion in a given compound from a knowledge only of the position of the first allowed transition. In this investigation, by using data we obtained on crystalline SmCl₃ and CfBr₃,¹⁶ we have supplied experimental proof to a theoretical speculation by Nugent and Vander Sluis¹⁷ that an allowed absorption band found in CfCl₃ is more probably an electron-transfer band than a postulated *f-d* band.¹⁸ From the data we have gathered for electron-transfer bands of many 6-, 8-, and 9-coordinated trivalent rare-earth halides, it appears that the coordination number of the ion can be established spectrally. The results presently appear to correlate well for rare-earth oxides if the band of interest occurs at lower energy than a limiting band possibly attributable to the oxide ion. For *f-d* bands it appears that there are some exceptions to the unequivocal assignment of a coordination number from a knowledge of the absorption. The problems may arise from fluorescence or a requirement that another parameter, namely the *d*-level splitting, must be included in the theoretical treatment. In gathering the data for these studies, we have used scattered transmission, Kel-F mull, single crystal, and diffuse reflectance techniques. It has been necessary to study the applicability of severe masking techniques to spectral studies with a Cary spectrophotometer, model 14H. In earlier work, masking was found to be effective¹⁹ for other spectrophotometers. The same techniques worked for the Cary 14H. In addition, it was demonstrated that solution absorption spectra can be obtained, in amenable spectral regions, with as little as 0.01 to 0.03 μl of sample when contained in a suitable masked 0.3-mm-OD silica tube. Again, with the Cary 14H, by suitable masking we obtained spectra from a 10-μg CfBr₃ crystal, mounted behind a 150-μm aperture, over the spectral region from 700 to 300 nm, where the crystal absorbs strongly. Spectral studies with these small samples were carried out without any beam condenser optics.

13. A. S. Meyer et al., "Spectral Studies of Solute Species in Molten Fluoride Salts," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 27.

14. 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 Metal Halides," *J. Phys. Chem.* 70, 472 (1966).

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

16. Crystal supplied by J. R. Peterson, consultant from University of Tennessee.

17. L. J. Nugent and K. L. Vander Sluis, "Electron-Transfer Bands in the Absorption Spectrum of CfCl₃," *J. Chem. Phys.*, in press.

18. W. T. Carnall, S. Fried, and F. Wagner, Jr., "Absorption Spectrum of BkCl₃," *J. Chem. Phys.* 58, 3614 (1973).

19. J. P. Young and G. W. Clark, "Apparatus for the Spectrophotometric Study of Small Crystals," *Rev. Sci. Instrum.* 37, 234 (1966).

There is interest in generating and characterizing various oxidation states of actinide ions in order to gain further knowledge of these elements both in a theoretical and experimental sense. More such studies are being carried out in nonaqueous solvents, where there is a wider range of electrochemical stability for the generation of unusual oxidation states. An obvious class of nonaqueous solvents, molten salts, has received a little attention elsewhere and only indirect attention at ORNL. We are presently evaluating several molten salt systems for such studies. In characterizing various oxidation states of actinides, or in some cases lanthanides as nonradioactive stand-ins, we will make use of both *f-f* and allowed electronic transitions such as were described above. In this latter respect the Ce(III) spectrum we reported¹³ would seem to fit the expected spectrum of an 8-coordinated ion in the molten solvents LiF-BeF₂-ZrF₄ or LiF-NaF-KF over the temperature range of 500 to 600°C. The spectral studies of Pa(IV) in molten LiF-BeF₂-ThF₄ have also been submitted for publication.²⁰

Since apparatus for handling the transuranic ions has not been fabricated as yet, our molten-salt studies have been concerned with solvent melts that might be useful, and we have studied some rare-earth, notably cerium and uranium, and some other transition-metal ions. Molten salts in general would be ideal solvents for radioactive ionic species because of these solvents' radiation stability as compared with water or organic systems. Thermal instabilities²¹ of high-oxidation ionic states pose some problems at temperatures in the range of 500°C. This possible thermal instability has caused us to consider primarily molten solvent systems in the 100 to 250°C range, such as hydroxides, nitrates, HF-KF, and chloroaluminates. Based on our results and results of others, it seems that the HF-KF solvent

system might be a very useful system. An apparatus is being designed for use in this system.

Spectral studies of transition metals. In the course of hydroxide melt evaluation, we carried out spectral studies of Cu²⁺ and Ni²⁺ in molten NaOH-KOH at temperatures of 130 to 250°C. We find that Cu(II) dissolves in molten NaOH-KOH, with or without the presence of dissolved H₂O, to yield a blue solution which exhibits an absorption peak at 662 nm at ~250°C. The position of this absorption peak is shifted to an energy considerably higher than that of Cu(II) in H₂O or molten fluoride media, near 800 nm, and indicates that the hydroxide produces a stronger ligand field than does H₂O or F⁻. The shift of the band in hydroxide melts is only somewhat less than the shift in Cu(II) spectra caused by amines, to ~600 nm. The fact that the peak does not shift as a function of H₂O concentration in molten NaOH-KOH suggests that the species is Cu(OH)₆⁴⁻ rather than a CuO_n²⁽ⁿ⁻¹⁾⁻ anionic complex. For spectral work, all hydroxide melts have been contained in MgO or Al₂O₃ cells.

Although Ni(II) did not dissolve in molten NaOH-KOH that contained H₂O, some solubility was noted in the presence of excess O²⁻, and the resultant Ni(II) exhibited a weak absorption peak near 620 nm. The position of this peak would be in line with a belief that the Ni(II) was tetrahedrally coordinated, as NiO₂²⁻, in this melt.

20. J. P. Young, C. E. Bamberger, and R. G. Ross, "Spectral Studies of *f-d* and *f-f* Transitions of Pa(IV) in Molten LiF-BeF₂-ThF₄," *J. Inorg. Nucl. Chem.*, to be published.

21. 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.* 35, 1553 (1973).

4. Nuclear and Physics Methods

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X-RAY AND ELECTRON PHYSICS

Scanning electron microscopy-x-ray fluorescence technique. The scanning electron microscope-x-ray fluorescence (SEM-XRF) technique is the most widely used method of microanalysis (analysis of individual microscopic particles) that the Analytical Chemistry Division offers. Two types of information are provided by this method: (1) high-resolution photomicrographs (200 Å) of the specimens and (2) a complete analysis for all elements heavier than neon. Images of specimens are generated in a point-by-point mode by scanning them with a beam of high-energy (20 to 30 keV) electrons while simultaneously measuring the intensity of secondary (low-energy) electrons emitted. The scan of a cathode ray tube is synchronized with the scan on the specimen. The intensity of the beam striking the face of the cathode ray tube is modulated according to

the intensity of secondary electrons emitted from the specimen. Scanning electron photomicrographs can thus be regarded as secondary electron "emission maps" of specimens. The beam striking the specimen also excites characteristic x rays from whatever elements are present in the specimen. By measuring the x-ray spectra with a suitable detector, Si(Li), one is able to perform an elemental analysis. Either the entire specimen or minute particles (0.1 to 1.0 μ) can be studied. The microscope can also be operated in the "x-ray map" mode; that is, instead of generating the image by measuring secondary electron emission, characteristic x rays of particular elements can be chosen. Images of this type indicate how elements of interest are distributed in the specimen. One can imagine a multitude of applications for which the SEM-XRF method is useful. Some case histories of some of the more interesting projects are described below.

The chemical state of cadmium in environmental samples. In the Hudson River swamp, a polluted area having a high concentration (3 to 6%) of cadmium has been discovered. The Environmental Sciences Division (T. Tamura, F. Sweeton, E. Bondietti) has been studying the chemical form of the cadmium by x-ray diffraction and has concluded that it may be in the form of a solid solution with calcium carbonate - $\text{Ca}_{1-x}\text{Cd}_x\text{CO}_3$. The cadmium-containing component of the mud was isolated by the zonal centrifuge technique,⁴ which will be described in more detail below. Upon examination of this component by the SEM-XRF method, we found that more than 50% of the particles contained both cadmium and calcium (Fig. 4.1). Most of the particles were 50 to 100 μ in diameter and were agglomerates of smaller crystallites 1 μ or less

1. General Hot Analyses Laboratory.

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3. ORAU summer trainee from Hardin-Simmons University, Abilene, Tex.

4. W. P. Bonner, T. Tamura, C. W. Francis, and J. W. Amburgey, Jr., "Zonal Centrifugation - a Tool for Environmental Studies," *Environ. Sci. Technol.* **4**, 821-25 (1970).

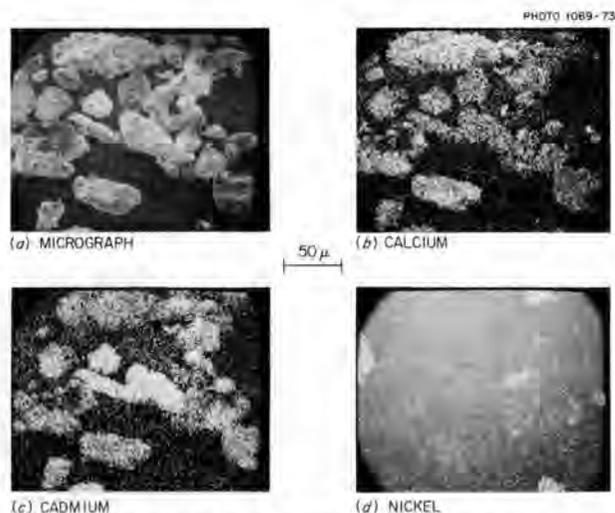


Figure 4.1. Distribution of calcium, cadmium, and nickel in the dense component of swamp mud as determined by the scanning electron microscope-x-ray fluorescence method. The distribution maps *b*, *c*, and *d* were generated by recording the emission of characteristic x rays from the elements indicated.

in dimension. By measuring distribution maps at high magnification of calcium and cadmium in the small particles, we determined that the calcium and cadmium were uniformly distributed within each other. This lends support to the conclusion by Tamura, Sweeton, and Bondietti that the cadmium is in a solid solution state.

The zonal centrifuge has proved to be very valuable in the preparation of soil samples for SEM-XRF examination. The principle of the method – separation of particles by density difference – is not new, but some important refinements have been added that make the technique more workable. Probably the most important improvement is the use of a surfactant – polyvinyl pyrrolidone – to make the particles disperse properly in the density gradient fluid. We have used this improved method in the next case history also.

The chemical state of lead in pollution samples. In Galena, Kansas, there is a controversy over whether or not a smelter is polluting its vicinity with lead. Soil samples taken 4000 yd downwind contain 1200 ppm lead. The smelter officials claim that the pollution is coming from the numerous piles of tailings left by other mining operations many years ago. Samples taken from the tailings piles and from areas downwind of the smelter were sent to the Analytical Chemistry Division for examination. The information requested was whether or not the chemical state of the lead in the soil was the same as in the tailings pile. We suspected that most of the lead in the tailings pile was in inorganic forms such as oxides, sulfides, or sulfates, all of which

have densities greater than 3. Using the zonal centrifuge, we separated the dense components from the downwind samples and the tailings pile samples. In the heavy fraction from the tailings pile, we found discrete particles containing high concentrations of lead. In the heavy fraction from the downwind sample, no individual lead-containing particles were found. This suggests that lead in the downwind sample is not in the same chemical state as in the tailings pile.

Inclusions in geological samples. The final case history to be described involves the coordination of more than one type of examination. In microanalysis it is often desirable to be able to study the same small spot on a specimen by more than one technique. This requires that the specimen be mounted so that it can be transported from one instrument to another and that a researcher or some other coordinator be able to memorize the features of the specimen so that the area of interest can be located again. This is the type of problem that we have solved routinely for the geologic specimens of R. V. Gentry, Chemistry Division. Gentry is studying inclusions of heavy elements that were once radioactive in mica. His procedure is to locate the inclusions in mica using an optical microscope. He then transports the specimen to the ion microprobe at the Y-12 Plant, where an isotopic analysis on the inclusion is made. The ion microprobe results have been indicating unusually high concentration of ^{206}Pb . Since the ion microprobe technique is rather new, many people are suspicious of Gentry's results and have suggested that lead is not present at all in the inclusions of his specimens. Using the SEM-XRF technique, we located and analyzed one of the inclusions previously studied by the ion microprobe. Our spectra show unequivocally that lead is present. This is a strong indication that the high ^{206}Pb concentration indicated by the ion microprobe is correct.

When problems in a highly specialized field such as microbiology are encountered, it is often necessary for the researcher to be present in order to direct the examination or to operate the microscope himself. For this reason we have encouraged researchers from other Divisions of the Laboratory to learn to use the microscope and to do their own work. Sidney Draggan, of the Environmental Sciences Division, has been one of the more active participants of this type. This arrangement has been beneficial to us as well as him since we have learned more about specimen preparation and other aspects of microbiology. Thus we have been able to manage the SEM-XRF equipment, which is very expensive (\$110,000), so that both routine service and specialized research projects can be accommodated.

X-ray-induced x-ray fluorescence. There has been an accelerated interest in the last three to five years in this technique because new instrumentation has greatly improved its sensitivity. The most important innovations have been (1) the use of monochromatic x-ray sources for excitation and (2) the use of Si(Li) crystals for detection. Monochromatic excitation sources greatly reduce background of spectra. The Si(Li) detector, when used with a multichannel device, increases by at least a factor of 100 the rate at which data can be taken. Several research groups and electronics companies across the country have contributed to the improvement of the method. At ORNL, the effort has been led by C. J. Sparks, Metals and Ceramics Division. His group, working under an NSF/RANN grant, has been able to achieve detection sensitivities less than 1.0 ppm for many elements. They have also shown that the technique can be made into an absolute method of quantitative analysis, such that individual standardization for different matrices is unnecessary. Using borrowed equipment, the Nuclear and Physics Methods group has assembled a system with sensitivities equal to that of Sparks' design. Some slight changes have been made in specimen holder construction, and a Ag $K\alpha$ monochromator source, instead of Mo $K\alpha$, has been used. Many environmental specimens, including the NBS standard orchard leaves and coal specimens, have been studied. The Analytical Chemistry Division is in the process of acquiring permanent equipment so that this improved x-ray fluorescence technique can be offered as a standard service. This is a cooperative effort with C. J. Sparks and J. C. Ogle of the Metals and Ceramics Division.

Photoelectron spectroscopy (ESCA). The ESCA (electron spectroscopy for chemical analysis) technique is a versatile tool for analyzing surfaces. The principle of the method involves the photoelectric effect. Surfaces of solids are irradiated with soft x rays — Al $K\alpha$ or Mg $K\alpha$ — which cause photoejection of electrons from core levels of atoms. By measuring the kinetic energies of the photoelectrons, the binding energies of the levels from which they came can be deduced. Inner core binding energies are unique to particular elements; thus a qualitative analysis technique is provided. There is a slight shift in binding energies with chemical state, so the method also provides information about chemical environments of elements. Since the photoelectrons cannot escape from large depths within the solids, the method provides information about surface layers only.

In the Environmental Sciences Division, T. Tamura and F. H. Sweeton have been studying the uptake of cadmium and other heavy metals by kaolinite and

montmorillonite clays. The understanding of the surface reactions of this process is the central goal of the study. It is believed that one of the mechanisms of adsorption of heavy metals is by cation exchange with calcium. Calcium appears to be bound at ion exchangeable sites on the surface of kaolinite. Using the ESCA technique, we have determined that for pure kaolinite substrates there is a reciprocal relationship between surface concentrations of calcium and cadmium. For clay specimens for which the photoelectron peaks of cadmium were intense, the calcium peak was low, and vice versa. Thus it appears that ion exchange with calcium is one of the mechanisms for cadmium uptake.

Tamura has observed in previous work that the adsorption of iron or aluminum on clay surfaces greatly increases the degree of cobalt adsorption. His adsorption measurements were made using tracers. We have found this to be true for cadmium adsorption also. If the kaolinite is treated with $FeCl_3$ solutions and then with cadmium, the uptake of cadmium is 20 times greater than for untreated clay. Using the ESCA technique, we have examined the clay surface after treating with iron and are currently studying the surface after the addition of cadmium.

A joint problem involving C. Helling of USDA has been started in which the adsorption of paraquat (a herbicide) on montmorillonite clay is being studied. Paraquat is a quaternary amine; its presence on the clay is revealed by the unique binding energy of nitrogen. It appears that the paraquat is also adsorbed by cation exchange with calcium. We have found that exposure to uv light removes or destroys the adsorbed paraquat. We are conducting experiments to determine the effects of sunlight.

TRACE-ELEMENT PROFILES THROUGH A COAL-FIRED STEAM PLANT

We are now into the second full year of our NSF/RANN program to determine experimentally the trace elements in the influent and effluent materials of the Thomas A. Allen Steam Plant in Memphis, Tennessee. A detailed account of this project and results is presented in another ORNL report,⁵ as well as in several journal publications which are listed in the Appendix.

5. N. E. Bolton et al., *Trace Element Measurements at the Coal-Fired Allen Steam Plant*, ORNL-NSF-EP-43 (March 1973).

As indicated in the 1972 annual report,⁶ our specific objectives this year were: "(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." Our efforts to accomplish these objectives and how they fared are discussed below.

Soil and particulate samples were obtained during September 1972, and these samples were analyzed for trace elements by spark-source mass spectrometry, neutron activation analysis, and atomic absorption (mercury only). The samples were taken along a north-south transection for a distance of 40 miles at 1-mile intervals. These sampling locations were selected after studying wind directions and velocity data and utilizing the best atmospheric model available for falldown. After hundreds of elemental determinations on these soils were made and the data correlated, no effect of Allen Plant particles was seen. Part of the reason for this was the similarity between the composition of soil around Allen and that of the particulates. A restudy of the problems of falldown by the modelers resulted in a conclusion that most of the falldown probably would occur within 0.5 mile of the stacks. Flooding of the land surrounding Allen would further tend to obscure any effect of particulates, and these effects, in any event, would tend to be small since our balance data show the precipitator to be about 99% efficient. Attempts to use fallout buckets and air samplers in December 1972 fell victim to heavy rainfall that eventually caused flood conditions throughout the Mississippi Valley.

In January 1973, preliminary in-plant samplings were performed to test a new impinger system for trapping mercury (whose presence in the gas is expected but not yet quantitatively found) and other toxic volatile elements. This system consists of an Na_2CO_3 trap (for SO_2 removal), a sodium acetate trap (for selenium and perhaps arsenic, antimony, etc.) and ICl (specific for mercury). These experiments paved the way for a complete resampling performed (after several postponements) in August 1973. Eleven Oak Ridgers, three TVA experts, and one EPA observer descended on the Allen Plant for one week of complete sampling, including coal, slag, precipitator inlet and outlet, and gas. A

second week of specialized air and vegetation sampling was carried out by a considerably reduced crew. Throughout the sampling period, the TVA personnel at Allen were most helpful in providing information, lab space for solution preparation, and operating assistance. The samples have been returned and are now being processed. Preliminary data indicate we have successfully trapped mercury and selenium. This latter element was determined using the GC-MES system discussed in Sect. 1 of this report. Throughout this project we have drawn heavily on the expertise of scientists in many disciplines and divisions, particularly Ecological Sciences, Industrial Hygiene, and our own Division.

Our plans for the next year are to concentrate on the volatile elements and to attempt to follow them through the combustion process in the plant and out into the environment. Our experience in attempting to sample at Allen convinces us that better sampling equipment and strategies are needed; we hope to develop these. The Allen Plant is one of the few steam plants equipped with cyclone furnaces. These have a much lower ratio of particulate to slag-tank ash than pulverized coal furnaces. Thus we feel studies should be repeated at a plant using the latter combustion equipment. We believe SO_2 may be used as a tracer for volatile toxic elements. In cooperation with air model experts at ORNL, AEC, and TVA, we hope to develop a method to predict falldown from other meteorological data and to test this model. As in the past, we will publish and publicize our results and continue to cooperate with other investigators in making our data available for decision making concerning air pollution prevention.

COOPERATIVE ISOTOPES PROGRAM

For many years the Isotopes and Analytical Chemistry Divisions conducted a cooperative program concerned with characterization, analysis, and application of isotopes. AEC support was withdrawn and the program was accordingly terminated in March. The following paragraphs summarize our work during the six-month period since the previous report. Most of the activities of the Isotopes Division have been reported elsewhere.⁷

Characteristics of radioisotopes. A tabulation⁸ was prepared of specific activities and other properties of

6. W. S. Lyon et al., "Trace Element Profiles through a Coal-Fired Steam Plant," *Anal. Chem. Div. Annu. Progr. Rep. Sect. 30, 1972*, ORNL-4838, p. 31.

7. *Isotopes Development Programs - 1972*, WASH-1220 (February 1973).

8. S. A. Reynolds, *Theoretical and Practical Specific Activities and Other Properties of Common Radionuclides*, ORNL-TM-4167 (March 1973).

over 170 radioisotope products, and much of this information was used in a new edition of the isotopes catalog.⁹ We answered numerous inquiries, notably about half-lives and decay schemes, and reviewed reports, including data sheets for ²⁴⁴Cm. A new determination of the half-life of ¹⁷⁰Tm, 128.7 ± 0.3 days, was in agreement with our previously published one.

Quality control. The most important aspect of our quality control effort has been assay of radioisotopes. A review¹⁰ of more than a quarter century of measurement methodology was prepared, and a shorter version has been submitted for publication in a journal. Intercomparisons of assays by competent laboratories are obviously useful. An important one was concerned with the medical radionuclide ⁶⁷Ga, of which preparations were obtained from the British Radiochemical Centre and a domestic supplier. Our measurements, using two independently calibrated instruments in each of two laboratories, were 0.8% below RCC and 1.6% above the domestic supplier. The RCC value was obtained by coincidence counting and was therefore little affected by assumptions about the decay scheme, but our measurements required utilization of data we selected from the literature, which are quite different from those in the 1967 *Table of Isotopes*. In particular, a 30% error in spectrometric assay would have resulted from using the old percentage for the 300-keV gamma radiation. Details of this study were made available to domestic suppliers and users, NBS, and standards groups and may contribute to resolution of discrepancies some have reported.

¹³³Xe is another isotope of importance in medicine. The ionization chamber used for local assay of shipments was recalibrated using mass-analyzed samples. The overall precision was about 6%, and the previous calibrations were confirmed within 0 to 7%. According to data received from a commercial supplier, taking an NBS measurement as unity, ours would be 1.07, the supplier's 1.19, and a foreign source 1.73. It must be noted that the NBS measurement was made on a small sample, and the above comparison is tentative. Resolution of the discrepancies awaits issuance of an NBS standard of appropriate level. Other intercomparison measurements included NBS preparations of ⁶⁰Co, ¹³⁷Cs, ³⁷Ar, and ³²P, plus one for CAP (below).

9. *Research Materials, Separated Isotopes, Radioisotopes, Special Preparations*, Oak Ridge National Laboratory publication, April 1973.

10. S. A. Reynolds, *Some Radioisotope Assay Methods*, ORNL-4788 (March 1973).

Since some radioisotope products are now being made in HFIR for the first time, we recommended that careful attention be given optimum irradiation times to minimize impurities. Analysis of ¹⁸¹Hf products was reviewed and found satisfactory. In particular, the relative amount of ¹⁷⁵Hf by-product agreed with that estimated from the cross sections. Calibrations and decay-scheme information for ^{110m}Ag and ¹¹¹Ag were reviewed. We suggested calorimetry for assay of large quantities of ¹⁴⁷Pm and gamma spectrometry for trace levels of ¹⁴⁶Pm impurity. Analytical methods were recommended for flux monitors and other special sources being prepared at ORNL. Isotope dilution mass spectrometry was suggested for enriched uranium isotopes and plutonium, alpha counting for neptunium, and activation analysis for impurities in cladding.

Work with national organizations. We worked actively for several months on behalf of ANS-16, the standards subcommittee of the ANS Isotopes and Radiation Division (IRD). A major concern was how to obtain readily usable and timely nuclear data. A suggestion had been made to handle tabulation and dissemination through the proposed ANS Information Center on Radiation and Radioisotopes, but the Center was not established.¹¹ Discussion of the problem took place at the special session on gamma counting which ANS-16 and IRD arranged.

We had considered preparation of "weightless" planchet sources of ¹⁴C to be used, for example, as reference sources for counters and survey instruments. A survey of needs and potential suppliers was made through ANS-16 by means of a questionnaire. Seventy-four organizations were contacted and 39 responded. Twenty-six checked "not interested." Nine indicated interest in sources somewhat like those proposed, and four companies reported willingness to supply them. It was accordingly decided not to pursue the matter further.

The problem of tritium contamination of heavy water (reported last year) was reviewed by ANS-16. No action was required because it was found by contacts with vendors that the ³H level had become very low, and it was subsequently confirmed that it had dropped about five orders of magnitude.¹²

We continued to advise the College of American Pathologists on their intercomparison program and assayed ¹²⁵I, one of the preparations distributed. On

11. "Absolute Gamma Counting," *Trans. Amer. Nucl. Soc.* 16, 67-69 (1973).

12. J. R. Campbell, "Tritium Contamination of Deuterium Compounds," *Nature* 241, 449 (1973).

that assay, our results and those of two other experienced groups and NBS were all within 2%. We did statistical analyses of the data from all the inter-comparisons and furnished decay-scheme information for a number of the nuclides of interest to CAP.

COOPERATIVE PROGRAMS IN APPLIED NEUTRON ACTIVATION ANALYSIS

MONSTR, the PDP-15 program for analyzing gamma-ray spectra obtained from Ge(Li) detectors and for isotope identification, has been essentially completed this year. The last addition has been a new routine to store spectra and parameters more efficiently on Dec-tape. Two tables required for isotopic identification have been completed. The first table is a list of 1200 gamma rays of the isotopes arranged in increasing energy, while the second table contains 320 isotopes, their gamma-ray intensities, cross sections, half-lives, and mass. These data are necessary for the calculation of disintegration rates and micrograms per gram. This program gives us the capability of multielement analysis by *absolute* neutron activation analysis, using radioactive nuclides with half-lives ranging from a few seconds to several years. The program has been used successfully with samples from a number of sources and has given good agreement on several standard NBS samples. Cooperation with institutions and universities has continued this year. Tours were made of the activation analysis facility at the ORR by the classes of the ORAU Summer Training Program. The study of aluminum in lung tissue was continued with Prof. Gale Norris and his research students (Denison University). We are cooperating with Dr. R. L. Tyndall (ORAU Microbiology Division) in the study of uterine proteins for possible complexing metals, copper, zinc, and manganese. These proteins had been separated by electrophoresis using (polyacrylamide) gels. Impurities of sodium, chlorine, and mercury in the gels have presented problems. Ion exchange techniques are presently being investigated.

Two experiments were conducted last summer by personnel of the USDA Forestry Service on the release and trapping of gold-tagged elm bark beetles.¹³ One experiment failed because of a cold front which prevented trapping of beetles. In the other experiment, tagged beetles were released at the USDA Experiment Station in Delaware, Ohio. The traps were placed on radii of 132, 264, 528, and 792 ft from a central release

point. The beetles were trapped for several days, but the total number collected was small, again due to rainy weather. The number of tagged and untagged beetles recovered was insufficient to predict the population, but almost all the trapped tagged beetles were from the southwest to northwest direction, which seemed to indicate the beetle flight path was in that direction. The beetles collected in the easterly direction were essentially all nontagged beetles.

A reactor coolant leak of approximately 7 gal min⁻¹ at the ORR was located using ²⁴Na and ²⁷Mg ($t_{1/2}$ = 15 hr and 9 min respectively) present in the coolant water as tracers. The ²⁴Na activity was used to estimate the dilution of the leak water by natural groundwater, and the ²⁷Mg activity was used to locate the leak. The leak was suspected to be somewhere under the concrete floor of the primary system pump house. This building contains five pumps and is about 68 ft long. The main discharge pipe runs the length of the pump house and is embedded in gravel approximately 6 ft below the floor. Small wells were drilled near each of the pumps to the bottom of the gravel bed. Samples of water from each well were counted for ²⁷Na and ²⁷Mg; those from No. 1 and No. 2 pump sites indicated the most ²⁷Mg. Changing the water flow direction through the gravel bed failed to indicate where the leak was located between these pumps, primarily because we found that the gravel bed was a good ion exchange material for ²⁷Mg. Digging at the No. 1 pump discharge line uncovered a small leak of 2 to 3 gal min⁻¹ at the gravel bed surface, and excavation at the No. 2 pump uncovered a larger leak in the main pump discharge line. This sampling and tracing technique clearly resulted in considerable savings both in reactor downtime and expense, since it was thought at one time that the entire line under the pump house would have to be uncovered.

SPECIAL MEASUREMENTS; FISSION PRODUCT AND RADIOACTIVE RELEASE STUDIES

Determination of fallout radionuclides in grass and air filter samples from the vicinity of operating nuclear power stations. The Atomic Energy Commission Office of Regulation conducted an "iodine pathways" study of radioiodine deposition in the vicinity of several operating nuclear power stations to obtain a valid assessment of ¹³¹I levels expected in the environment. We were asked to provide measurement assistance for grass and air filter samples collected at three nuclear power stations (Oyster Creek, Monticello, and Dresden), whereas other laboratories measured milk and other samples. Samples were collected regularly during

13. W. S. Lyon et al., "Elm Bark Beetle Tagging," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 33.

the summer months and continued until results were obscured by fallout from the Chinese nuclear weapons tests.

We measured 39 samples in the program (one-third air filters, two-thirds grass samples). Grasses were measured in an "as received" condition to prevent loss of volatile iodine. We adapted our low-level spectrometric techniques, developed for lunar sample analysis, to accommodate the environmental samples. Grass samples ranged in size from 50 to 800 g (wet basis). The volume of grass was reduced by hand compressing the larger samples so that they would fit into an 8-in.-diam by 2-in.-high container. Counting times were adjusted to accommodate the sample load and were in the range of 200 to 400 min. All the grass samples were analyzed in our 9- by 5-in. NaI(Tl) dual parameter system, and all filter samples were measured with our low-level Ge(Li) spectrometer in addition to the NaI(Tl) system.

Since our measurement techniques involve spectrometric equipment and least-squares data analysis we are able to determine several gamma-emitting nuclides with the single measurement. We were able to provide quantitative values for potassium (due to radioactive ^{40}K), ^{137}Cs , ^{131}I , and ^7Be in all grass and filter samples. In many samples collected in July, we were able to quantitatively determine ^{140}Ba , ^{140}La , ^{95}Zr , ^{95}Nb , and ^{103}Ru .

Potassium values ranged from 9.1 to 36.6 mg per gram of dry grass, with the mean value being 17.8 mg g^{-1} . Iodine-131 levels were near the detection limit for most small samples prior to the Chinese fallout arrival. Typical ^{131}I values were 0.02 to 0.08 pCi g^{-1} , with counting statistic uncertainties of approximately 50%. The highest level of ^{131}I observed in these samples was 6.4 pCi g^{-1} ; however, this same sample showed elevated levels of other fission product activities characteristic of nuclear weapons fallout. Cesium-137 values ranged from 0.006 to 1.1 pCi g^{-1} prior to the atmospheric weapons test, with posttesting samples having levels up to twice as high. Beryllium-7 was ubiquitous in the grass and filter samples and accounted for most of the gamma-ray activity in several samples. This radionuclide was present at levels of 3 to 27 pCi g^{-1} .

The success of adapting the lunar sample measuring equipment to environmental problems stems largely from the ability to modify data analysis techniques to fit various sample types, coupled with the ability to manufacture our own calibration standards for a variety of radionuclides. Another positive feature of this study has been the demonstration that our low-level Ge(Li) spectrometer is a useful adjunct for environmental sample analysis. This is a cooperative effort with G. D. O'Kelley, of the Chemistry Division.

✓ **Radioanalysis of environmental materials.** Analytical and general radiochemical studies related to programs of the Environmental Sciences Division are in progress. We have initiated an investigation of methodology for determination of actinides in environmental materials such as soil, water, and biological matter. Plutonium is the element of primary interest at this time because of its radiological significance in the LMFBR and radioisotope-source programs. A substantial literature search is being made on analytical methods for plutonium and on its environmental behavior. We have consulted a number of specialists in AEC, EPA, national laboratories, and other organizations and have resumed work with ASTM Committee D-19 on water, especially the heavy-element and sediments sections of its radiochemistry subcommittee.

We suggested that the National Bureau of Standards supply calibrated solutions of ^{236}Pu to be used for simultaneous evaluation of recovery and counting efficiency in plutonium analysis. However, NBS and the AEC Health and Safety Laboratory (HASL) have chosen to use ^{242}Pu for this purpose, and we shall receive a preparation of that nuclide. Soils and vegetable matter of known plutonium content are being obtained from the International Atomic Energy Agency (IAEA) and from C. W. Sill (AEC, Idaho), and ASTM D-19 is planning a "round robin" on plutonium in water.

It was desired to have a substitute for plutonium to permit exploratory work outside containment. A review of the radiochemical behavior of similar elements led to our suggestion that thorium would probably be best, and ^{234}Th is a satisfactory tracer. Plutonium-237 is a useful isotopic tracer and emits x and gamma radiations, thus avoiding complexities of alpha counting and permitting in situ measurements. Its properties and methods of production have been reviewed in anticipation of obtaining a supply. Advice is being given on facilities to be installed by Environmental Sciences personnel in Building 3508. Basic equipment has been assembled for liquid-scintillation measurement of alpha activity. System evaluation and experimental application will begin when additional components are installed by personnel of the Instrumentation and Controls Division.

Methodology and calibrations for routine radioanalysis are being reviewed at the request of Analytical Chemistry personnel responsible for the work. Efficiency of leaching low-level ^{90}Sr from soil is to be evaluated by destroying the residue by further leaching and fusion and determining the remaining ^{90}Sr . Methods and standards were suggested for gross alpha, beta, and gamma measurements on low-level waste samples,

as well as for other gross measurements using a new beta counter. Tritium and ^{147}Pm standards are to be obtained from NBS; a ^{90}Sr standard from IAEA has been put to use, and "known" environmental materials have been ordered from IAEA. For trace radium determinations, the radon-emanation method was found to be the only satisfactory one, and information is being collected on availability and cost of equipment.

^{235}U determinations for safeguard inventories.

Studies were begun early this year to improve gamma-ray spectrometric techniques for field measurements of the ^{235}U content of nuclear fuels and scrap materials.

A mobile assay system containing a modern computer-based pulse-height analyzer coupled to sodium iodide detectors was assembled and tested at ORNL to determine optimum operating conditions for several fuel types. We studied the accuracy of a proposed method involving the determination of ^{235}U by means of the 185-keV transition that occurs in 54% of the decay. By measuring a series of low-enriched oxide fuels (1.2 to 3.1%) that had been characterized by mass spectrometry and chemical means, we were able to show that the amount of ^{235}U present in such materials could be determined to an overall inaccuracy of approximately 1%.

We found that suitable beta-particle absorbers must be present in the system to eliminate spectral distortions caused by the presence of high-energy negatrons from the decay of ^{238}U daughters. It was also found necessary to hold the counting geometry constant so that severe attenuation problems associated with the 185-keV gamma ray could be properly corrected.

Operating conditions for the determination of the ^{235}U content of UO_2 powder and oxide pellet samples were determined with the mobile analyzer housed in an ORNL laboratory. The analyzer equipment and lead shield were then reassembled and transported to the Westinghouse Nuclear Fuel Plant in Columbia, South Carolina. We provided field assistance to the Region II USAEC staff for the gamma-ray spectrometric determination of ^{235}U content of 37 uranium oxide samples and 41 oxide pellet samples. These measurements were accomplished in three days field measurement time, with the data analysis completed at ORNL. Analysis of all collected data showed that the field techniques were adequate and that future field trips could be made self-sustaining; that is, the data analysis as well as measurements could be conducted in the field.

Future development activities will be directed to optimizing counting conditions for a variety of additional fuel types and enrichments. Application of high-resolution detectors [$\text{Ge}(\text{Li})$] to the safeguards

program will be investigated by making correlation measurements with both $\text{NaI}(\text{Tl})$ and $\text{Ge}(\text{Li})$ detectors on the same set of ^{235}U fuel types.

Nuclear products from nuclearly stimulated natural gas. S. A. Reynolds was assigned for three months to the Plowshare group in the Environmental Sciences Division. A study was made of hypothetical levels of radioactivity in various products made from natural gas from nuclearly stimulated wells. Tritium is the only significant radionuclide in such gas, and the level is predicted to be about 1 pCi cm^{-3} . The information was gathered to supplement that in an earlier report.¹⁴

The most-used drug is aspirin, and a literature survey was made of its production and its metabolism in humans. A plausible and conservative metabolic model involves oxidation of the tritium-containing acetyl hydrogen and its incorporation in body water. On this basis, the annual dose to an individual from a reasonable intake of aspirin, eight tablets per day, would be $0.012 \text{ millirem year}^{-1}$, about 43% of that from contemporary drinking water. "Natural gasoline" is that separated from gas, and it may make up 15% of fuel gasoline. It was estimated that the tritium dose rate from automotive use of such a product would be $0.003 \text{ millirem year}^{-1}$ for a person staying full time on a Los Angeles freeway. Among the roughly 2500 materials added to foods, three that are now used, or likely to be used, were selected on the basis of possible preparation from Plowshare gas. These were modified starch used in infant foods, sorbitol, a "dietetic" sweetener, and synthetic protein supplement. Postulating realistic intakes, the respective tritium doses would be 0.025, 0.011, and $1.0 \text{ millirem year}^{-1}$. The latter is slightly less than that from natural ^{14}C .

An outgrowth of the above work was a brief assignment for A. S. Meyer and S. A. Reynolds as consultants to Amoco Oil Company. In using radioactive tracers, HT , CH_3T , and ^{85}Kr , in an oil field, very poor analytical results were received. Company representatives wished to assure better data in a similar study in another field and requested that we visit their research laboratory in Tulsa. They were advised that ionization chambers were inadequate at the levels required (below 1 pCi cm^{-3}) and internal proportional counters should be used. Interference from radon was discussed and found to be insignificant; regulatory aspects and other matters were also covered.

14. C. J. Barton, D. G. Jacobs, and M. J. Kelly, *Quarterly Progress Report on Radiological Safety of Peaceful Uses of Nuclear Explosives: Consumer Products from Nuclearly Stimulated Gas Wells*, ORNL-TM-3123 (September 1970).

Fission product behavior in HTGR coolant circuits.

We have continued our assistance to the ORNL high-temperature gas-cooled reactor (HTGR) nuclear safety program. During the past year in our study of the Peach Bottom HTGR (owned and operated by Philadelphia Electric Company), we completed examinations of two coolant samplers, measured the fission gases in the primary coolant and core purge helium, and remeasured the fission product distribution in the primary circuit large ducts. We also began a postirradiation examination of a power fuel element. In a cooperative effort with the Instrumentation and Controls Division, we developed a powerful program for a Nuclear Data 4410 small computer to acquire and analyze Ge(Li) gamma spectra. This computer-analyzer system with a 16K 12-bit word memory has been used to acquire most of the spectra obtained in the ORNL HTGR Nuclear Safety and Fission Product Technology Programs.

Our objective in studying the Peach Bottom reactor is to compare measured and predicted distributions of fission products in an operating reactor. The Peach Bottom reactor has been powered with two cores during its operation. The first core had to be removed prematurely in 1970 due to fuel breakup and excessive fission product leakage. Because the primary coolant circuit was contaminated with fission products by Core I, the release of nongaseous fission products from Core II has been more difficult to determine than anticipated. In 1973, for the first time, we simultaneously operated coolant samplers upstream and downstream of a steam generator. Also, we were able to remove and analyze the samplers in time to measure ^{131}I . The purpose of these samplers is to determine the concentrations of the various forms (molecular and dust-borne) of nongaseous fission products in the coolant. By operating samplers upstream and downstream of a steam generator, the rate of deposition of fission products in the steam generator can be estimated. From their samplers it was found that the coolant leaving the core in May 1973 contained about $4 \times 10^{-4} \mu\text{Ci}$ of ^{131}I per pound of helium. This concentration has increased about 10% since April 1971. Between 13 and 39% of this iodine deposited on the steam generator and ducting between the samplers. At the reactor exit temperature of 720°C , iodine was not associated with dust. However, 0.7 to 1.2% of the ^{131}I was found on organic iodine traps in the sampler; this iodine is thought to be bound in an organic compound. At the downstream sampler position with a temperature of 325°C , between 5 and 30% of the ^{131}I was associated with dust, and the organic iodide had increased to 6–12%. We have thus assumed that organic iodides are

being generated in the steam generator. The ^{131}I content of one steam generator is estimated to be about 6 mCi, $\sim 2 \times 10^{-9}$ of that in the core. Recent measurements during shutdown on the Peach Bottom large ducts with a collimated Ge(Li) spectrometer have revealed the presence of ^{131}I . These results have not been quantitatively analyzed.

Several useful conclusions have been drawn about the release and behavior of ^{137}Cs and ^{134}Cs in the Peach Bottom reactor. In brief, the two cesium isotopes are mainly associated with dust. A small amount of molecular cesium species can be detected in the upstream sampling position. The total cesium inventory deposited in the primary coolant circuit that reached a relatively high level with Core I has been decreasing faster than can be accounted for by radioactive decay. The surface deposit apparently reentrains in the coolant and is removed by the coolant cleanup plant.

Additional conclusions regarding the behavior of fission products and the nature of the particulate and chemical effects that occur in the Peach Bottom reactor have been reported at a British Nuclear Energy Society Conference.¹⁵

Fission product release. In a cooperative program with the Reactor Chemistry Division,¹⁶ the release rates of ^{134}Cs , ^{137}Cs , ^{90}Sr , ^{141}Ce , and ^{144}Ce were measured from several types of castings and matrices in microspheres and bonded beds. Last fall, one or more experimental bonded beds leaked fission gas upon irradiation in the HFIR. Another bonded bed of each type was irradiated in the ORR for 8 hr and heated after 6 hr decay in vacuum to collect the fission gases $^{85\text{m}}\text{Kr}$, ^{135}Xe , and ^{133}Xe . This fission gas release was measured weekly by gamma spectrometry, and the tests showed that only one type of bonded bed had leaked.

We developed a method for determining ^{131}I on silver filters in the presence of a large amount of $^{110\text{m}}\text{Ag}$. The silver filter is dissolved in HNO_3 with iodine carrier present, perchloric acid and sodium vanadate are added, and the solution is heated in a distillation flask. A solution of AgNO_3 is used in the distillate tube to precipitate the distilled iodide. The solution is heated until all the dust particles are dissolved. After distillation, the residual solution in the

15. H. J. de Nordwall et al., "An Interim Report on Fission Product Release during Operation of the Second Peach Bottom Core," International Conference on Nuclear Fuel Performance, British Nuclear Energy Society, October 15–19, 1973.

16. W. S. Lyon et al., "Fission Product Release," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 36.

distillation flask is diluted, and the remaining AgI is reprecipitated. The distilled iodide is precipitated as AgI and combined with the AgI from the distillation flask. The AgI is metathesized in a basic solution with formaldehyde whereupon the silver metal precipitates. The solution is made acidic, and iodine is precipitated as AgI for radioactivity measurements.

ACTIVATION ANALYSIS DEVELOPMENT

Quality control methodology for determination of environmental base lines by absolute nondestructive NAA. We have continued our development work at the High Flux NAA Laboratory to apply nondestructive absolute multielement NAA to the determination of environmental base lines.¹⁷ Absolute NAA can be an extremely useful method for multitrace analysis, provided that very strict requirements are met. Until very recently, activation analysts had not favored this technique because of (1) lack of reliable nuclear data and of adequate data handling equipment, (2) reluctance to engage in very strict calibration and checking procedures to avoid systematic error. Absolute NAA began to flourish as the needs of (1) were met, and, naturally, this made necessary the reliability controls of (2).

J. F. Emery's absolute NAA program MONSTR — for the PDP-15 computer — has proved to be extremely useful and successful for the rapid and simple determination of over 20 elements. We also concluded that the optimum procedure for multielement analysis consists of two bombardments of the same sample: first, one for short-lived nuclides lasting 5 to 10 sec, immediately followed by a count, and by another 2 to 3 hr later. A second 5- to 10-min bombardment is followed by counts after 24 hr and one week for long-lived nuclides. The last count should be carried out overnight. This does not affect the simplicity of the method, since no attention is needed, and it uses the facility during normally off-duty hours.

On the other hand, three serious causes of error were observed: a shift of the Ge(Li) detector efficiency calibration, a bias in the bombardment timing, and a pronounced influence of sample shape in counting results.

Detector efficiency. We analyzed the NBS orchard leaves SRM-1571 and found that use of the old counting setup resulted in determinations with large inaccuracies (16 to 64%) with respect to the NBS

certified values. To correct this situation a new set of counting spacers was constructed — more rigid and mechanically stable than the former — and our system's efficiency for detector-sample distances of 3, 10, 27, and 39 cm was recalibrated with NBS, IAEA, and other calibrated standards.

The MONSTR program fits the efficiency curves with polynomial equations. With the new calibration we could reproduce our four curves — by using said polynomials — with errors smaller than the following: for 3 cm, 5.7%; 10 cm, 6.9%; 27 cm, 8.9%; 39 cm, 3.8%. The internal consistency of calibration among the four positions was checked by determining the absolute activity of two radioactive sources — ^{110m}Ag at 27 and 39 cm and ^{75}Se at 3, 10, and 27 cm. The independent determinations for ^{110m}Ag were within a standard deviation of 1.6%, while those for ^{75}Se were within 3.5%.

The NBS and IAEA sources originally used are being rerun to see if the certified absolute values can be reobtained. The NBS orchard leaves standard is also being analyzed. Results from these tests are now being processed.

Bombardment timing. We observed systematic errors introduced in short-irradiation timing, which we attributed to interfacing problems between a newly installed electronic timer and the electronic relays that govern the rabbit system. Timing errors as large as 13.6% were observed during repeated stopwatch determinations of bombarding time, that is, time elapsed between "rabbit in pile" light automatic turn on and off. Accuracy was worst for bombardments of 15 sec or less. This was serious because our HFIR flux measurements are based on 5- or 6-sec bombardments — where the error is greatest — and are used in each one of the samples' analytical calculations.

After correcting this malfunction, we determined the following quite acceptable accuracies in a similar stopwatch test: for a 5-sec bombardment, 1.2% (5 determinations); 10 sec, 1.0% (5); 60 sec, 0.13% (3); and 300 sec, 0.03% (2).

Sample shape. The drastic bombarding conditions at the HFIR cause damage to many organic samples. Filter papers and other samples used in environmental baseline analyses, for example, tend to crumble. Thus it is advantageous to weigh our samples into polyethylene inserts that are later sealed and placed in the regular rabbit capsules for irradiation. The samples are then counted inside the inserts.

As detector efficiency curves are usually determined by counting calibrated point sources, we studied differences in detector response between these sources and insert-size samples. For this, equal aliquots of ^{24}Na ,

17. W. S. Lyon et al., *Anal. Chem. Div. Annu. Progr. Rep.* Sept. 30, 1972, ORNL-4838, p. 37.

^{82}Br , and ^{75}Se solutions were measured on counting cards and in water-filled inserts. Counting of these sources gave ratios point-source/insert for 26 gamma rays, from 66.04 to 2754.10 keV. We found varying ratios whose maximum values were 1.16 for the 3-cm geometry, 1.15 for 10 cm, 1.12 for 27 cm, and 1.29 for 39 cm. These ratios are used to correct insert-counting results for each gamma-ray energy.

Obviously, it is important for sensitive multielement analysis that the inserts be significantly free from trace impurities. Table 4.1 shows weighted average concentrations for 15 elements, determined by absolute nondestructive NAA in two inserts at our high-flux facility. The last column lists results for Whatman No. 42 filter paper for the purpose of comparison. The latter were obtained during a somewhat less sensitive determination. Except for chromium and iron, the trace-element contents of the inserts are one or more orders of magnitude smaller than those of the filter paper; clearly, then, the interference of the insert in the counting is either small and easy to correct or negligible. The filter paper is representative of samples that are encountered in our base-line work. However, this comparison is established each time a new type of sample is subjected to bombardment.

For several years we have been plagued with the problem of rabbits hanging up in the pneumatic system at HFIR. Almost always these difficulties were associated with sticking valves. Consequently, the HFIR

pneumatic tube has been modified with ball valves in the off-gas manifold system. By changing the electrically controlled seat valves to ball valves, problems caused by sticking pistons and debris collecting on the valve seats were eliminated. Valve ECV-114 was removed from the system since it did not properly rotate the rabbit because of unbalanced air flow in the exit ports.

Simple approach to ^{252}Cf neutron activation analysis. Over the last few years, several laboratories — including our Division at ORNL¹⁸ — have been engaged in the evaluation and use of ^{252}Cf sources for neutron activation analysis (NAA) with different configurations and setups. To ascertain the analytical capabilities of these sources, the AEC — through its New Brunswick, New Jersey, laboratory — has provided synthetic standard samples to ^{252}Cf users for NAA; the results thus obtained will be compared and are expected to provide the AEC with a set of consistent and well-defined data on the utility of ^{252}Cf .

Two standard samples — a dilute HNO_3 solution and a powdered mixture of 70% SiO_2 , 20% Fe_2O_3 , and 10% $\text{Ca}(\text{NO}_3)_2$ — to be analyzed for Na, Al, V, Mn, Co, Cu, Zn, As, Se, Mo, Cd, Eu, and Hg were received. For this purpose, in collaboration with the Chemical Technology Division, a simple ^{252}Cf bombardment system was installed in accordance with recommendations made in a former paper.¹⁹ It consists of a 28-cm-diam, 28-cm-high high-density polyethylene cylinder, which is kept 4.3 m under water in a pool. Three ^{252}Cf sources (35.4, 25.3, and 19.5 mg each) are located 12.4 cm deep in holes drilled at 3.2 cm from the cylinder top center, 120° apart. The sample is placed in a fourth hole — at the very center of the cylinder and at approximately the same depth as the sources — simply by means of a long aluminum rod handled from the edge of the pool. The thermal neutron flux, determined with manganese and gold monitors, was $1.1 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$, with a thermal to resonance ratio of 15.4, at the sample bombardment site. The total flux gradient along the length of the irradiated sample was only 1.8%.

We used nondestructive comparative NAA; thus, neither pre- nor postirradiation treatments were made. For the analyses we weighed 0.3 to 0.4 g of the solid mix, or 0.5 ml of the solution was introduced, into 1-ml polyethylene inserts that were bombarded inside a 2-ml polyethylene container fixed at the tip of the long

Table 4.1. Multielement absolute nondestructive NAA of rabbit polyethylene insert

Element	Polyethylene insert		Whatman No. 42 (ppm)
	Parts per million	Approx error (%)	
Na	0.58	2.7	32.8
Al	1.54	1.9	Decayed
Cl	4.7	5.5	515
Sc	0.00008	28	
Cr	0.687	0.66	0.414
Mn	0.0165	5.6	0.291
Fe	3.2	7.2	
Co	0.0326	2.8	0.344
Zn	0.09	15	3.78
As	0.001	20	0.334
Br	0.0074	3.9	0.502
Ag	0.028	5.5	
Ba			3.02
Eu			0.055
W	0.0019	25	1.84
Au	0.000395	1.1	0.0023
Hg	0.0025	21	

18. W. S. Lyon et al., *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1970*, ORNL-4636, p. 29.

19. E. Ricci and T. H. Handley, "Activation Analysis with Californium-252," *Anal. Chem.* **42**, 378 (1970).

aluminum rod. The multielement comparator contained 0.2 to 33 mg of each of the corresponding elements. The samples were irradiated for periods of 18.7 to 72.0 hr to determine most of the elements, and then for 8 to 15 min to determine aluminum and vanadium. Decay times ranged from 5 min for determination of the latter elements, to 1 hr for manganese, to one day for the rest. Counting times were from 15 min for the short-lived products to 2 hr for the other radionuclides, with a Ge(Li) detector of 6.5% sensitivity – relative to a 7.62×7.62 cm NaI(Tl) crystal – and 2.1 keV resolution for the 1333-keV gamma of ^{60}Co .

We obtained satisfactory results – within the expected ranges – for all 13 elements, except aluminum and copper, in the solid mix. Aluminum, copper, vanadium, manganese, and zinc escaped detection in the solution, but the remaining eight elements were easily determined. The concentrations found ranged from 37 ppm of europium in both samples, to 2940 ppm of zinc in the mix, and to 4620 ppm of cadmium in the solution. Detection limits are defined as the amount of element that yields 900 dis min^{-1} at end of bombardment, calculated from the actual complex sample spectrum. These values ranged from $280 \mu\text{g}$ for selenium in the solution ($150 \mu\text{g}$ in the mix) to a low of 63 ng for manganese in the mix. In conclusion, we have demonstrated the feasibility of simple, reasonably sensitive multielement ^{252}Cf NAA. Results from other laboratories were not available for comparison at this writing.

Photon activation analysis with thick-target 110-MeV electron bremsstrahlung at the ORELA. The usefulness of our photon activation analysis (PAA) facility at the Oak Ridge Electron Linear Accelerator (ORELA) has been described in former reports.²⁰ ORELA's operation conditions are primarily designed for neutron production. They result in a 30- to 50-kW electron beam impinging on a massive (3.03 cm thick) tantalum target and, thus, are quite different from those characterizing most PAA experiments to date. On the basis of existing theoretical and experimental data, we studied the influence of our photon angular distribution on bombardment homogeneity and compared our sensitivities with those from other authors to put our system in perspective. Results of these studies follow, as well as a specific application of PAA to environmental samples.

Flux gradient during photon bombardment. Figure 4.2 shows the basic design and operation of our PAA

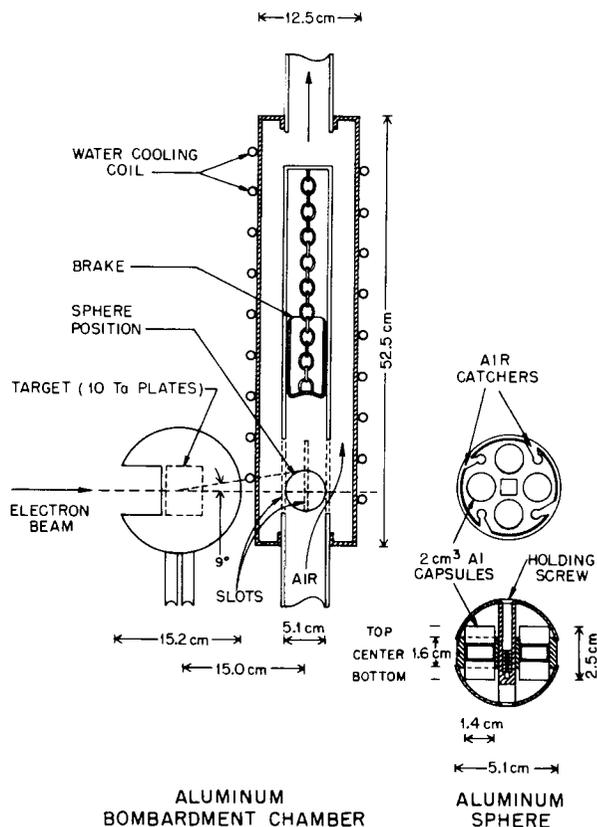


Figure 4.2. Photon bombardment chamber at the ORELA and sphere rabbit.

bombardment chamber in the target room of the ORELA. The rabbit is an aluminum sphere – carrying four sample capsules – which is supported, cooled, and induced to spin at the irradiation position by air upstream.

Theoretical and experimental information about photon intensity and angular distribution in our working conditions is scarce. Yet these data are important to understand photon activation inside ORELA's rabbit sphere. We have calculated the angular distribution of the energy radiated from the converter, without photon energy discrimination, by using the equation suggested by Koch and Motz.²¹ We also replotted analogous values calculated by the Monte Carlo method for 2- to 10-MeV photons produced in conditions that approach those at ORELA.²² Though incomplete, this informa-

21. H. W. Koch and J. W. Motz, "Bremsstrahlung Cross-Section Formulas and Related Data," *Rev. Mod. Phys.* **31**, 920 (1959).

22. R. G. Alsmiller and H. W. Moran, "Electron Photon Cascade Calculations and Neutron Yields from Electrons in Thick Targets," *Nucl. Instrum. Methods* **48**, 109 (1967).

20. W. S. Lyon et al., *Anal. Chem. Div. Annu. Progr. Rep.* Sept. 30, 1971, ORNL-4749, p. 35; *ibid.*, Sept. 30, 1972, ORNL-4838, p. 36.

tion is enough to indicate that at low angles ($<35^\circ$) with respect to the electron beam direction, one should expect a significant photon intensity angular gradient (25 to 74%) and also some photon energy spectrum variations.

As the sphere subtends a 9° angle (Fig. 4.2), we have run two experiments to assess this gradient quantitatively. First, sodium nitrate was bombarded in the center of all four capsules to produce ^{24}Na while, simultaneously, the same nuclide was induced in samples of magnesium and aluminum placed at the top and bottom (see figure). Two capsules carried magnesium at the top and aluminum at the bottom; in the other two the sample positions were inverted. The second experiment was analogous, but vanadium pentoxide was placed in the center of all four capsules this time, to test with a short-lived product (^{52}V); samples of tin were added at the top of two capsules and at the bottom of the other two. ^{52}V and ^{47}Sc from vanadium activation and ^{111}In from tin were counted.

As expected, we found that activation was uniform (only 1.2 to 5.5% difference) for samples in analogous positions inside the capsules, while divergences of 9.0 to 28.2% appeared between samples placed at the top and the bottom of the capsules. The conclusion is that, if samples and standards are irradiated simultaneously but in different capsules, care should be taken to place them in analogous positions inside the capsules. If more accuracy were required, there is enough room in each capsule to irradiate sample and standard together. This procedure proved satisfactory – in another experiment – even when a short-lived nuclide is produced in a short, purposely nonuniform bombardment.

Comparison of PAA sensitivities at ORELA with those from other laboratories. The systematic survey of PAA sensitivities at the ORELA has been completed. To put these data in perspective with values obtained in more conventional conditions – bremsstrahlung from 25- to 40-MeV electrons on thin targets – we plotted thin-target (platinum) bremsstrahlung spectra for electron energies from 19 to 160 MeV from Penfold and Leiss²³ and a thick-target (tantalum) spectrum for 100-MeV electrons from Alsmiller and Moran. All these spectra appear remarkably similar for photon energies below 20 to 25 MeV. Considering now that photon activation occurs significantly only in the region of the “giant resonance” (8 to 25 MeV from heavy to light elements), we conclude that PAA sensitivities at the ORELA should compare well with results from other workers for thin-target, low-energy electrons.

This was confirmed by taking ratios between our sensitivities and results of this type obtained both

experimentally²⁴ and by calculation²⁵ for thin-target bremsstrahlung from 25- and 30-MeV electrons. Average ratios (for C, N, O, F, Na, Mg, P, Ni, Cd, and Pb) are 0.5 and 1.4, respectively, for those two electron energies; ratios are analogous for both experimental and calculated data. Therefore, our sensitivities (average ratio 1.0) fall between those for the stated bombardment conditions, as we had expected from the above comparison of bremsstrahlung spectra.

PAA determination of fluorine in pine needles. We have determined fluorine in two samples of pine needles from the Oak Ridge Gaseous Diffusion Plant area. One set of pine needles (*Pinus virginiana*) was dry and clean, while the other had apparently been on the ground a long time and was partially decomposed.

The samples were bombarded at the ORELA facility in polyethylene inserts with Teflon comparators wrapped around them. A standard of calcium fluoride was also irradiated to check the fluorine concentration in the Teflon. Samples and standards, sandwiched in Lucite, were counted with a Ge(Li) detector, and the decay of the annihilation photopeak of ^{18}F (511 keV, 110 min) was analyzed by using Cummings' least-squares program. Results follow:

Sample	Water (%)	Ppm F (wet)	Error (%)
<i>P. virginiana</i>	10.2	1140	7.4
Ground needles	34.2	1120	6.8

The two samples show the same rather high contamination in their original state, despite their different water content. The Teflon standard proved unsatisfactory, because it becomes brittle under bombardment. The results of four fluorine analyses in different samples of Teflon by different methods – including the one mentioned above – yielded $69.8 \pm 2.9\%$ fluorine.

RADIOACTIVITY MEASUREMENTS FOR THE APOLLO PROGRAMS

Activation of NaI(Tl) detector aboard the Apollo 17 flight. During the Apollo 15 and 16 flights, NaI(Tl) spectrometers were employed to map from lunar orbit the chemical composition of the lunar surface by means

23. A. S. Penfold and J. E. Leiss, *Analysis of Photo Cross Sections*, University of Illinois report (May 1958).

24. C. Engelmann, *Contribution to the Study of Activation Analysis by Charged Particles and Photons*, French report CEA-R-4072 (1970).

25. G. J. Lutz, “Calculations of Sensitivities in Photon-Activation Analysis,” *Anal. Chem.* **41**, 424 (1969).

of emitted gamma radiation.²⁶ Spectra recorded during the transearth-coast phase of the flights gave interesting results on the shape of the cosmic photon spectrum²⁷ from 0.4 to 30 MeV. A major source of interference, especially in the cosmic photon spectrum, is the background due to proton-induced radioactivity in the NaI(Tl) detector itself. The detectors used on Apollos 15 and 16 were deployed from their respective service modules and so were consumed on reentry.

To determine the spectral distribution and intensity of the proton- and neutron-induced activity in the NaI(Tl) detectors, a detector crystal assembly similar to those of Apollos 15 and 16 was flown in the command module of the Apollo 17 spacecraft. The experiment was passive; that is, no measurements were made during flight.

After splashdown the NaI(Tl) detector, activated during flight, was measured in a low-background shield aboard the recovery ship. Direct measurements of induced activities were made by optically sealing a photomultiplier tube to the activated crystal. An identical crystal not flown aboard Apollo 17 was used as a control throughout the measurement program. Counting began about 1.5 hr after the command module reentered the earth's atmosphere. After about 30 hr of measurement, the detector was flown to Oak Ridge National Laboratory, where the direct measurements were continued to follow the decay of long-lived components. Indirect measurements were also made with the Ge(Li) and large scintillation gamma-ray spectrometers of low background at ORNL, following procedures very similar to those used for lunar samples.

Qualitative identification has been obtained for ²⁴Na, ¹²³I, ¹²⁴I, ¹²⁵I, ¹²⁶I, ¹²⁸I, and possibly ²²Na and ¹²⁷Xe. Our analysis so far indicates that the induced activity can be attributed mainly to species with half-lives of about half a day or longer. Dominant nuclear reactions are of the (*p,pxn*) type. Neutron interactions did not seem to play an important role in producing the induced radiation seen here during the Apollo 17 post-flight measurements. We are confident that after absolute calibration, quantitative concentra-

tions of these nuclides will be obtained, from which we can derive an adequate correction to the Apollo gamma-ray spectrometer flight data.

This is a cooperative program with a number of other investigators, primarily NASA personnel.

Radionuclide concentrations in Apollo 16 samples.

Twenty-six samples from Apollo 16 were analyzed by nondestructive gamma-ray spectrometry. The equipment and techniques of nondestructive gamma-ray spectrometry are essentially those we developed for earlier Apollo missions.^{28,29} Spectrum libraries for all sample studies were constructed from exact replicas which reproduce the electronic and bulk densities of the lunar samples.

Primordial radionuclide (potassium, thorium, uranium) contents of 11 soil samples from eight sampling stations are strikingly similar, with average concentrations of 940, 1.95, and 0.54 ppm for potassium, thorium, and uranium respectively. Sample 63501, <1 mm fines from a rake sample at station 13 (North Ray Crater ejecta blanket),³⁰ contains primordial radionuclide concentrations that are 22% less than the average values shown above. Subtle differences also exist for samples 64801, 65901, and 68501, fines from stations 4, 5, and 8 respectively. These stations probably include ejecta from South Ray Crater.³⁰ Samples 64801, 65901, and 68501 contain primordial radionuclide concentrations that are approximately 10% greater than the average values. To the extent that those results and sampling locations are representative of the ejecta blanket from the two ray craters, differences in chemical compositions of soil at depth may be inferred in comparison with the average regolith at the Descartes site.

Concentrations of cosmogenic radionuclides ²⁶Al and ²²Na in the 11 soil samples show some interesting variations. The general level of ²⁶Al concentrations in

28. G. D. O'Kelley, J. S. Eldridge, E. Schonfeld, and P. R. Bell, "Primordial Radionuclide Abundances, Solar Proton and Cosmic-Ray Effects and Ages of Apollo 11 Lunar Samples by Non-Destructive Gamma Ray Spectrometry," Apollo 11 Lunar Science Conf., *Geochim. Cosmochim. Acta*, Suppl. 1, vol. 2, p. 1407, Pergamon, 1970.

29. J. S. Eldridge, G. D. O'Kelley, K. J. Northcutt, and E. Schonfeld, "Non-Destructive Determination of Radionuclides in Lunar Samples Using a Large Low-Background Gamma-Ray Spectrometer and a Novel Application of Least-Squares Fitting," Proc. 1st International Summer School on Radionuclide Metrology, *Nucl. Instrum. Methods* (in press).

30. Apollo Lunar Geology Investigation Team, *Documentation and Environment of the Apollo 16 Samples: A Preliminary Report*, U.S. Geological Survey interagency report Astrogeology 51 (1972).

26. A. E. Metzger, J. I. Trombka, L. E. Peterson, R. C. Reedy, and J. R. Arnold, "Lunar Surface Radioactivity, Preliminary Results of the Apollo 15 and Apollo 16 Gamma-Ray Spectrometer Experiments," *Science* **179**, 800-803 (1973).

27. J. E. Trombka, A. E. Metzger, J. R. Arnold, J. L. Matteson, R. C. Reedy, and L. E. Peterson, "The Cosmic γ -Ray Spectrum between 0.3 and 27 MeV Measured on Apollo 15," NASA Goddard Space Flight Center report GSFC X-641-72-421 (November 1972).

Apollo 16 samples is considerably higher than for Apollo 15 samples. In many cases the concentrations of ^{26}Al are about twice as great in Apollo 16 soils. This difference is probably related to the high Al_2O_3 content of Apollo 16 soils ($\sim 26\%$, compared with $\sim 13\%$ for Apollo 15). Three soil samples show distinct differences from the general pattern for ^{26}Al concentrations. These soils are 64801, 65901, and 68501, the same rake soils from stations 4, 5, and 8 that showed slightly higher primordial radionuclide concentrations. These soils have ^{26}Al concentrations that are about half those of the majority of other soils in our suite; however, the ^{22}Na concentrations are not greatly different from those in the other soils. Three possibilities exist for explaining the low ^{26}Al values: (1) The Al_2O_3 content of these soils is greatly lower than that of the other soils; (2) sampling conditions for these soils were such that the average depth of sampling was considerably below the surface; and (3) the surface exposure time for these soils is of the order of 1,000,000 years due to "gardening" or ejection from depth. Condition 2 does not seem likely, since ^{22}Na values are not depressed, and another rake soil, 63501, has the highest ^{26}Al concentration in our suite. The other possibilities will be explored when other information concerning these samples is available.

Microbreccia 61195, from a 4-part radial sample collected at the rim of Plum Crater, shows a distinctly low concentration of ^{26}Al , which indicates a short exposure time on the lunar surface if the chemistry is normal. Field geology studies³⁰ indicate a lack of filleting and burial for this sample, suggesting a short exposure time. A companion sample, 61135, showed normal ^{26}Al content. Soil 61181,19, collected at the same site, shows a saturation value for ^{26}Al and typical primordial radioelement concentrations.

Sample 67937, from the House Rock area on the rim of North Ray Crater, is described as a piece of the "shatter cone." This sample shows ^{26}Al concentration at less than one-half the saturation value, with normal ^{22}Na concentrations. With proper chemical values, this sample may be used to calculate the age of ejection from depth or of the cratering event.

Three of our crystalline rock samples have been categorized as type II (igneous and high-grade metamorphic rocks), which have the greatest variations in chemical composition of the Apollo 16 samples. Sample 60315, a KREEP basalt type, contains the highest concentration of primordial radionuclides (~ 4 to 5 times as great as the soils and breccias). A comparison of potassium, thorium, and uranium concentrations for sample 60315 with those of sample 15382 (possibly

pure KREEP)³¹ shows that 60315 is a very important sample for future study of the mineral isochron.

Sample 62295, another type III rock, exhibits unique chemistry as shown by its K/U ratio of 768. This is the lowest value we have observed in any of our previous lunar samples from all other Apollo sites. Detailed chemical studies of this rock should be performed to explain its anomalous position in the K/U systematics of lunar samples. However, the Th/U ratio of 3.9 for rock 62295 is not greatly different from that found for other lunar rocks.

Breccia samples in our suite exhibit similar primordial radionuclide contents to soils and are similar to the low-potassium samples of Apollo 15 soils and breccias.

This is a cooperative project with G. D. O'Kelley, of the Chemistry Division.

Solar-flare-induced radionuclides and primordial radioelement concentrations in Apollo 17 rocks and fines — preliminary results. Solar and galactic cosmic rays produced neutron-deficient radionuclides in lunar samples returned from the previous five Apollo missions. Half-lives of the activation products measured in those samples ranged from a few days (^{52}Mn and ^{48}V) to three-quarters of a million years (^{26}Al).³² Due to differences in excitation functions for the production of these species, it has been possible to draw conclusions concerning relative magnitudes of previous solar flares, orientation of undocumented lunar samples, erosion rates of surface samples, exposure ages (in some cases, dating of cratering events), etc. From ^{60}Co determinations it has been possible to calculate the contemporary neutron flux on the lunar surface.³³

One of the largest flares of the 20th solar cycle occurred during August 4–7, 1972. The integrated flux of protons >10 MeV was 10 times greater than the flare of April 12–17, 1969. The August 1972 flare was also

31. E. Schonfeld, G. D. O'Kelley, J. S. Eldridge, and K. J. Northcutt, "K, U, and Th Concentrations in Rake Sample 15382 by Nondestructive Gamma-Ray Spectrometry," in *The Apollo 15 Samples*, ed. J. W. Chamberlain and C. Watkins, Lunar Science Institute, Houston, 1972.

32. G. D. O'Kelley, J. S. Eldridge, E. Schonfeld, and P. R. Bell, Proc. Apollo 11 Lunar Sci. Conf., "Primordial Radionuclide Abundances, Solar Proton and Cosmic-Ray Effects and Ages of Apollo 11 Lunar Samples by Non-Destructive Gamma Ray Spectrometry," *Geochim. Cosmochim. Acta*, Suppl. 1, vol. 2, p. 1407 (1970).

33. G. D. O'Kelley, J. S. Eldridge, E. Schonfeld, and P. R. Bell, Proc. Second Lunar Sci. Conf., "Cosmogenic Radionuclide Concentrations and Exposure Ages of Lunar Samples from Apollo 12," *Geochim. Cosmochim. Acta*, Suppl. 2, vol. 2, p. 1747 (1971).

Table 4.2. Radionuclide concentrations in Apollo 17 rocks and soils

Decay corrected to 1800 EST, December 14, 1972.

Radionuclide	Rocks			Soils			
	70135	76295	79155	76501	78501	79221	79261
K, ppm	460 ± 100	2300 ± 400	410 ± 40	900 ± 50	770 ± 40	700 ± 40	700 ± 40
Th, ppm	0.32 ± 0.06	5.6 ± 0.11	0.31 ± 0.06	1.39 ± 0.14	1.10 ± 0.11	1.12 ± 0.06	1.08 ± 0.05
U, ppm	0.11 ± 0.02	1.4 ± 0.3	0.12 ± 0.03	0.38 ± 0.04	0.28 ± 0.03	0.36 ± 0.03	0.31 ± 0.02
²⁶ Al, dis min ⁻¹ kg ⁻¹	37 ± 8	70 ± 14	70 ± 10	90 ± 9	90 ± 9	130 ± 7	45 ± 4
²² Na, dis min ⁻¹ kg ⁻¹	45 ± 9	60 ± 12	77 ± 10	90 ± 9	105 ± 10	165 ± 10	43 ± 4
⁵⁴ Mn, dis min ⁻¹ kg ⁻¹	42 ± 10		110 ± 20	60 ± 10	96 ± 10	215 ± 20	44 ± 6
⁵⁶ Co, dis min ⁻¹ kg ⁻¹	59 ± 20	40 ± 25	155 ± 30	120 ± 12	150 ± 10	470 ± 25	26 ± 10
⁴⁶ Sc, dis min ⁻¹ kg ⁻¹	30 ± 10	9 ± 8	62 ± 10	18 ± 4	30 ± 6	65 ± 7	15 ± 4
⁴⁸ V, dis min ⁻¹ kg ⁻¹	10 ± 5			15 ± 10	10 ± 8	30 ± 20	

distinctive in having a greater abundance (40 times) of >60 MeV protons than the April 1969 flare.³⁴

The great intensity and character of the August 1972 flare leads one to predict that solar-proton-induced radionuclides would be ubiquitous in the Apollo 17 samples, especially for radionuclides with half-lives of a few months to a few years. Indeed, this has been the case for three rocks and four soil samples we have measured by nondestructive gamma-ray spectrometry.³⁵ Table 4.2 lists the radionuclide concentrations (preliminary values) measured in this early suite of Taurus-Littrow samples.

Sample 70135 was taken from the "geophone rock" at the ALSEP station and described as a gabbro from a very large, partly buried boulder.³⁶ From the values of ²⁶Al and ²²Na determined for this sample, it is probable that the "geophone rock" and the accompanying material partially burying it have been on the surface less than a million years. Soils 76501 and 78501 are <1 mm fines sieved from 1-kg samples from stations 6 and 8. To the extent that these samples are representative of the regolith from North Massif and the Sculptured Hills, these regions are quite similar in primordial radioelement concentrations. However, sample 76501 has thorium and uranium concentrations

only 60% of those of the shadow soil taken from under the boulder from which 76295 was chipped.³⁷ Radionuclide abundances shown for samples 79221 and 79261 reflect differences due to sampling at depth as well as possible chemical differences as seen by differences in color of the two soils. Sample 79221 is described as "normal" dark gray soil taken from within 2 cm of the surface of a trench at station 9. Sample 79261 is described as a light gray soil taken >7 cm below the surface.³⁶

This is a cooperative project with G. D. O'Kelley, of the Chemistry Division.

34. J. H. King, attachment to: Study of mutual consistency of IMP 4 solar proton data. NSSDC 72-14, 1972.

35. J. S. Eldridge, G. D. O'Kelley, K. J. Northcutt, and E. Schonfeld, Proc. 1st International Summer School on Radionuclide Metrology, "Non-Destructive Determination of Radionuclides in Lunar Samples Using a Large Low-Background Gamma-Ray Spectrometer and a Novel Application of Least-Squares Fitting," *Nucl. Instrum. Methods* (in press).

36. Apollo Lunar Geology Investigation Team, *Preliminary Report on the Geology and Field Petrology at the Apollo 17 Landing Site*, U.S. Geological Survey Interagency report Astrogeology 69 (1972).

37. J. E. Keith and R. S. Clark, private communication - unpublished data, 1973.

5. Mass and Emission Spectrometry

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MASS SPECTROMETRY DEVELOPMENT

Computer-operated densitometer. An interactive, computer-operated data acquisition and processing system to read photographic plates produced by a spark-source mass spectrometer is under development. The system uses an 8K PDP-8/E computer that has a 10-bit analog-to-digital converter (ADC), a real-time clock, a TD8-E Dectape (magnetic tape) unit, and an ASR-33 teletypewriter (TTY) for input/output.

We have reassembled the subroutine for operation of the magnetic tape as part of the core memory to be compatible with the FOCAL interpretive compiler. A program was written to handle the transfers between core memory and the magnetic tape. Programs are stored on Dectape. Transfers of any desired program from Dectape to core memory are operator-controlled. We have found it advantageous in program development to store several compilers on Dectape. Thus we can use

1. Instrumentation and Advanced Methodology Group.
2. On leave of absence to I.A.E.A., Vienna, Austria.
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more variables, larger tests, and several different data acquisition and data handling functions.

An emulsion calibration program takes percent T (transmittance) data for two isotopes and computes a relative intensity data table using the Churchill two-line method. A second program does isotope dilution calculations for 11 different elements, Cd, Zn, Hg, Pb, Cu, W, Cr, Fe, Se, Zr, and U. These basic programs were translated from IBM 1130 FORTRAN into FOCAL for operation on the PDP-8/E.

Before making a measurement on a spectral line, the dark current is determined, and the range is set from 0 to 100% T . After the densitometer scans the line, the data points are stored in the memory. Signal enhancement and 60-Hz noise rejection are also achieved by a signal-averaging data handling procedure.

Data analysis is accomplished by ascertaining the minimum transmittance and base-line information. Relative intensity values are calculated for each of the data points using the emulsion calibration curve. Peak areas can be calculated either by simple numerical integration or by the application of Simpson's rule. The conversion time can be reduced by use of a modified Hull equation:

$$RI = K \left(\frac{100 - T}{T} \right) R^{-1},$$

where

RI = relative intensity,

T = percent transmittance,

R = empirical value,

K = constant.

The work load on the IBM 1130 has been lightened, and the card punching step for these programs has been eliminated.

Measurements of nitrogen and nitrogen isotopic ratios using reductive pyrolysis coupled with mass spectrom-

etry. An analytical system for measuring total nitrogen and its isotopic abundance in a variety of environmental samples has been developed. A reductive pyrolysis system and a directional-focusing 6-in. gas mass spectrometer were combined into the analytical system. In the reductive part of the system, nitrogen species are converted to ammonia with an atmosphere of hydrogen in the presence of a heated nickel catalyst. Five percent of the gas stream is split away for measuring total nitrogen by a conductivity detector. The ammonia is removed from the gas stream using a cold finger reaction vessel.

The hydrogen-free ammonia is decomposed thermally to nitrogen and hydrogen at 1000°C using a hot rhenium filament. The nitrogen produced from the decomposition is used for measuring the abundance of masses 28 and 29 by mass spectrometry. From this ratio, the ^{15}N atom fraction is calculated.

Standard samples of nitrogen, ammonia, orchard leaves, and urea have been successfully analyzed to determine isotopic compositions. Samples containing as little as 20 μg of total nitrogen could be analyzed by this system. By the addition of multireaction vessels, three samples may be completed per hour. A paper⁴ describing this work has been submitted for publication.

Analysis of entrapped gases in salt crystals. One of the more interesting and difficult analyses that we are called upon to perform in the Mass Spectrometry Group is the determination of entrapped gases in a solid matrix. A particular case in point is that of gases in irradiated salt crystals. A customary attack on this problem is to dissolve the crystal in degassed distilled water, pump off the residual gases, and determine them spectrometrically. The obvious disadvantage of this technique is that it is applicable only to those materials that are soluble in water. In addition, the completeness of the degassing process is never known with certainty, so the validity of the results remains in some doubt.

In an attempt to improve the reliability of the analysis, a simple device has been designed to crush the sample and thereby release the gases entrapped in the salt crystal. This device was tested on crystals of sodium chloride which were baked under high vacuum to remove adsorbed surface gases and then crushed, after which the released gases were directed into the mass spectrometer. A particle-size examination of the

crushed salt showed that 60% of the particles were $<2\text{ mm}^3$ and 40% were between 2 and 3 mm^3 ; the largest particle was 3 mm^3 .

The analyses of the gases from unirradiated and irradiated NaCl salt crystals are summarized in Table 5.1. This method is an obvious improvement over the dissolution technique and provides additional information on entrained gases in crystals. Further refinements are under way to ensure complete release of gases and to ascertain the extent, if any, of contamination from surface gases adsorbed on the crusher.

Strontium isotopic analysis. Collaborative research with a geochemist, Dr. Lois M. Jones, at the University of Georgia, has resulted in several publications during this period. Dr. Jones is interested in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and has no mass spectrometer available. We have found that by using the $^{86}\text{Sr}/^{88}\text{Sr}$ as an internal standard we can make some very precise measurements on our two-stage machines. This research is primarily aimed at weathering experiments and geochronology using the rubidium-strontium method.

Absolute abundance of krypton in the earth's atmosphere. Three additional measurements of the natural abundance of elemental krypton in the earth's atmosphere were made during this period. These results, along with the seven that were reported in last year's report, were used to give a final result of 1.1074 ± 0.0083 ppm by volume. A manuscript⁵ describing this work has been accepted for publication.

Age dating of speleothems. Procedures for uranium-thorium and uranium disequilibrium dating of speleothems were developed, making use of alpha spectrometry for thorium determinations and mass spectrometry for uranium determinations. Thorium was removed from calcite in a three-step process using an anion exchange separation followed by LaF_3 precipitation

5. J. R. Walton, A. E. Cameron, R. L. Walker, and T. L. Hebble, "Determination of the Abundance of Krypton in the Earth's Atmosphere by Isotope Dilution Mass Spectrometry," *Int. J. Mass Spectrom. Ion Phys.*, in press.

Table 5.1. Gas analyses of unirradiated and irradiated salt

Gas	Unirradiated NaCl (mole %)	Irradiated (mole %)
H_2	0	54.76
H_2O	93.78	30.08
$\text{N}_2 + \text{CO}$	6.23	10.90
O_2	0	4.27

4. J. A. Carter, D. R. Matthews, R. L. Walker, and J. R. Walton, "Measurement of Nitrogen and Nitrogen Isotopic Ratios Using Reduction Pyrolysis Coupled With Mass Spectrometry," *Anal. Lett.*, in press.

and thenoyltrifluoroacetone extraction. Uranium was separated from the calcite by extraction with tributyl phosphate.

The stalagmites tested were generally beyond the age range of the uranium-thorium age-dating method, and, as a result, $^{234}\text{U}/^{238}\text{U}$ ratios provided the most useful dating technique. Because stalagmites are enriched in ^{234}U beyond the equilibrium value at the time of deposition, they are potentially datable by measuring their progress toward equilibrium from their original state of ^{234}U enrichment, which can be inferred from the $^{234}\text{U}/^{238}\text{U}$ ratio of the present-day cave waters. Stalagmites up to 1,500,000 years old are potentially datable using this method.⁶ A paper describing this work has been submitted to *Geochimica et Cosmochimica Acta*.

ENVIRONMENTAL SPECTROMETRY

Our Mass and Emission Spectrometry Group has performed analytical developmental studies as part of a matrix evaluation for various NSF-funded RANN projects and for EPA during the past year. Additionally, we have carried out quality control and referee analyses for these groups, including the Purdue University Program on the Environmental Aspects of Cadmium.

ORNL-Purdue environmental studies. Many elements, including Cd, Pb, Cu, Zn, and Hg, may be determined by excitation with a radio-frequency spark followed by spectrometric measurement of the resulting ions according to their mass-to-charge ratio. This technique is applicable to virtually any matrix but gives only semiquantitative results with many "environmental" samples. Therefore, to obtain quantitative Cd, Zn, and Pb results for the Purdue samples, we used isotope dilution techniques employing spark-source mass spectrometry and the stable ^{106}Cd , ^{204}Pb , and ^{67}Zn isotopes as enriched spikes. The success of the isotope dilution technique depends to a great extent on establishing equilibrium between the enriched spikes and "normal" Cd, Pb, and Zn in the sample. After the spikes are added to a sample, isotopic equilibrium is established and the organic matter is destroyed by acid digestion with purified HNO_3 and HClO_4 acids. Once isotopic equilibrium is reached, any technique may be used that permits one to transfer about 10 ng of each element of interest from the solution to the surface of a suitable substrate such as a pair of graphite electrodes.

6. Glenn Thompson, "Uranium Series Dating of Stalagmites from Blanchard Springs Caverns, Stone County, Arkansas," M.S. thesis, Memphis State University, May 1973.

Solvent extraction may be employed to concentrate the Cd, Pb, and Zn prior to transfer to the substrate, if this is necessary. Extraction with dithizone or APDC (ammonium pyrrolidine dithiocarbamate) is suitable. High extraction efficiencies are not required since the analysis at this point depends only on establishing a ratio between two isotopes, for example, ^{114}Cd and ^{106}Cd . When it has been necessary to use an extraction procedure, the APDC method is usually the method of choice because APDC extractions are carried out at lower pH values. The accuracy is limited to about 5% because of the characteristics of the Ilford Q-2 emulsion used as the detector. The real advantage of the IDSSMS approach is that it is virtually free of matrix effects. The detection limit for the method can be in the ppb range, depending somewhat on the sample size, the isotopic distribution of the element of interest, and the matrix.

As an example of a typical sample spiked with enriched ^{106}Cd , Fig. 5.1 shows a typical spectrum of cadmium. The solid line at mass position 106 represents the ^{106}Cd spike, and the dashed lines represent the relative abundances for the other cadmium isotopes. The dashed line in juxtaposition at m/e 106 is the relative abundance of ^{106}Cd as it occurs in nature.

A computer program for an IBM 1130 computer is used for data reduction. The program is flexible in that the spike size, sample size, spike composition, and percent transmittance can all be variables.

Atomic absorption spectrometry experiments were carried out to see if determinations of Cd, Zn, and/or Pb could be made in HNO_3 extracts of Purdue soils with little or no chemical treatment of the extract. It was found that accurate results could be obtained for zinc at the levels encountered ($>100 \mu\text{g/g}$) but that high results were obtained for lead and cadmium. This was due to the fact that continuous absorption by major components, within the band pass of the monochromator, was substantial compared with the absorption due to the lead or cadmium.

In the APDC extraction of Cd, Zn, and Pb from soil extracts, high concentrations of iron interfere. Iron forms an insoluble precipitate with APDC and thus tends to overload the system when only the Cd, Zn, and Pb are desired. Iron can be removed by a preliminary extraction, but this extra step can be avoided by making two changes in the procedure: (1) Heptanone-2 (methyl *n*-amyl ketone) is used as the extractant instead of methyl isobutyl ketone. The Fe-APDC reaction product is quite soluble in heptanone-2, making the extraction easier to handle. (This solvent is also a much more efficient extractant for the Cd, Zn, and Pb

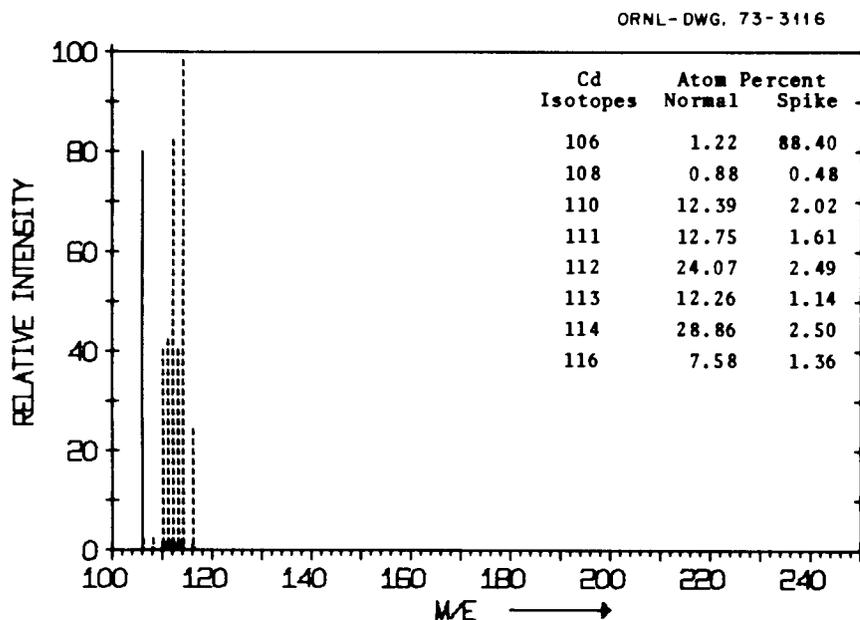


Fig. 5.1. SSMS spectrum of cadmium spiked with enriched ^{106}Cd .

compounds, permitting one-step extractions in most cases.) (2) The Cd, Zn, and Pb are stripped from the organic with 6 N HCl containing ~5% HNO₃. This oxidizes the Fe²⁺ to Fe³⁺, which is retained in the organic layer.

It was found that the sensitivity of analysis could be considerably improved by using heptanone-2 as noted. This improvement results from the high aqueous:organic volume ratios which could be used and from the fact that direct aspiration of the heptanone-2 gave a three- to fourfold improvement in the sensitivity of atomic absorption determinations.

During the past year, some 260 samples were analyzed with over 2000 results reported. Sample types included soil, litter, vegetation, steel plant samples, coal, coal distillates in methanolic KOH, coke, limestone, dolomite, fuel oil, ores, sludges, plating bath solutions, etc. Many of these diverse samples required development and special handling in order to obtain meaningful results.

Thermal emission isotope dilution mass spectrometry. For the quantitative measurement of lead and uranium in coal and fly ash and lead in gasoline, we use a three-stage thermal emission mass spectrometer (TEMS) that was constructed at ORNL. The addition of an electrostatic third stage increased the abundance sensitivity to 10⁸.

Ions are detected by a secondary electron multiplier behind the receiver slit. The pulses from the multiplier

are accumulated in a 400-channel analyzer used in the time-base mode. This arrangement allows the maximum sensitivity with respect to sample size. Mass measurements are made by sweeping the accelerating voltage across the regions of interest, 233 through 238 for uranium and 204 through 208 for lead. The determination of uranium and lead in coal and fly ash and lead in gasoline, both quantitatively and isotopically, is done by isotope dilution with enriched spikes of ²³³U and ²⁰⁴Pb.

Lead analyses are made utilizing the gel technique described by Cameron et al.⁷ Lead ions are thermally produced at rhenium filament temperatures ranging between 1100 and 1300°C, depending somewhat on the sample size. A loading of 10 ng provides enough sample to allow an analysis consisting of ten runs of 200 sweeps across the masses of interest. Uranium ions are thermally produced at rhenium filament temperatures ranging from 1700 to 1850°C. Small quantities (10 to 100 ng) of uranium in the form of UO₂(NO₃)₂ produce sufficient ions for a precise analysis. A benzene reduction procedure has been developed at ORNL which produces only metal ion signals. This procedure produces a very clean uranium spectrum and increases the sensitivity of the measurement. As in the analysis of

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

lead, an analysis consists of at least 200 sweeps across the masses of interest.

Preparation of coal and fly ash for TEMS isotope dilution analysis. Separate aliquots of coal and fly ash are weighed out and spiked with ^{204}Pb and ^{233}U respectively. The chemical treatment and extraction of lead and uranium from coal and fly ash are identical except that coal is ashed at 450°C before chemical treatment. The samples are dissolved with a mixture of HF, HNO_3 , and HClO_4 in Teflon beakers. The lead is separated by dithizone extraction, evaporated to dryness, and redissolved in dilute HNO_3 , and 10 ng is loaded on filaments with silica gel for mass analysis. Uranium is separated, after dissolving the sample as described for lead, by extraction with TBP from 4 M HNO_3 . After the organic phase is scrubbed with 4 M HNO_3 , the uranium is back extracted into distilled water and evaporated to dryness. The uranium is loaded on a rhenium filament for analysis after dissolving the purified sample in a small volume of 0.05 M HNO_3 .

Preparation of gasoline for TEMS isotope dilution analysis. Aliquots of gasoline are spiked with ^{204}Pb and treated by either a wet chemical method or the bromine oxidation method. The wet chemical procedure consisted of refluxing first with HNO_3 until the initial reaction subsided; then HClO_4 was added and the reflux continued until the reaction was complete. The resulting solution containing the inorganic lead was finally evaporated to near dryness, adjusted to a suitable lead concentration with dilute HNO_3 , and loaded onto rhenium filaments.

In the bromine method, Br_2 in CCl_4 was added to the gasoline in a test tube. Complete conversion to lead bromide was assured by heating. The resulting lead bromide precipitate was dissolved with dilute ~ 1 M HNO_3 . The mixture was centrifuged and the organic layer discarded; the aqueous solution was adjusted for mass spectrometry analysis. Either of the procedures works satisfactorily, but the bromine method is much easier and faster and has less possibility for contamination.

Trace metals in gasoline by SSMS. Work has continued during this past year on improving the spark-source technique for analyzing the priority I and priority II elements. The trace elements from these lists that can be analyzed by SSMS include: Be, Cd, As, V, Mn, Ni, Sb, Cr, Zn, Cu, Pb, Se, B, Li, Ag, Sn, Fe, Sr, Na, K, Ca, Si, and Mg. The general coverage for all of these elements is by a procedure employing an addition of normal erbium. By the use of erbium and the corresponding sensitivity values that can be placed in the computer program, quantitative results are possible.

The preparation procedure that offered the greatest utility involved an oxidation step with bromine after the addition of the erbium spike, followed by freeze-drying to remove the liquid, and finally drying at 62°C in a vacuum oven until little or no gasoline odor could be detected. A sample of 5 ml of gasoline in a plastic beaker treated with 1 ml of 1:3 Br_2 in CCl_4 will produce sufficient carbonaceous material so that the residue can be mixed with pressing graphite. The homogenized mixture of sample and pressing graphite is then loaded into AEI polyethylene slugs for pressing isostatically at 25,000 psi for 1 min. The two electrodes, having a nominal size of 1 cm by 0.15 cm, are used to produce a graded set of spectra on Ilford O-2 photoplates. A microdensitometer is used to measure the intensities of the lines produced by the ions of the major isotope of each element desired and the line produced by one of the isotopes of erbium. These transmittancy data are then processed through the IBM 1130 computer.

Cadmium in coal by isotope dilution spark-source mass spectrometry. Cadmium in coal may be determined directly by SSMS; however, the cadmium results are usually biased because of molecular ion interferences. Corrections could be made, but the results at best are only of a semiquantitative nature. To circumvent this serious drawback, coal samples are analyzed for cadmium by the isotope dilution technique. The highly enriched stable isotope ^{106}Cd is used as the spike.

Samples of coal are low-temperature ashed to remove the bulk of the organic matter. The coals are spiked with ^{106}Cd prior to the ashing step by evaporating the small spike solution over the surface of the coal. The ashing step starts with a cool furnace at about 50°C , and the temperature is increased periodically in steps of 50° until a final temperature of 450°C is reached and maintained for 1 to 2 hr. The ash is dissolved in the platinum dish with a mixture of HNO_3 , HF, and HClO_4 . The dissolution should be complete to ensure equilibrium of the ^{106}Cd spike and the naturally occurring cadmium in the coal and/or fly ash. The solution is then treated with about 2 g of citric acid and the acidity adjusted with NaOH (solid) and finally with aqueous ammonia to pH 8. The equilibrated cadmium is concentrated by dithizone extraction, and about 10 ng is loaded onto graphite electrodes for spark-source mass spectrometry.

The results for a series of 20 coals analyzed by the isotope dilution technique had a spread of values from 0.1 to over 5 ppm cadmium. Generally there is some correlation of the cadmium concentration to the ash

content, that is, when the ash content of coal is high the cadmium concentration is high. Our cadmium results on the NBS-EPA round-robin coal and fly-ash samples were in good agreement with the NBS values.

Mass spectrometry studies on the Allen Steam Plant samples. In the Allen Steam Plant study, the multi-element capabilities of SSMS were used extensively. A total of 51 elements were analyzed on a semiquantitative basis. These results, along with a number of isotope dilution results, are summarized in the progress report,⁸ however, in general, the SSMS results, on the average for trace metals and for major elements, show an imbalance of -14% and -32%, respectively, for the Steam Plant. By isotope dilution mass spectrometry, the imbalance for such elements as Pb, Zn, and Cd was less than -10%.

Isotopic lead ratios in environmental samples from the University of Illinois. It is well established that the isotopic abundance of lead is variable in nature. Based on this fact, the ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ have been measured on several samples for H. Laitinen. The variation of lead ratios was determined on soil samples taken from depths of 1 to 30 in. and on rodents, vegetation, and gasoline. The values we obtained on the soil samples in particular have been used as secondary standards for ion microprobe lead isotopic ratio measurements.

ORGANIC MASS SPECTROMETRY

The single-stage mass spectrometer has been used to analyze approximately 900 samples during the past year. Most of the samples were of a biological nature and originated in the Body Fluids Analysis Program of the Chemical Technology Division and in various programs of the Biology Division. Considerable effort was also devoted to analysis of a series of nitrosamines in cooperation with W. Lijinsky of the Biology Division. In addition, the number of samples received from production and development facilities has increased because of growing emphasis on more thorough knowledge of exposure of personnel to possibly hazardous chemicals used in plant processes. Rather interesting results have also been obtained in GC-MS studies of organomercury, -arsenic, and -vanadium compounds of interest to ecological problems.

The single-stage instrument has been interfaced to the IBM 1130 computer to transfer the spectrum from the

spectrometer to the computer during the time the data are being generated. The interface alternately samples the output from the Hall probe gaussmeter and the multiplier detecting the ion current at selectable rates up to 5000 times per second. A mass calibration curve is generated by the computer using a least-squares fit from a spectrum of the standard perfluorokerosene mixture. This calibration curve is stable to an accuracy of ± 0.2 amu over the mass range of 20 to 505 for a period of at least 15 min. The calibration curve is then used to determine masses of the peaks in the sample spectrum, and the reduced data are available for further processing, either printed out or plotted as a bar graph. The computer program is in need of further modification to handle problems of base-line shift and metastable peaks.

Extensive modifications have been made to the high-vacuum system of the high-resolution mass spectrometer to allow interfacing a Varian model 1400 gas chromatograph. The titanium-sublimation sputter ion pump used to evacuate the ion source region would not handle the gas load and has been replaced by a 1200-liter/sec oil diffusion pump with a line-of-sight water-cooled baffle. A 4-in. gate valve is used to isolate the diffusion pump from the ion source when access to this region is required. The availability of a gas chromatograph inlet will allow us to analyze classes of compounds that we previously could not handle. Many compounds of biological interest (carbohydrates, glucuronides, etc.) are too thermally sensitive to be run via the direct insertion probe. Many of these compounds can now be derivatized and admitted to the instrument through the gas chromatograph. In addition, as the Laboratory becomes more involved in energy and pollution programs, the gas chromatographic inlet will be valuable in identification of components in mixtures. These can be separated on the gas chromatograph, and the peak of interest can then be admitted to the mass spectrometer for mass analysis.

The data acquisition and reduction programming system⁹ has been further improved as the need dictated. The next major change anticipated is going to be hardware thresholding of the incoming data as opposed to software thresholding. This will allow higher data rates to be maintained and is of importance in the analysis of gas chromatograph samples where the sample lifetime is relatively short.

8. N. E. Bolton et al., *Trace Elements Measurements at the Coal-Fired Allen Steam Plant, Progress Report, June 1971-January 1973*, ORNL-NSF-EP-43 (March 1973).

9. W. H. Christie, D. H. Smith, and H. S. McKown, "Data Acquisition and Processing for High-Resolution Mass Spectrometry Using a Small Nondedicated Computer," *Chem. Instrum.*, in press.

During the past year, 150 samples were submitted for high-resolution spectrometry. Mass spectra were first obtained on the single-stage instrument to determine necessary instrumental conditions and peaks of interest in the spectrum. As is often the case, low-resolution data may be sufficient to identify a sample, especially if spectra of known compounds are available for comparison. However, with many of the samples of biological origin, compounds are often new identifications, and high-resolution data, including possible empirical formulas, are of major importance in interpretation of the mass spectra. The high-resolution instrument has been of great value in several instances when studying reaction mechanisms, especially when ambiguity existed concerning identification of fragments (e.g., whether a loss of 17 amu was due to elimination of NH_3 or OH). A study of rearrangements occurring in a series of phenols (as trimethylsilyl derivatives), in cooperation with D. H. Ohrt and J. A. Mrochek of the Chemical Technology Division, required this capability.

Interesting and unexpected results were obtained in studying with W. Lijinsky the fragmentation of nitrosamines under electron bombardment in the mass spectrometer.^{10,11} The spectra of N-nitrosamides, such as nitrosoethylurea, were quite different from the N-nitrosamines. One outstanding difference was the presence of an m/e 44 peak in the nitrosamide spectra. Generally, in organic mass spectra, an m/e 44 peak is expected to be due to CO_2 formed by rearrangement or decomposition of organic material. However, in these cases, the ion proved to be CH_2NO , an expected product. This elimination requires rather unusual rearrangement of the amide, and, to date, no satisfactory explanation of its formation has been determined. A paper giving detailed information on the mass spectra of the nitroso compounds and their rearrangements is in preparation.

An interesting short project was successfully completed during the year for the Viking mission to Mars. One of the Viking landing units will include a gas chromatograph-mass spectrometer for analysis of organics in soil samples. Samples are to be pyrolyzed in a hydrogen stream prior to the GC unit, and effluent GC peaks are to be passed through a silver-palladium separator for removal of the hydrogen and thence into

the mass spectrometer. During testing with standard mixtures of possible organic products, it was noted that several compounds (notably phenylacetonitrile) were not detected by the mass spectrometer. It was suspected that the "electroless" nickel deposit used in valve manufacture could be causing the problem. Subsequent work using the single-stage GC-MS combined instrument showed that the flash precoating of pure nickel rather than the "electroless" nickel was responsible for the loss of material. Thicker coatings of "electroless" nickel, heavy gold plating, or change of construction material alleviated the problem. The GC-MS work showed that phenylacetonitrile in nanogram quantities was adsorbed on nickel surfaces at temperatures below 200°C in a hydrogen stream. Heating the nickel to $>250^\circ\text{C}$ resulted in desorption of the material, and the mass spectra proved it to be desorbed as ethylbenzene. Since ethylbenzene is not adsorbed by nickel surfaces and since phenylacetonitrile is not adsorbed from helium carrier streams, it is felt that the nitrile is adsorbed as a partially reduced material, perhaps by complexing with the nickel surface.

SPECTROMETRY SERVICES

Mass Spectrometry Service Laboratory. This laboratory performs the mass spectrometric measurements on a wide variety of elements and gases. More than 17,250 results were reported — a decrease of about 7% from the previous year. During the past year, isotopic analyses were made on more than 50 metallic and nonmetallic elements. Most of the isotopic analyses are for programs in the Isotopes and Chemical Technology Divisions. In the gas laboratory, gas compositions are determined on many inorganic and a few simple organic gases. Certification analyses for welding gases are the major single source of gas samples.

Actinides. Nearly 5700 results were reported by the TRU Spectrometry Laboratory last year, the same number as in the previous year. The Chemical Technology Division accounted for about 61% of the analyses. These included samples in the transuranium programs, in the support of the LWBR program, and in the spectrometry of alpha-active materials program. Samples of the actinides, uranium through californium, are analyzed routinely. Occasionally, requests for isotopic determinations of other radioactive samples are received. We recently analyzed a sample of ^{151}Sm for the Isotopes Division. Using the triple-spike methods, we continued to make quantitative analyses for ^{148}Nd , uranium, and plutonium in fuel rods for use in burnup calculations. We continued to participate in the Euro-

10. W. Lijinsky, W. H. Christie, and W. T. Rainey, *Mass Spectra of N-Nitroso Compounds*, ORNL-TM-4359 (in press).

11. W. Lijinsky, W. T. Rainey, and W. H. Christie, "Identification of N-Nitroso Compounds by Mass Spectrometry," Twenty-First Annual Conf. on Mass Spectrometry and Allied Topics, May 20-25, 1973, San Francisco, Calif.

pean "Safeguards" program and analyzed the samples from the MOL IV experiment. We analyzed about 60 uranium and plutonium fuel rods for the Los Alamos Scientific Laboratory.

Stable isotopes. Isotopic analyses were made on 38 different stable elements in the past year. The vast majority of this work is for the Isotopes Division in their calutron separations program. Preliminary samples are received from them prior to being composited into lots. After the lot is mixed and before it is placed into inventory, a final result is obtained. When material is returned from customers, it is analyzed before being put back into inventory. Among the unusual samples analyzed were a ^{28}Si sample greater than 99.99% purity and a ^{10}Be sample of about 57% purity.

Gases. A wide variety of gas samples were analyzed. The number of cylinders certified has continued to drop as more batching of cylinders is done. This past year we analyzed about 225 cylinders of argon, helium, and nitrogen. We made isotopic analyses on krypton, xenon, and hydrogen. Several tritium samples were analyzed for purity and for isotopic content for the Isotopes Division. We also made a boron isotopic analysis on a sample of $\text{BF}_3\text{-CaF}_2$. During the year we added a micromanometer to the instrument to make standardization easier and more accurate. We have continued to provide gas analysis service to the Y-12 mass spectrometry laboratory when needed.

Spectrochemistry and spark-source mass spectrometry. In these service laboratories, we have provided spectrochemical analyses and trace analyses by spark-source mass spectrometry to 18 ORNL divisions and/or ORNL projects. A total of 54,630 results were reported

during the past year. This represents an increase of 12% for this integrated effort. The five largest divisional suppliers of samples in decreasing order were: Metals and Ceramics, Chemical Technology, Isotopes, Environmental Sciences, and Health.

Besides the normal flow of alloys and metal samples from Metals and Ceramics, two major projects contributed to the sample load. These still active projects are the production of iridium sheet and the HTGR fuel program. In the iridium work, we developed and used an isotope dilution technique for certifying the tungsten concentration in the iridium metal sheet, as well as check for trace impurities. Efforts are continuing for selecting a sampling method that will provide reliable impurity measurements of coated HTGR fuels; these data will be used to calculate boron poison factors.

The production of reactor-grade $^{233}\text{UO}_2$ by the Chemical Technology Division for Westinghouse was a source of many samples for the spark-source mass spectrometer equipped to handle radioactive samples. We make specification checks during the processing and on the final $^{233}\text{UO}_2$ products for the following elements: Al, B, Br, Ca, Cl, Co, Cr, Cu, F, Fe, Mg, Mn, Mo, Ni, P, S, Si, Th, Ti, V, and Hg. All of these analyses are part of the quality assurance program.

The Paschen direct-reading emission spectrometer continues to serve well as a means of checking alloy and metal specifications. Isotope dilution techniques are used routinely for Pb, Cd, Zn, Cu, Zr, W, Pt, and a number of the rare-earth elements. The computer programs (PDP-8/E) described earlier in this section have aided in the data reduction.

6. Method Development and Special Projects

D. A. Costanzo, Head

J. L. Botts	D. R. Matthews ³
D. C. Canada ¹	F. L. Moore
L. G. Farrar	R. R. Rickard
D. E. LaValle	G. R. Wilson ²
J. R. Lund ²	

W. E. Bayless

REACTOR FUEL AND MATERIALS ANALYSES

Electrolytic disintegration of HTGR fuel compacts.

An electrochemical method was evaluated to disintegrate HTGR fuel compacts.⁴ These compacts are fabricated from a mixture of (Th,U)O₂ or UO₂ particles, graphite, and suitable binder. They are compacted to the desired shape and heat treated to give them rigidity. This heat treatment also makes the carbon matrix extremely hard to decompose. The compacts must be disintegrated to study the condition of the coated particles.

Electrochemical disintegration of these compacts was accomplished by placing them close to a platinum anode in a glass tube immersed in an electrolyte. A graphite electrode is used as the cathode. Nitric acid is used as the electrolyte. The current is supplied by a dc generator with adjustable voltage. The best results have been obtained using 8 N HNO₃ as the electrolyte and a current of 2 A.

These fuel compacts, once disintegrated, are then leached in nitric acid, and the leach solution is analyzed

for thorium and uranium to determine the extent of broken particle coats.

A disintegration cell has been fabricated for hot cell applications. Irradiated compacts will be disintegrated remotely and the particles separated for visual inspection, gamma spectrometry, and burnup determination.

Determination of damaged particles in HTGR fuel compacts. A series of experiments was begun on HTGR fuel particles (spherical particles of thorium and/or uranium oxide or carbide, coated with pyrolytic carbon and/or silicon carbide) to determine whether high-temperature chlorination (1000°C) will remove the fuel as volatile chlorides from cracked and from intact particles. Determinations on uncoated ThO₂ and UO₂ particles have demonstrated 98% transport for ThO₂ and practically 100% for UO₂.

Hydrogen release from HTGR pyrolytic-carbon-coated fuel particles. A detailed kinetic study of the total hydrogen release from the pyrolytic carbon coat of HTGR fuel particles was undertaken for the Metals and Ceramics Division. Since the carbon coat of these microspheres is derived from a hydrocarbon, it is important to know the amount of hydrogen that will be released at various temperatures for reactor applications. Time-volume relationships were determined for the hydrogen release at 1150°C, 1350°C, 1650°C, and 1950°C using induction heating. For example, at 1650°C, a sample size of 250 mg will release approximately 4 cm³ of hydrogen in 2 hr.

Open porosity of pyrocarbon-coated HTGR fuel particles. A unique method was developed to determine the depth to which the pyrolytic carbon surface of HTGR fuel particles is permeable. The ceramicists are interested in this property since the open porosity may influence the tendency for failure of coatings during carbonization of fuel rods. In this method the open pores are impregnated with nickel by removing all gases under a vacuum, introducing nickel carbonyl vapor, and

1. Leave of absence.

2. Environmental Analyses Laboratory.

3. Mass and Emission Spectrometry Group.

4. P. Koss and H. Bildstein, *Testing and Evaluations of Reactor Fuel Particles*, A.E.E. Winfrith, Dorchester, Dorset, England, D.P. report 295, September 1964, p. 16.

decomposing the carbonyl with subsequent deposition of nickel on the walls of the open pores. Light microscopic examination of metallographically polished samples is used to determine the depth of penetration of the nickel.

Particle size distribution of UO_2 powder. In support of the Westinghouse/Bettis LWBR Assistance Program, a Micromeritics Instrument Corporation 5000/GB particle size analyzer was evaluated and installed in a glove box to determine the particle size distribution of $^{233}\text{UO}_2$ powder. The analyzer measures the sedimentation rates of particles in suspension by means of a finely collimated beam of x rays and automatically presents these data in terms of the Stokesian or equivalent spherical diameter in the size range 0.1 to 100 μm . In this method, the UO_2 powder is ultrasonically suspended in an aqueous 40 wt % glycerol solution plus a surfactant, 0.02 wt % Daxad 23. The sample does not have to be precisely weighed and measured. The precision and accuracy of the measurement is $\pm 1\%$.

Dissolution of noble-metal alloys and refractory oxides. The sealed-tube method was evaluated for the dissolution of difficultly soluble materials.⁵ One of its applications has been the dissolution of some of the noble metals such as platinum, iridium, and rhodium and some of their alloys, such as Pt-Rh-W. The solvent for these metals is concentrated hydrochloric acid containing three to four drops of nitric acid. The dissolution temperature is kept at 300°C for about 16 hr. Another application of this method will be for the dissolution of refractory plutonium and thorium oxides. The Metals and Ceramics Division is interested in the analysis of these noble-metal alloys since they develop alloys for space applications. Also in this regard a series of iridium alloys and standards containing rhenium, tungsten, and ruthenium were dissolved by anodic dissolution for analysis by atomic absorption.⁶

Infrared spectrophotometry. The Beckman IR-12 spectrophotometer was used to determine the presence and amount of OH^- species in the $\text{NaF}\cdot\text{NaBF}_4$ eutectic which was of interest to the Reactor Chemistry Division.⁷ 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. The IR-12 was also used to verify samples of Teflon and various polymers as authentic and to identify or compare other organic compounds. The spectra obtained using the Varian A60A NMR spectrometer were much more informative than infrared spectra when used to confirm that two disubstituted cyclohexanes were hydroxylaminocyclohexanecarboxylic acid and cyclohexyl- α -hydroxylamine nitrile.

ENVIRONMENTAL AND BIOLOGICAL ANALYSES

Total organic analyses. Analysis for carbon, nitrogen, and sulfur in environmental field specimens continues to be an important part of our work.⁸ The instrument used for this work, a reductive pyrolysis-gas chromatograph, has been altered slightly by the addition of a new flame ionization detector for CH_4 measurement. Before this addition, H_2S and CH_4 were analyzed in the same effluent stream. This created problems when carbon or sulfur differed greatly in concentration. Now, these elements are analyzed in different effluent streams, therefore broadening the analytical range of the instrument. A paper was published describing the recent data obtained with this instrument.⁹

A program has been initiated by the Environmental Sciences Division that attempts to measure carbon movement in the Walker Branch Watershed location between ORNL and Y-12 sites. An analytical method was needed that would handle large numbers of samples for dissolved and particulate organic carbon and would be sensitive enough to determine dissolved organic carbon at 0.5 mg of carbon per liter. Several methods were considered. We studied reductive pyrolysis, combined with flame ionization detection, but were unable to eliminate a system blank which limited our lower limits of detection to approximately 10 mg of carbon per liter. We then tried oxidation of organic carbon to CO_2 on hot copper oxide in a helium stream, followed by reduction of CO_2 to methane with hydrogen on nickel and flame ionization detection. We were able to completely reduce CO_2 to methane and measure the

5. E. Wichers, W. G. Schlecht, and C. L. Gordon, "Attack of Refractory Platiniferous Materials by Acid Mixtures at Elevated Temperatures," *J. Res. Nat. Bur. Stand.* **33**, 363-81 (November 1944).

6. W. D. Box, "Dissolution of Metals by A.C. Electrolysis," *Nucl. Appl.* **2**, 299 (1966).

7. A. S. Meyer et al., "Infrared Spectral Studies of Molten and Solid $\text{NaBF}_4\cdot\text{NaF}$," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 24.

8. D. A. Costanzo et al., "Carbon, Nitrogen, and Sulfur in Ecological Materials," *Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1972*, ORNL-4838, p. 50.

9. A. D. Horton, W. D. Shults, A. S. Meyer, and D. R. Matthews, "Determination of Nitrogen, Sulfur, Phosphorus, and Carbon in Solid Biological Materials via Hydrogenation and Element-Selective Detection," *Environ. Sci. Technol.* **7**, 449 (1973).

methane satisfactorily with a flame ionization detector, but again the limit of detection was not low enough for the Walker Branch samples. We considered both the Dohrmann total organic carbon (TOC) analyzer, which is based on flame ionization detection of methane, and the Beckman TOC instrument, which is based on oxidation to carbon dioxide and measurement via nondispersive infrared spectrometry. Neither of these has the necessary sensitivity — both are limited to 1 to 2 mg or more of carbon per liter.

We then decided to use a sealed-tube wet chemical oxidation technique using persulfate as oxidizing agent, based on a method by Menzel and Vaccaro.¹⁰ Carbon is converted to CO₂ and then determined by infrared spectrometry. This method has lower limits of 0.1 to 0.2 mg of carbon per liter. Sealed-tube wet oxidations are not usually considered rapid methods, but Oceanographic International Instrument Company recently marketed an analytical system that speeds up the whole procedure. Dissolved organic, dissolved inorganic, particulate organic, and particulate inorganic carbon analyses can be made with this instrument.

We analyze the dissolved and particulate organic carbon by oxidation of the carbon to carbon dioxide with potassium persulfate at 130°C in sealed glass ampules. The organic carbon samples are acidified with phosphoric acid and purged of inorganic carbonates and CO₂ with purified oxygen. Ten-milliliter aliquots can be used, and this accounts for much of the instrument's increased sensitivity. This instrument can analyze 86 such aliquots per day. The precision is approximately 0.1 mg of carbon per liter or ±5%, whichever is larger. The blank is about 0.12 to 0.16 mg of carbon per liter.

Carbonate analyses are very easily accomplished by injecting an aliquot containing dissolved carbonates into a phosphoric acid solution contained in a special ampule equipped with a septum and then measuring the evolved CO₂. Solid carbonate may be analyzed by injecting a phosphoric acid solution through the septum onto the samples. Several thousand samples have been analyzed for carbon with this system during the past few months.

Mercury by cold-vapor atomic absorption spectrometry. The cold-vapor atomic absorption technique has been used to determine mercury in a wide variety of biological, ecological, and commercial materials down to the sub-ppb level.¹¹ More than 1200 samples of fish, fish organs, vegetation, soils, sediments, stream and river water, coal, fly ash, and various solutions have been analyzed for members of the Environmental Sciences, Operations, Health, and Chemistry Divisions and in support of such programs as the Allen Steam

Plant study, the ORNL/Purdue project, and our Smoking and Health Programs.

Toxic metals in the environment. During this period, we completed laboratory studies of the pertinent variables for the pollution abatement of toxic metals in industrial brine effluents. The chemical and engineering details are described in three recent publications.¹²⁻¹⁴ This work is supported by the National Science Foundation (RANN) through the Ecology and Analysis of Trace Contaminants Program.

On the basis of our laboratory studies, we have designed and fabricated a miniplant solvent extraction unit for evaluating toxic metals removal from industrial waste streams of interest. Currently the major interest is on waste effluents containing Cd, Hg, Zn, and Pb. Shakedown tests to define the operating characteristics are now in progress.

An interesting spinoff¹⁵ of this project is a field concentration method for toxic metals in natural waters. Chemists have found selected quaternary amines to be very effective at the ppb level for Pb, Hg, Cd, Cu, and Sb. The organic extracts are directly amenable to analysis via the atomic absorption method.

Laboratory recycling of toxic materials. Vacuum distillation was used to repurify tetrabromoethane (TBE) used in the gradient-density procedure when the used TBE cannot be decolorized by heating with charcoal. The density of the distilled material was within 0.1% of the handbook value, whereas small amounts of benzene impurity remain in the TBE repurified by decolorization with charcoal at approximately 100°C.

During the period September 1972 to September 1973, 1132 lb of mercury was cleaned and recycled for

10. D. W. Menzel and R. F. Vaccaro, "The Measurement of Dissolved Organic and Particulate Carbon in Seawater," *Limnol. Oceanogr.* 9, 138 (1964).

11. 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.

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

13. F. L. Moore, *Ecology and Analysis of Trace Contaminants Semiannu. Progr. Rep. January 1973*, ORNL-NSF-EATC-1, p. 349.

14. W. S. Groenier, *The Application of Modern Solvent Extraction Techniques to the Removal of Trace Quantities of Toxic Substances from Industrial Effluents*, ORNL-TM-4209 (July 1949).

15. A. Anders, *Ecology and Analysis of Trace Contaminants Monthly Progr. Rep. June 25, 1973*, ORNL-NSF-EATC-73-3.

use at ORNL and Y-12 laboratories. The countercurrent liquid-liquid extraction column procedure modification of the Hanford method was used.¹⁶

INORGANIC PREPARATIONS

The Inorganic Preparations facility supports other divisions by synthesizing compounds and preparing materials not otherwise available and by processing or carrying out experiments on existing materials. During the past year, we have made the following compounds: RbClO_4 , ND_4ClO_4 , NaBF_3OD , FeCoS_4 , BaTbO_4 , TbF_4 , and $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 2.3\text{H}_2\text{O}$, the latter of interest in superconductivity. We also made the ferrites $\text{Ni}_{0.3}\text{Fe}_{2.7}\text{O}_4$ and $\text{Ni}_{0.3}{}^7\text{Li}_{0.3}\text{Fe}_{2.4}\text{O}_4$ and the intermetallics AuSb_2 , Ni_3Al , and Ni_3Ga , the latter in a series doped with small amounts of iron. A preparation of 10 g of the stable isotope ${}^{140}\text{Ce}$ in the metallic form was made by the reduction of the fluoride with calcium. Multiple preparations of purified anhydrous salts included kilogram quantities of LiNO_3 , KNO_3 , and CsNO_3 (all fused); $\text{Cd}(\text{NO}_3)_2$ and K_2SO_4 (anhydrous); and the specific hydrate $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

As an example of a preparation-processing program, we may mention the preparation of a series of thin films (0.5 mil) of high-purity iron doped with 0.005 to 10.0 at. % Co. The iron was dissolved in dilute HNO_3

and high-purity $\text{Co}(\text{NO}_3)_2$ was added, followed by evaporation and ignition to the oxides and reduction of the oxides to metal. The metal mixtures were melted in MgO crucibles in an induction furnace underneath weights to yield disks about 1 mm thick, a prerequisite to beginning rolling these nonductile alloys. Intermediate annealings between rollings enabled the thickness of 0.5 mil to be achieved.

In another experiment, we successfully grew single crystals of the 50 mole % solid solution of CoS_2 in FeS_2 by vapor-phase transport of the disulfides in an atmosphere of bromine at 100 torr and sulfur vapor at 1 atm with a temperature gradient of 735° to 685° .¹⁷

Other procedures carried out were the saturation of high-purity palladium with hydrogen to the extent of $\text{PdH}_{0.97}$ by an electrolytic method, the preparation of 10 and 50 mole % solid solutions of NH_4I in RbI , and the doping of Eu_2O_3 with CaO in the range from 2.5 to 10% by the precipitation of the oxalates at a pH of 3.0.

Finally we recovered a number of valuable materials during the year from various matrices: platinum, ${}^{57}\text{Fe}$, ${}^{54}\text{Fe}$, ${}^{154}\text{Sm}$, and ${}^{61}\text{Ni}$.

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

17. S. R. Butler and R. J. Bouchard, "Single Crystal Growth of Pyrite Solid Solutions," *J. Cryst. Growth* **10**, 163 (1971).

Part B. Service Analyses

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

Table B-1. Summary of analytical work

Organization	Number of results reported by –				Total
	Elemental Spectrometry ^a	Mass Spectrometry Service Laboratory ^b	General Analyses Laboratory ^c	General Hot Analyses Laboratory ^d	
For ORNL divisions					
Analytical Chemistry	399	959	333	58	1,749
Biology	50		392	1	443
Chemistry	286	50	111	15	462
Chemical Technology	8,786	3,798	8,702	26,927	48,213
Director's				168	168
Environmental Sciences	2,342		46,986	588	49,916
Health	4,416				4,416
Health Physics			591	1,740	2,331
Inspection Engineering	42			30	72
Instrumentation and Controls	30			3	33
Isotopes	16,139	6,752	63	3,194	26,148
Metals and Ceramics	13,272	19	3,466	973	17,730
Neutron Physics	1,322		85	44	1,451
Operations	1,318	71	1,033	10,553	12,975
Physics	435	5	20	791	1,251
Plant and Equipment		270		16	286
Reactor	1,268	905	369	18	2,560
Reactor Chemistry	1,252	215	645	417	2,529
Solid State	1,494	18	521		2,033
Thermonuclear	12	10			22
For others					
Los Alamos Scientific Laboratory		306		53	359
Miscellaneous	685	2,807	573	100	4,165
Y-12	1,082	1,070	270	7	2,429
Total	54,630	17,255	64,160	45,696	181,741

^aAverage number in group: 3.5 scientists and 3 technicians.

^bAverage number in group: 1 scientist and 3 technicians.

^cAverage number in group: 5 scientists and 10 technicians.

^dAverage number in group: 17 scientists and 10 technicians.

7. General Hot Analyses Laboratory

J. H. Cooper, Head

C. E. Lamb	M. E. Pruitt
G. Goldberg	C. K. Talbott
F. L. Layton	J. S. Wike
E. C. Lynn	H. C. Meyer
H. A. Parker	J. M. Peele
W. H. Akers	W. C. Massey
R. Burns	P. W. Pair
J. H. Davidson	J. D. Pendleton
E. C. Fearnow	S. H. Prestwood
C. C. Foust	W. F. Rogers
L. R. Hall	T. G. Scott
R. A. Jones	C. K. Talbott
R. E. Jones	

More than half of the 46,000 analyses done by the General Hot Analyses Laboratory were for the Chemical Technology Division in support of the Transuranium Processing Plant and the LWBR fuel production program. The LWBR program provided several batches of $^{233}\text{UO}_2$ powder which required quality control analyses. Qualifying certification was completed on four new methods: (1) moisture, (2) nitrogen, (3) average particle size, and (4) particle size distribution.

The Low Level Radiochemical Laboratory formerly at Y-12 has been moved into Building 2026 to further consolidate facilities. Because of the interest in environmental problems, the sample load in the Low Level Laboratory has increased. We are updating the counting

equipment and revising some of our analytical procedures.

Specimens of protective coatings for nuclear reactor containment facilities have been tested for performance under various conditions to which they will be exposed. Steel and concrete panels coated with the various paints to be tested were submitted for three different tests. In the first test the specimens were contaminated with different reagents. Counting the gamma activity of the specimens before and after the various decontamination steps enabled us to calculate the decontamination factors for each nuclide. The second test (on different specimens) consisted in subjecting the specimens to a circulating bath of corrosive liquid at a temperature of about 280°F and a pressure of 60 psi. Half of the coupons were immersed in the liquid, and duplicate coupons were placed in the vapor phase. After 28 hr in this environment, the specimens were removed and examined for coating damage. The final test exposed the coupons to a total of 5×10^9 rads of gamma radiation. The radiation source was a spent fuel element from the HFIR. Details of these testing procedures may be found in American National Standards Institute reports N5.9-1967 and N101.2-1972.

A waste tank monitor outside Building 2026 repeatedly showed contamination. Investigation by Operations Division personnel revealed a leak in the line leading to the tank. The line was replaced with a preformed Hastelloy line, and no further contamination has been detected.

8. General Analyses Laboratory

W. R. Laing, Head

L. J. Brady H. G. Davis

M. R. Childs

C. J. Coley

P. S. Gouge

J. H. Hackney

A. H. Matthews

B. Philpot

K. I. Webb

Work for the Environmental Sciences Division increased 17% to 47,000 determinations. Four new determinations contributed substantially to this total. An Oceanographics Total Carbon Analyzer was used to measure carbon in area streams, rainfall, throughfall, and filtered particulates with a sensitivity of 0.1 ppm of carbon. Humic acid in solution was determined by its absorption at 520 nm in an $(\text{NH}_4)_2\text{HPO}_4$ buffer at pH 8. Humic acid sorbed on clay was measured by a Leco carbon analyzer. Manifolds for the Technicon Auto-analyzer were constructed for the determination of nitrate and ammonia. Sensitivities obtained were 2 ppb nitrate nitrogen and 5 ppb ammonia nitrogen.

For other environmental samples, the ethylene blue¹ method was adapted for 1 to 10 ppm levels of sulfate. This chromogenic agent is twice as sensitive as methylene blue. Both graphite furnace atomizers and radio-

frequency furnace atomizers were used for trace levels of lead, zinc, and cadmium. The Teflon-lined Parr bomb was used for dissolution of plant material for tellurium determination.

Development and method modification continued for the HTGR Program. Minimum aliquot sizes of 1 ml were established for mercury density measurements. All standards for density gradient columns were recalibrated to establish their value to the fourth decimal place. A complex procedure consisting of a burn, fusion, leach, fusion, and precipitation was used to completely dissolve 15-g portions of Triso-coated microspheres for uranium and thorium analyses. A nitric acid-hydrofluoric acid reflux was used to dissolve uranium and thorium from broken microspheres.

For purposes of monitoring plant effluents, a regular sampling schedule for dissolved oxygen was established. Stripping polarography was used to determine lead, bismuth, and copper in water samples from Melton Branch, White Oak Creek, and White Oak Dam. Composite samples for Cr, Zn, P, NO_3 , Pb, Hg, ^3H , and phenol were analyzed monthly.

In other work, the Davies and Gray volumetric uranium procedure was used with weighed aliquots and dichromate to obtain an RSD of 0.5%. This method was also used to determine uranium in $\text{UO}_2 \cdot \text{NbO}_2 \cdot \text{ZrO}_2$ cermet. Atomic absorption was used to measure Ru, Rh, Re, W, and Ir in alloys and cutting scrap. Condensate from molten NaBF_4 was analyzed for free acid, free fluoride, bound fluoride, and boron. An apparatus was set up for the determination of hydrogen in potassium metal by amalgamation followed by gas chromatography.

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

9. Industrial and Radiation Safety

G. R. Wilson

J. S. Wike

Most of the 12 medical treatment cases we had in the past year involved glass, chemicals, finger contusions, abrasions, and strains; none were lost-time accidents. Quarterly safety and housekeeping inspections have resulted in obvious improvements in the appearance of the Division laboratories and in removal of unused equipment and old chemicals.

To meet fire protection requirements, $\frac{1}{4}$ -in.-thick steel plates approximately 5 ft high and $1\frac{1}{2}$ ft wide are

being constructed; when completed, they will be firmly mounted between cylinders of hydrogen and oxygen or breathing air.

Forty-six radiation work permits were issued for hazardous work areas. All work was completed without incident or overexposure to ionizing radiation. The leaking radiochemical drain serving the center hoods in room 205, Building 2019, was replaced. The leaking radiochemical drain header at Building 2026 was replaced, and the interior of HRLAF cell No. 3 was renovated and decontaminated. The exhaust fan filters were replaced in Building 2019; this increased the pressure difference between the interior of the building and the outside.

10. Quality Control Program

G. R. Wilson

The relative limit of error expected at the 95% confidence level has been set at 5% for the very low levels of Ca, Mg, K, and Na determined by atomic absorption and at 20% for the calorimetric phosphorus method (at the ppb level) with the Technicon Auto-analyzer. These control programs were initiated in April 1972. Control programs for low levels of Cr, Fe, Ni, and Co by atomic absorption and for soluble organic carbon by infrared absorption were started in April 1973.

The total number of control programs available is now 36; however, some of these are not used frequently enough for the data to be statistically meaningful and will be dropped next quarter. The overall quality level increased from 92.5% to 93.4%, and the number of control results increased from 1616 to 1952. 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 1972–June 1973

Laboratory	Number of control results		Quality level ^a (%)	
	Total	Outside fixed limits	1972	1973
General Hot Analyses	942	78	95.1	91.7
General Analyses	<u>1010</u>	<u>51</u>	<u>90.7</u>	<u>95.0</u>
Total	1952	129	Av 92.5	93.4

^aControl results within 2S limits.

Table 10.2. Distribution by method of control results for July 1972–June 1973

Type of method	Constituent	No. of programs	No. of results	Total for method
Atomic absorption	Calcium	1	66	279
	Cobalt	1	2	
	Chromium	1	3	
	Iron	1	5	
	Magnesium	1	71	
	Nickel	1	6	
	Potassium	1	54	
	Sodium	1	<u>72</u>	
Colorimetric	Chloride + bromide	1	16	442
	Chromium	1	23	
	Fluoride	1	31	
	Iron	1	50	
	Molybdenum	1	23	
	Nickel	1	33	
	Nitrogen	1	44	
	Phosphate	1	10	
	Phosphorus	1	75	
	Thorium	2	109	
	Uranium	1	<u>28</u>	
Coulometric	Uranium	4	<u>608</u>	608
Flame photometric	Lithium	1	43	50
	Sodium	1	<u>7</u>	
Fluorimetric	Uranium	2	<u>124</u>	124
Gravimetric	Carbon	2	<u>150</u>	150
Infrared absorption	Carbon	1	<u>37</u>	37
Polarographic	Uranium	1	<u>52</u>	52
Volumetric	Nitrate	2	56	210
	Thorium	1	104	
	Uranium	1	<u>50</u>	
Total		36		<u>1952</u>

11. Environmental Analyses Laboratory

R. R. Rickard, Head

N. Marion Ferguson J. R. Lund

C. A. Clark

J. D. Hill

J. H. Oxendine

An Environmental Analyses Laboratory has been established with facilities in Building 2026 (rooms 131 and 132) and in Building 2024 (room 42). Clean-room capabilities provided by room 131 in Building 2026 will be used for special sample preparation. The other

laboratories will have instruments for atomic absorption spectrometry, semiautomated spectrophotometry, and special analytical measurement techniques for the determination of carbon, nitrogen, and sulfur in environmental materials.

The Environmental Analyses Laboratory will coordinate the analytical requirements of the Environmental Sciences Division, the Ecology and Analysis of Trace Contaminants (EATC) Program, and other activities that involve environmentally related materials. The laboratory will also serve as a liaison between requesters with analytical problems and the various specialists within the Analytical Chemistry Division.

Part C. Activities Related to Education

The Division continues to maintain liaison with the academic community through the assistance of its Advisory Committee and consultants and through the use of its facilities and supervision for student and faculty research and training programs.

ADVISORY COMMITTEE

This year, again, the Divisional Advisory Committee was 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

CONSULTANTS

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.

A. E. Cameron advises Spectrometry Group of Division.

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

M. T. Kelley advises and works with computer programs, in particular.

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

GRADUATE THESIS RESEARCH PROGRAM

J. D. Lodmell. Mr. Lodmell has completed the requirements for the Ph.D. degree from the University of Tennessee under the direction of A. S. Meyer, W. D. Shults, and J. A. Dean. His research for this degree involved the development and utilization of a wavelength-selective multielement flame spectrometric detector for the gas chromatograph.

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

R. V. Crosmun. A graduate student from the University of Tennessee, Mr. Crosmun has initiated research on multielement trace analysis using flame and/or flameless spectrometry under the direction of Y. Talmi and J. A. Dean.

Sandra T. Crosmun. Mrs. Crosmun has initiated research on pulse polarography and stripping techniques under the direction of J. R. Stokely and J. A. Dean. She is a graduate student from the University of Tennessee.

G. M. Thompson. Mr. Thompson was awarded the M.S. degree in geology from Memphis State University. He completed his research on uranium series dating of stalagmites from Blanchard Springs Caverns, Stone County,

Arkansas, under the direction of J. A. Carter, R. L. Walker, and D. N. Lumsden to fulfill the requirements for the degree.

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

GREAT LAKES COLLEGES ASSOCIATION EDUCATIONAL PROGRAM

This cooperative program is now in its fourth year. L. R. Wilson, Professor of Chemistry from Ohio Wesleyan University, Delaware, Ohio, has been our guest this year. Dr. Wilson worked with L. D. Hulett on x-ray and electron physics methods in the Nuclear and Physics Methods Group.

Three GLCA students were assigned to the Division's staff. They are: M. C. Dale from Earlham College in Richmond, Indiana, to the Tobacco Smoke and Inhalation Program under the direction of M. R. Guerin; Irene I. Devadason from DePauw University, Greencastle, Indiana, to work on electrophoresis with John Caton; and Mr. S. L. Eck, from Kalamazoo College, Kalamazoo, Michigan, to Y. Talmi on the environmental analyses program. These three students were in residence in the Division during the fall semester.

NSF PRESIDENTIAL INTERN PROGRAM

G. E. McGuire. Dr. McGuire completed his NSF Presidential Intern appointment in the Division as a member of the Nuclear and 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 high school graduates. G. Goldstein serves as "Dean" for these guests during their visit.

Co-Op Students

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

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

ORAU Summer Research Participant

Dr. James A. Kinsinger, Tougaloo College, Tougaloo, Mississippi, worked on computerization of gas chromatographic information with R. W. Stelzner (Instrumentation Group) and M. R. Guerin (Bio-Organic Analysis Group).

ORAU Summer Student Research Trainees

K. D. Cook, Colorado College, Colorado Springs, Colorado, worked on analysis techniques using x rays under the direction of L. D. Hulett.

J. C. Lechleiter, Xavier University, Cincinnati, Ohio, worked with R. W. Stelzner investigating applications involving a dedicated small computer in the field of coulometry.

Janet A. Mercer, Hardin-Simmons University, Abilene, Texas, assisted J. F. Emery on activation analysis program.

D. W. Magouyrk, Arkansas College, Batesville, Arkansas, investigated the preparation and operating characteristics of uranium ion-selective electrodes under the direction of D. L. Manning.

W. J. Barringer, Eckerd College, St. Petersburg, Florida, conducted research under the direction of Y. Talmi using gas chromatographic techniques with RFF and microwave detectors. (January 1973)

Kathleen L. Lowry, New College, Sarasota, Florida, worked under the direction of J. E. Caton on the MAN Program. (Fall 1972 semester)

Part D. Supplementary Professional Activities

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

J. A. Carter

Councilor: East Tennessee Section, ACS
Viking Mission Pin Award for GCMS work

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

D. A. Costanzo

Program Chairman: East Tennessee Section, ACS

J. S. Eldridge

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

J. F. Emery

Vice President: DECUS East Tennessee Local Users Group

Cyrus Feldman

Member: Committee E-2, Emission Spectrochemical Analysis, ASTM
Subcommittee on Photographic Photometry
Subcommittee on Atomic Absorption Analysis
Publications Committee, Society for Applied Spectroscopy

Scientific Editor: *Optics and Spectroscopy* (English translation of Russian journal
Optika i Spektroskopiya)

N. Marion Ferguson

Secretary-Treasurer: Analytical Chemistry Group, East Tennessee Section, ACS

Gerald Goldstein

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

- Chairman: Subcommittee on Nucleotides and Related Compounds
 Member: Committee on Specifications for Adenine for Use in Anti-coagulant Solutions, NAS-NRC
 President: Tennessee Institute of Chemists, AIC
- M. R. Guerin**
 Member: Tobacco Working Group, National Cancer Institute
 Data Analysis Subgroup, Tobacco Working Group, National Cancer Institute
 Filtration Subgroup, Tobacco Working Group, National Cancer Institute
 Chairman: Chemistry Subgroup, Tobacco Working Group, National Cancer Institute
 Member: ORNL Ph.D. Recruiting Committee
 Committee on Tobacco Smoke Generation for Biological Exposure, ASTM
- A. D. Horton**
 Member: Committee E-19, Chromatography, ASTM
 Subcommittee 3, Research
- L. D. Hulett**
 Treasurer: Sigma Xi-RESA, Oak Ridge Chapter
 Member: Editorial Board, *Journal of Electron Spectroscopy*
- W. R. Laing**
 Secretary: Committee C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, ASTM
 Subcommittee 5
 Chairman: Subcommittee 1, Nomenclature, Committee C-26, ASTM
- W. S. Lyon**
 Member: Committee D-5, Coal and Coke, Subcommittee on Methodology, Task Group on Trace Elements, ASTM
 Committee E-10, Radioisotopes and Radiation Effects, ASTM
 Subcommittee 1, Burnup
 Subcommittee 3, Tracer Application
 Subcommittee 5, Neutron Dosimetry
 Organizing Committee, 5th International Conference on Modern Trends in Activation Analysis
 Scientific Committee 25 on Radiation Protection in the Use of Small Neutron Generators, NCRP
 Committee N43-3, Equipment for Nonmedical Radiation Applications, United States of America Standards Institute
 Regional Editor: *Journal of Radioanalytical Chemistry*
 Associate Editor: *Radiochemical and Radioanalytical Letters*
- H. S. McKown**
 Treasurer: Oak Ridge Section, Instrument Society of America

T. R. Mueller

Councilor: Analytical Chemistry Group, East Tennessee Section, ACS

W. T. Rainey, Jr.

Viking Mission Pin Award for GCMS Work

S. A. Reynolds

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

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

Councilor: Analytical Chemistry Group, East Tennessee Section, ACS

Chairman: ORNL Graduate Selection Panel, ORNL

Coordinator: ORNL-NSF Ecology and Analysis of Trace Contaminants Program

Member: Industrial Cooperation Committee
 Panel on Chlorine and Vapor Phase Hydrogen Chloride, NAS
 Environmental Quality Advisory Board, City of Oak Ridge
 Site Review Teams, NSF/RANN

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: Editorial Board, *Analytical Letters*
 Analytical Chemistry Division Executive Committee, ACS

Titular Member and Secretary: Commission V.7, Analytical Radiochemistry and Nuclear Materials, IUPAC

Chairman-Elect: Federation of Analytical Chemistry and Spectroscopy Societies

Member: Analytical Specialists Group, Union Carbide Corporation Technology Subcommittee

J. P. Young

Chairman: Analytical Chemistry Group, East Tennessee Section, ACS

Part E. Presentation of Research Results

The scope of the Division's work has continued the change this past year which has been the trend during the last several years; much basic research and development work accompanies our involvement in the environmental and biochemical fields, as well as in continuing programs in such areas as metallurgy, reactor development, and nucleonics. The "multidisciplinary" approach continues as an effective method of problem solving; therefore, many of the publications listed below reflect collaborative efforts with investigators outside the Analytical Chemistry Division. Those persons are designated by an asterisk.

PUBLICATIONS

Contributions to Books

AUTHOR(s)	TITLE	PUBLISHER
Eldridge, J. S., G. D. O'Kelley,* K. J. Northcutt	"Radionuclide Concentrations in Apollo 16 Samples," pp. 219-221 in <i>Lunar Science IV</i> , ed. by J. W. Chamberlin and C. Watkins	Lunar Science Institute, Houston, Tex., 1973
O'Kelley, G. D.,* J. S. Eldridge, K. J. Northcutt	"Solar Flare Induced Radionuclides and Primordial Radioelement Concentration in Apollo 17 Rocks and Fines - Preliminary Results," pp. 572-574 in <i>Lunar Science IV</i> , ed. by J. W. Chamberlin and C. Watkins	Lunar Science Institute, Houston, Tex., 1973
Thomas, W. A.,* G. Goldstein, W. H. Wilcox*	<i>Biological Indicators of Environmental Quality</i>	Ann Arbor Science Publishers, Ann Arbor, Mich., 1973

Articles

Anderson, N. G.,* D. W. Holladay,* J. E. Caton, L. B. Peterson*	"Isolation of Tumor Associated Macromolecules Using Immun subtraction"	<i>Fed. Proc.</i> 32 , 961 (1973)
Bate, L. C.	(See Lyon, W. S.)	
Bell, J. T.,* C. F. Coleman,* D. A. Costanzo, R. E. Biggers*	"Plutonium Polymerization - III. The Nitrate Precipitation of Pu(IV) Polymer"	<i>J. Inorg. Nucl. Chem.</i> 35 , 639 (1973)
Cameron, A. E.	"Atomic Weights and Mass Spectrometry"	<i>Int. J. Mass Spectrom. Ion Phys.</i> 10 , 209 (1972)
Carter, J. A., R. L. Walker, J. R. Sites	"Trace Impurities in Fuels by Isotope Dilution Mass Spectrometry"	Div. of Fuel Chemistry Preprint, 166th Nat. ACS Meeting, Chicago, Ill., 18(4) , 79-91 (1973)
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Lodmell, J. D.	<i>The Development and Utilization of a Wavelength-Selective Multi-Element Flame Spectrometric Detector for the Gas Chromatograph</i>	University of Tennessee, Knoxville, August 1973
Thompson, G. M.	<i>Uranium Series Dating of Stalagmites from Blanchard Springs Caverns, Stone County, Arkansas</i>	Memphis State University, Memphis, Tenn., March 1973

Reports

AUTHOR(s)	TITLE	REPORT NO. AND DATE
Bolton, N. E.,* R. I. Van Hook,* W. Fulkerson,* W. S. Lyon, A. W. Andren,* J. A. Carter, J. F. Emery	<i>Trace Element Measurements at the Coal-Fired Allen Steam Plant</i>	ORNL-NSF-EP-43 (March 1973)
Carter, J. A.	Progress Report: <i>Trace Metal Analyses Developments and Analyses for EPA by Mass Spectrometry</i>	ORNL-CF-73-6-42 (June 30, 1973)
Corbin, L. T.	<i>Statistical Quality Control Report, Analytical Chemistry Division, October through December 1972</i> <i>January through March 1973</i> <i>April through June 1973</i> <i>July through September 1972</i>	ORNL-CF-73-1-32 (Jan. 11, 1973) ORNL-CF-73-4-15 (Apr. 6, 1973) ORNL-CF-73-7-25 (July 11, 1973) ORNL-CF-72-10-24 (Oct. 11, 1972)
Dyer, F. F., L. C. Bate	<i>Decaygam – Radioactive Decay Gamma-Ray Spectra Compilation</i> <i>Nuclear Data Tables, RISC Data Library Collection</i>	ORNL-DLC-19 (March 1973)
Fulkerson, W.,* W. D. Shults, R. I. Van Hook*	Progress Report: <i>Ecology and Analysis of Trace Contaminants Program</i>	ORNL/NSF-EATC-1 (March 1973)
Guerin, M. R., P. Nettesheim*	<i>Tobacco Smoke Research Program Progress Report</i>	ORNL-4879 (April 1973)
Handley, T. H., C. J. Barton*	<i>Home Ventilation Rates: A Literature Survey</i>	ORNL-TM-4318 (September 1973)
Lijinsky, W.,* W. H. Christie, W. T. Rainey	<i>Mass Spectra of N-Nitroso Compounds</i>	ORNL-TM-4359 (September 1973)
Meyer, A. S.	<i>Methods for the Analysis of MSRP Samples and Process Stream</i>	ORNL-CF-72-7-16 (July 12, 1972)
Reynolds, S. A.	<i>Some Radioisotope Assay Methods</i> <i>Theoretical and Practical Specific Activities and Other Properties of Common Radionuclides</i> "Radioisotope Characterization, Quality Control, and Standards," pp. 23–24 in <i>Isotopes Development Programs – 1972</i>	ORNL-4788 (March 1973) ORNL-TM-4167 (March 1973) AEC rep. WASH-1220 (1973)
Shults, W. D., J. J. Beauchamp	<i>Summary Report: The Development of Air Quality Indices</i>	ORNL-NS-EP-56 (July 1973)
Shults, W. D.	<i>Analytical Chemistry Division Research and Development Monthly Summary –</i> <i>October 1972</i> <i>November 1972</i>	ORNL-CF-72-11-10 (Nov. 1, 1972) ORNL-CF-72-12-10 (Dec. 1, 1972)

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	<i>March 1973</i>	ORNL-CF-73-4-18 (Apr. 2, 1973)
Shults, W. D., L. T. Corbin	<i>April 1973</i>	ORNL-CF-73-5-31 (May 1, 1973)
	<i>May 1973</i>	ORNL-CF-73-6-7 (June 1, 1973)
	<i>June 1973</i>	ORNL-CF-73-7-7 (July 2, 1973)
	<i>July 1973</i>	ORNL-CF-73-8-6 (Aug. 1, 1973)
	<i>August 1973</i>	ORNL-CF-73-9-9 (Sept. 4, 1973)

ORAL PRESENTATIONS

As in previous years, staff members have presented papers at many local, national, and, in some instances, international meetings. These papers have covered a variety of subjects, as our interests have expanded into environmental, biological, and health-related areas.

Seventeenth Conference on Analytical Chemistry in Nuclear Technology

The theme of this conference, which was held at the Riverside Motor Lodge in Gatlinburg on October 23–25, was "New Techniques in Analytical Chemistry." Nine sessions included papers on the following topics: Analyses for Reactor Programs, Biochemical Applications, Ion Microprobe Mass Analyzers, Instrumentation for Chemical Analysis, Application of Lasers for Chemical Analysis, and Trace Analysis and Environmental Base-Line Measurements. In addition, the program included a panel discussion on Control of Costs in Analytical Chemistry Laboratories.

Roger F. Hibbs, President, Nuclear Division, Union Carbide Corporation, was the speaker at the dinner on October 23.

Members of the Conference Committee were: L. J. Brady, Chairman; H. R. Beatty, Treasurer and Exhibits Coordinator; H. H. Ross, Technical Program Chairman; J. E. Caton; W. H. Christie; D. A. Costanzo; J. M. Dale; G. Goldstein; W. R. Laing; C. E. Lamb; T. R. Mueller; and J. C. White.

The list of attendees included representatives from AEC Laboratories, universities, other government-sponsored laboratories, and industrial laboratories. Countries outside the U.S. which were represented at the Conference included France, Great Britain, and Canada.

At Meetings of Professional Societies, Conferences, and the Like

AUTHOR(s)	TITLE	PRESENTED AT
Attrill, J. E., J. E. Caton, D. W. Holladay,* N. G. Anderson*	"Affinity Chromatography of Human Serum Using Antisera against 'All but One' Human Serum Proteins"	165th American Chemical Society Meeting, Dallas, Tex., Apr. 9, 1973
Bolton, N. E.,* J. A. Carter, J. F. Emery, C. Feldman, W. Fulkerson,* L. D. Hulett, W. S. Lyon	"Trace Element Mass Balance around a Coal-Fired Steam Plant"	166th American Chemical Society Meeting, Chicago, Ill., Aug. 26–31, 1973

- Carter, J. A. "Isotope Dilution Mass Spectrometry" Symposium on Trace Element Analysis of Coal, Fly Ash, Fuel Oil, and Gasoline, EPA, National Environmental Research Center, Research Triangle Park, N.C., May 16-17, 1973
- "Inorganic Trace Analyses by Mass Spectrometry" Third Annual Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Athens, Ga., May 14-16, 1973
- "Spark-Source Mass Spectrometry" ORAU Summer Course on Trace Analysis for Environmental Pollutants, Oak Ridge, Tenn., Aug. 20, 1973
- "Environmental Measurements" ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Jan. 30, 1973
- Carter, J. A., L. D. Hulett, R. L. Walker "Spectrometry and Physics Methods" 16th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 24-26, 1972
- Carter, J. A., R. L. Walker, J. R. Sites "Trace Impurities in Fuels by Isotope Dilution Mass Spectrometry" 166th American Chemical Society Meeting, Chicago, Ill., Aug. 26-31, 1973
- Carter, J. A., J. R. Walton, D. R. Matthews, R. L. Walker "Measurements of Nitrogen and Nitrogen Isotopic Ratios Using Reduction Pyrolysis Coupled with Mass Spectrometry" First Annual NSF Trace Contaminants Conference, ORNL, Oak Ridge, Tenn., Aug. 8-10, 1973
- Caton, J. E. "The Potential of Polyacrylamide Gel Electrophoresis in Bioanalytical Chemistry" Seminar for Department of Microbiology, University of Mississippi, Jackson, Miss., Nov. 13, 1972
- "Analytical Chemistry and Gel Electrophoresis" Biology Division Plant Physiology Seminar, Oak Ridge, Tenn., Nov. 1, 1972
- "Analytical Chemistry and Gel Electrophoresis" Chemistry Department Seminar, University of West Florida, Pensacola, Fla., Feb. 14, 1973
- Caton, J. E., D. W. Holladay,* N. G. Anderson* "Immunosubtraction Electrophoresis on Gradient Polyacrylamide Gel" 165th American Chemical Society Meeting, Dallas, Tex., Apr. 8, 1973
- Clayton, F. R.,* G. Mamantov,* D. L. Manning "Electrochemical Studies of Uranium and Thorium in Molten LiF-NaF-KF (46.5-11.5-42.0 Mole %) at 500°C" 143rd Meeting of the Electrochemical Society, Chicago, Ill., May 14, 1973
- "Electrochemistry of Titanium in Molten Fluorides and Sodium Tetrafluoroborate" 143rd Meeting of the Electrochemical Society, Chicago, Ill., May 14, 1973
- Cooper, J. H., F. F. Dyer, W. S. Lyon, M. E. Pruitt, E. Ricci, J. R. Stokely, E. I. Wyatt, J. P. Young "Analysis of Radioactive Materials" 16th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 24-26, 1972
- Costanzo, D. A. "Activities of the Methods Development and Special Projects Group" ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Jan. 30, 1973
- Costanzo, D. A., C. Feldman, W. R. Laing "General Analyses of Nonradioactive Materials" 16th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 24-26, 1972
- Dyer, F. F., L. C. Bate "A Compilation of Modern Nuclear Decay Data for High Resolution Gamma Spectroscopy" IAEA Symposium on Applications of Nuclear Data in Science and Technology, Paris, France, Mar. 12-16, 1973
- Dyer, F. F., T. H. Handley, E. Ricci "Ultra-Sensitive Neutron Activation Analysis in the ORNL High-Flux Isotope Reactor" 24th ACS Southeastern Regional Meeting, Birmingham, Ala., Nov. 2-4, 1972

- Eldridge, J. S.,
G. D. O'Kelley,*
K. J. Northcutt
- "Radionuclide Concentrations in Apollo 17
Rocks and Soils"
- 54th Annual Meeting, American Geophysical Union,
Washington, D.C., Apr. 16-20, 1973
- "Radionuclide Concentrations in Apollo 16
Samples"
- Fourth Lunar Science Conference, Houston, Tex.,
Mar. 5-8, 1973
- Eldridge, J. S.
- "Nondestructive Determination of Radionuclides
in Lunar Samples"
- Chemistry Department Seminar, Democritus Nuclear
Center, Athens, Greece, Sept. 6, 1973
- "Radionuclide Metrology"
- University of Tennessee Chemistry Department
Lecture to Graduate Students, Knoxville, Tenn.,
May 15, 1973
- Feldman, C.
- "The Preservation of Dilute Mercury Solutions"
- 7th Annual Conference on Trace Substances in
Environmental Health, University of Missouri,
Columbia, Mo., June 12-14, 1973
- Guerin, M. R.
- "Analysis of Cigarette Tobacco Smoke and
Condensates"
- ORAU Traveling Lecture Series, Mercer University,
Macon, Ga., Jan. 11, 1973
- "Analysis of Cigarette Tobacco Smoke and
Condensates"
- ORAU Traveling Lecture Series, Maryville College,
Maryville, Tenn., Jan. 25, 1973
- Guerin, M. R.,
J. E. Caton,
G. Goldstein,
M. L. Moss,
W. T. Rainey
- "Bio-Organic Analysis"
- 16th Conference on Analytical Chemistry in Nuclear
Technology, Gatlinburg, Tenn., Oct. 24-26, 1972
- Guerin, M. R.,
P. Nettesheim*
- "Tobacco Smoke Chemistry and Inhalation
Bioassay Methodologies"
- Carcinogenesis Collaborative Conference, San
Antonio, Tex., Oct. 2-4, 1972
- Guerin, M. R.,
G. Olerich
- "Quantitative Utility of the Trimethylsilylation
of Smoke Condensate and Particulate Matter"
- CORESTA/TCRC Joint Conference, Williamsburg,
Va., Oct. 22-28, 1972
- Herz, N.,*
S. Banerjee,*
L. M. Jones,*
R. L. Walker
- "Ortho-Amphibolites Associated with Mn
Protore in Ampa and Minas Gerais, Brazil"
- 85th Annual Meeting, Geological Society of America
and Its Associated Societies, Minneapolis, Minn.,
Nov. 13-15, 1972
- Horton, A. D.,
M. R. Guerin
- "Chemical Characterization of a Little Cigar"
- Cigar Research Council Seminar, Center of Adult
Education, University of Maryland, College Park,
Md., Feb. 7-9, 1973
- "Gas Chromatographic Profiling of Fractions and
Subfractions of Cigarette Smoke"
- ORAU Summer Lecture Series, ORNL, Oak Ridge,
Tenn., July 25, 1973
- "Quantitative Gas Chromatographic Determination
of Smoke Components Using the Sulfur-Specific
Photometric Detector"
- CORESTA/TCRC Joint Conference, Williamsburg,
Va., Oct. 22-28, 1972
- Hulett, L. D.
- "Scanning Electron Microscopy"
- Molecular Structure and Dynamics Colloquium,
ORNL, Oak Ridge, Tenn., Apr. 30, 1973
- "Scanning Electron Microscopy"
- ORAU Summer Course on "Trace Analysis for
Environmental Pollutants," Aug. 6-24, 1973;
lecture on Aug. 20
- Hulett, L. D.,
L. R. Wilson,*
G. E. McGuire*
- "X-Ray Photoelectron Spectroscopy (ESCA) for
the Characterization of Materials"
- Middle Atlantic Regional Meeting, American Chemical
Society, Washington, D.C., Jan. 14-17, 1973
- Jones, L. M.,*
V. J. Hurst,*
R. L. Walker
- "Strontium Isotope Composition and Origin of the
Amphibolites of the Cartersville-Villa Rica
District, Georgia"
- Southeastern Section 22nd Annual Meeting, The
Geological Society of America, University of
Tennessee Student Center, Knoxville, Tenn.,
Apr. 11-14, 1973
- Kelley, M. T.
- "Use of Minicomputers in Analytical Chemistry"
- ORAU Traveling Lecture, Davidson College, Davidson,
N.C., Mar. 2, 1973
- "Use of Minicomputers in Analytical Chemistry"
- ORAU Traveling Lecture, Virginia Military Institute,
Lexington, Va., Apr. 4, 1973

- "Use of Minicomputers in Analytical Chemistry" ORAU Traveling Lecture, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., Apr. 6, 1973
- "Use of Minicomputers in Analytical Chemistry" University of Tennessee Department of Chemistry Colloquium, Knoxville, Tenn., Apr. 24, 1973
- "The Use of FOCAL in Real-Time Applications of Minicomputers" 165th American Chemical Society Meeting, Dallas, Tex., Apr. 8-13, 1973
- Kelley, M. T.,
 R. W. Stelzner,
 M. N. Ferguson "Application of a Small Computer in Atomic Absorption Analyses of Environmental Samples" International Symposium on Microchemical Techniques - 1973, Pennsylvania State University, University Park, Pa., Aug. 19-24, 1973
- Kubota, H. "Analysis of Cigarette Tobacco Smoke and Condensates" ORAU Traveling Lecture, Presbyterian College, Clinton, S.C., Feb. 5, 1973
- "Analysis of Cigarette Tobacco Smoke and Condensates" ORAU Traveling Lecture, Southeastern State College, Durant, Okla., Dec. 7, 1972
- "Analysis of Cigarette Tobacco Smoke and Condensates" ORAU Traveling Lecture, Tougaloo College, Tougaloo, Miss., Nov. 28, 1972
- Kubota, H.,
 M. R. Guerin,
 J. A. Carter "Inorganic Analytical Methods of Tobacco Smoke Analysis - a Comparative Study" CORESTA/TCRC Joint Conference, Williamsburg, Va., Oct. 22-28, 1972
- Laing, W. R. "Precision and Accuracy of Pipetting Devices" ORNL Biology Division Seminar, Oak Ridge, Tenn., Sept. 15, 1972
- Lijinsky, W.,*
 W. T. Rainey,
 W. H. Christie "Identification of N-Nitrous Compounds by Mass Spectrometry" 21st Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, Calif., May 20-25, 1973
- Lyon, W. S. "A Comparison of Analytical Methods" ORAU Summer Course on "Trace Analysis for Environmental Pollutants," ORNL, Oak Ridge, Tenn., Aug. 23, 1973
- "Nuclear and X-Ray Techniques" Interagency Conference on the Environment, Livermore, Calif., Oct. 17-19, 1972
- "Neutron Activation Analysis" Third Annual Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Athens, Ga., May 15, 1973
- McDonald, C. W.,*
 F. L. Moore "Solvent Extraction of Cadmium with High-Molecular-Weight Amines from Aqueous Solutions" Southwestern Regional Meeting, American Chemical Society, Baton Rouge, La., Dec. 6-8, 1972
- Maddox, W. L.,
 M. R. Guerin "High Speed Photometric Analyzer in the Tobacco Sciences" CORESTA/TCRC Joint Conference, Williamsburg, Va., Oct. 22-28, 1972
- Mamantov, G.,*
 D. L. Manning,
 J. P. Young "Electrochemistry and Some Chemistry in Molten Fluorides" 7th International Symposium on Fluorine Chemistry, Santa Cruz, Calif., July 15-20, 1973
- Moore, F. L. "Toxic Metals Abatement Program" NSF/RANN Site Review, ORNL, Oak Ridge, Tenn., Apr. 18-19, 1973
- "Pollution Abatement of Toxic Metals" ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Jan. 30, 1973
- Moore, F. L.,
 W. S. Groenier* "Toxic Metals Abatement Program" NSF-EPA Research Utilization Group Site Review, ORNL, Oak Ridge, Tenn., May 3-4, 1973
- Moss, M. L. "Early Prenatal Diagnosis of Genetic Disease" American Chemical Society "Men and Molecules," radio series, No. 647 (released May 11, 1973)
- "Prenatal Diagnosis of Birth Defects" Tennessee Institute of Chemists, Oak Ridge, Tenn., May 12, 1973
- "Prenatal Detection of Birth Defects" American Association of Clinical Chemists, Southeast Section, Gatlinburg, Tenn., Apr. 6, 1973
- "Current Research on Neuromuscular Disease" Catholic High School, Knoxville, Tenn., Physiology Classes, Oct. 23, 1972

- Moss, M. L.,
W. W. Harris*
"Ultramicro Approach to Prenatal Diagnosis" 165th American Chemical Society Meeting, Dallas, Tex., Apr. 12, 1973
"Enzyme Assays in Isolated Amniotic Cells" Symposium on Recent Developments in Research Methods and Instrumentation, Bethesda, Md., Nov. 30, 1972
"New Approach to Prenatal Diagnosis" World Press Institute Seminar, Oak Ridge, Tenn., Jan. 29, 1973
- O'Kelley, G. D.,*
J. S. Eldridge,
K. J. Northcutt
"Solar Flare Induced Radionuclides and Primordial Radioelement Concentrations in Apollo 17 Rocks and Fines - Preliminary Results" Fourth Lunar Science Conference, Houston, Tex., Mar. 5-8, 1973
- Rainey, W. T. "Progress in Organic Mass Spectrometry" ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Jan. 30, 1973
- Ricci, E. "New Activation Analysis Facilities at ORNL" Junta De Energia Nuclear, Madrid, Spain, Nov. 2, 1973
"Practical Aspects of Activation Analysis" University of Tennessee Chemistry Department Lecture to Graduate Students, Knoxville, Tenn., May 29, 1973
"Activation Analysis at the ORELA and the HFIR" Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Jan. 29-30, 1973
- Ricci, E.,
T. H. Handley,
F. F. Dyer
"Analysis of Traces at ORNL's New High-Flux Neutron Activation Laboratory" C.N.R.S. Colloquium in Activation Analysis, Saclay, France, Oct. 2-6, 1972
"Environmental Analysis at ORNL's High-Flux Neutron Activation Laboratory" American Nuclear Society 19th Annual Meeting, Chicago, Ill., June 10-15, 1973
- Ross, H. H.,
J. M. Dale,
D. J. Fisher,
M. T. Kelley,
A. S. Meyer,
T. R. Mueller,
R. W. Stelzner
"Analytical Instrumentation" 16th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 24-26, 1972
- Ross, H. H.,
G. T. Rasmussen*
"Modern Techniques and Applications in Cerenkov Counting" Plenary Lecture, International Symposium on Liquid Scintillation Counting, Sydney, Australia, Aug. 20-22, 1973
- Shults, W. D. "The Role of Electrochemistry in Transuranium Research" Chemistry Department Colloquium, Auburn University, Auburn, Ala., Oct. 9, 1972
"Environmental Research at ORNL" NAS/BEEP Committee Meeting, Washington, D.C., Feb. 15, 1973
- Shults, W. D.,
J. R. Stokely,
J. P. Young
"The Role of Electrochemistry in Transuranium Research" 165th American Chemical Society Meeting, Dallas, Tex., Apr. 8, 1973
- Talmi, Y.,
R. Crossmun
"Applicability of the RF-Furnace Technique for AA and AE Analysis of Trace Elements in Environmental Samples" 7th Annual Conference on Trace Substances in Environmental Health, Columbia, Mo., June 12-14, 1973
- Talmi, Y. "Environmental Applications of the Radio-Frequency Furnace Technique" Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, Mar. 5-9, 1973
- White, J. C.,
A. D. Horton,
H. Kubota,
W. L. Maddox
"Research on the Analysis of Cigarette Smoke" ORAU Summer Lecture Program, ORNL, Oak Ridge, Tenn., July 25, 1973

White, J. C., W. S. Lyon, J. A. Carter, C. Feldman, N. E. Bolton,* W. Fulkerson,* W. D. Shults	"Analytical Techniques for Determining Levels and Fates of Trace Elements in a Fossil-Fueled Steam Plant"	IAEA Symposium on Nuclear Techniques in Comparative Studies of Food and Environmental Contamination, Otaniemi, Finland, Aug. 27-31, 1973
White, J. C., W. D. Shults	"Analytical Problem Solving for a Diversified-Program Research Laboratory"	166th American Chemical Society Meeting, Chicago, Ill., Aug. 26-31, 1973
Young, J. P.	"Spectral Studies of Actinide Ions in Molten Fluoride Salts"	Tenth Rare Earth Research Conference, Carefree, Ariz., Apr. 30-May 3, 1973
	"Spectral Studies of Molten Salts: A Review"	Lecture in University of Tennessee "Molten Salt" Course, Knoxville, Tenn., May 28, 1973

Seminars

The Division continues to sponsor seminars covering a wide variety of topics in its commitment to keep current with new developments in analysis and measurement. The Divisional seminars (listed below) presented during the period covered by this progress report reflect our most recent efforts in this direction.

SPEAKER(s)	SUBJECT	DATE
Decker, John A., Spectral Imaging Inc., Concord, Mass.	"Hadamard Transform Spectroscopy"	Apr. 26, 1973
S. S. Cristy, Y-12 Development Department	"A New Analytical Instrument - Ion Microprobe Analyzer"	Feb. 20, 1973
Hanna, S. R., National Oceanic and Atmospheric Administration	"Calculation of Atmospheric Dispersion in Rockwood-Harriman, Tennessee"	Mar. 20, 1973
Harrington, H., Hewlett-Packard Company, Palo Alto, Calif.	"Photoelectron Spectroscopy Using Monochromatic X-Rays"	Feb. 27, 1973
Hise, E., ORNL	"The Wankel Engine and the Environment: From the Frying Pan into the Fire"	Oct. 10, 1972
Keliher, P. N., Villanova Univ.	"High-Resolution Echelle Flame Spectroscopy"	May 11, 1973
Kelley, M. T.	"Short Course in FOCAL for GeMSAEC"	Feb. 23, 1973
Levin, S. A., ORGDP	"Uranium Enrichment Expansion Planning"	May 15, 1973
Lyon, W. S.	"DELPHI - a Possible Tool for Predicting Future Technological Progress?"	Nov. 28, 1972
Moss, M. L.	"Techniques for Prenatal Detection of Birth Defects"	Dec. 19, 1972
Sparks, C. J., ORNL	"Quantitative Analysis for Trace Elements Using X-Ray Fluorescence"	July 31, 1973
Weeks, R. A., ORNL	"West of Suez - II"	June 20, 1973
Williams, L., Lunn, R., EDAX International, Inc.	"Si(Li) Detector Systems for X-ray Fluorescence - Questions and Answers"	Sept. 5, 1973

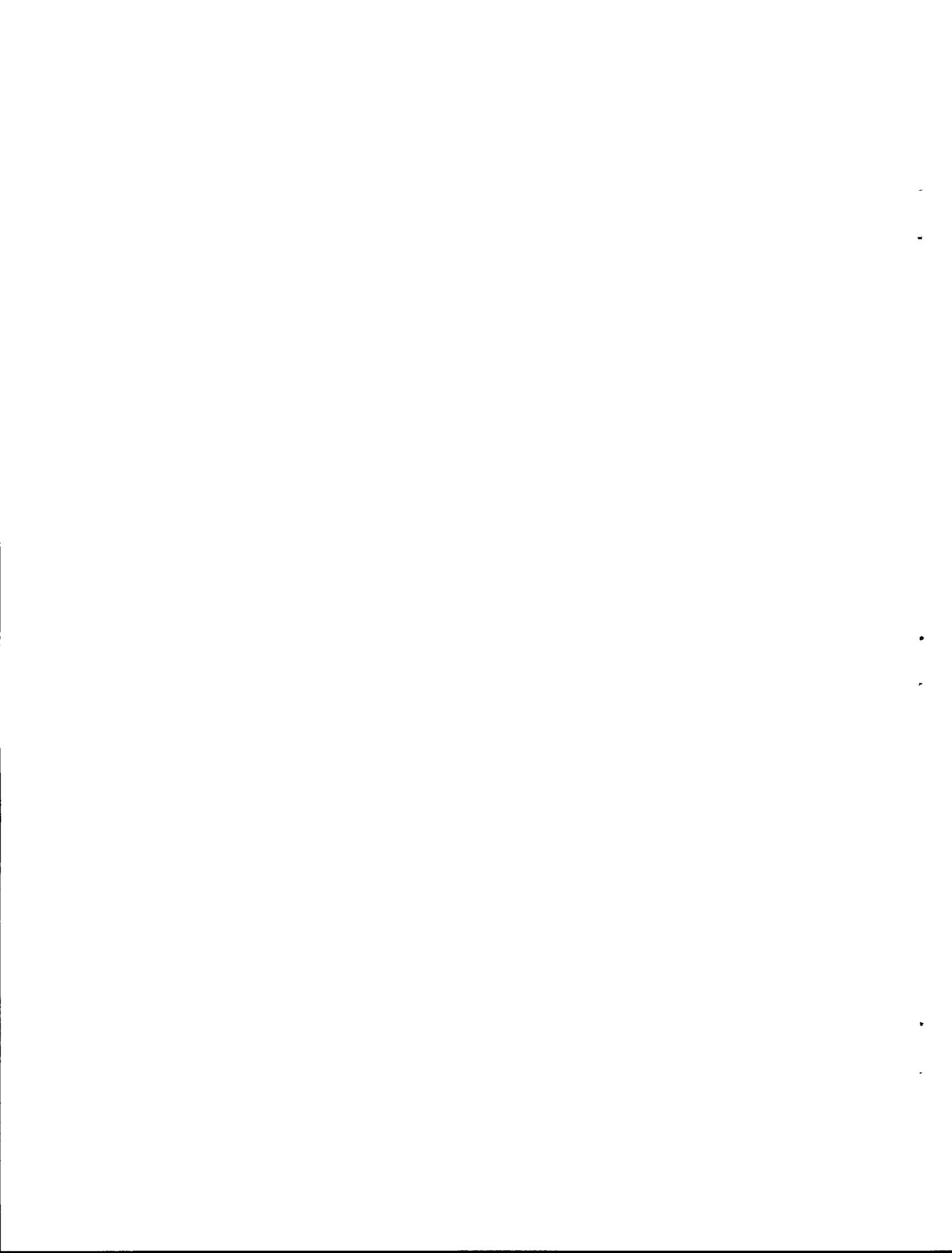
PATENTS

AUTHOR(s)	TITLE	PATENT NO.	DATE ISSUED
Maddox, W. L., R. L. Coleman, W. D. Shults	"Loading Disk for Photometric Analyzer of Rotary Cuvette Type"	3,744,974	July 10, 1973

Shults, W. D., J. R. Kuempel*	"Electrochemical Air Pollution Monitoring Device and Method of Use Thereof"	3,713,994	Jan. 30, 1973
Sturm, B. J., R. B. Quincy, C. T. Butler	"Preparation of High Bulk Density Magnesium Oxide Powder"	3,711,600	Jan. 16, 1973
Zittel, H. E., L. C. Bate, S. B. Lupica	"Base-Borate Reactor Safety Spray Solution for Radiolytic Hydrogen Suppression"	3,691,084	Sept. 12, 1973
Young, J. P.	"Slotted Probe for Spectroscopic Measurements"	3,733,130	May 15, 1973

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

Reviewer or referee	Number of articles reviewed or refereed for indicated periodical													
	<i>Anal. Chem.</i>	<i>Anal. Lett.</i>	<i>ASTM Methods</i>	<i>Chem. Instrum.</i>	<i>Clin. Chem.</i>	<i>Environ. Sci. Technol.</i>	<i>High Temp. Sci.</i>	<i>J. Electron. Spectrosc.</i>	<i>J. Inorg. Nucl. Chem.</i>	<i>Radiochem. Radioanal. Lett.</i>	<i>Science</i>	<i>Books</i>	<i>Proposals</i>	Total
Bate, L. C.											1			1
Caton, J. E.		1												1
Christie, W. H.	1													1
Feldman, C.												1		1
Fisher, D. J.				2										2
Goldstein, G.	1	1		1	1									4
Hulett, L. D.	1							1			1			3
Kubota, H.	1													1
Lyon, W. S.	6					1				4				11
Manning, D. L.	1						1							2
Mueller, T. R.				1	1									2
Pruitt, M. E.		1												1
Reynolds, S. A.			3						1			2		6
Ricci, E.	5													5
Shults, W. D.	1												3	4
Stelzner, R. W.	2			2										4
Walker, R. L.	3													3
White, J. C.	1										1		1	3
Young, J. P.													1	1
Total	23	3	3	6	2	1	1	1	1	4	2	4	5	56



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