OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

UCN-7969
(3 3-67)

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES
3 4456 0515801 2

cy. 124

ORNL-4636
UC-4 — Chemistry

ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

FOR PERIOD ENDING SEPTEMBER 30, 1970

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL-4636
UC-4 — Chemistry

Contract No. W-7405-eng-26

ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

For Period Ending September 30, 1970

M. T. Kelley, Director
J. C. White, Associate Director

Compiled and Edited by
W. S. Lyon

Assisted by
C. A. Horton

JANUARY 1971

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

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES
3 4456 0515801 2

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
ORNL-1113	Period Ending June 26, 1951
ORNL-1129	Period Ending September 10, 1951
ORNL-1233	Period Ending December 26, 1951
ORNL-1276	Period Ending March 26, 1952
ORNL-1361	Period Ending June 26, 1952
ORNL-1423	Period Ending September 26, 1952
ORNL-1474	Period Ending January 10, 1953
ORNL-1547	Period Ending April 20, 1953
ORNL-1639	Period Ending October 20, 1953
ORNL-1717	Period Ending April 20, 1954
ORNL-1788	Period Ending October 20, 1954
ORNL-1880	Period Ending April 20, 1955
ORNL-1973	Period Ending October 20, 1955
ORNL-2070	Period Ending April 20, 1956
ORNL-2218	Period Ending December 31, 1956
ORNL-2453	Period Ending December 31, 1957
ORNL-2662	Period Ending December 31, 1958
ORNL-2866	Period Ending December 31, 1959
ORNL-3060	Period Ending December 31, 1960
ORNL-3243	Period Ending December 31, 1961
ORNL-3397	Period Ending December 31, 1962
ORNL-3537	Period Ending November 15, 1963
ORNL-3750	Period Ending November 15, 1964
ORNL-3889	Period Ending November 15, 1965
ORNL-4039	Period Ending October 31, 1966
ORNL-4196	Period Ending October 31, 1967
ORNL-4343	Period Ending September 30, 1968
ORNL-4466	Period Ending October 31, 1969

Contents

Preface vii

Summary ix

Part A. Analytical Research and Development 1

1. Analytical Methodology 1

Environmental Activities 1
Water Laboratory 1
Applications of the GeMSAEC Photometric Analyzer 1
Pyrolysis–GC System for Determining P, N, S, and C 2
The Gas Chromatography of Aqueous Solutions: Inorganic Anions 2
Participation in the ORNL-NSF Project IDEA 2

Cigarette Tobacco Smoke Analysis Program 2
Facilities 3
Results and Methodology 3
Research Activities 3

Analytical Research and Support Activities in the Transuranium Research Laboratory 4
Complexometric Titration of Curium: Half-Life Measurement 4
Potentiostatic Coulometry of Plutonium in the Presence of Iron 4
Applications of Conducting Glass Electrodes 4
Analytical Support in TRL 5

Electrochemical Research 5
Controlled-Current Coulometric Titrator 5
Electrochemical Properties of Stannic Oxide Electrodes 5
New Instrumentation 6

Gas Chromatography 6
Survey of Pesticides in Animal Organs 6
Examination of the Aqueous Products of the Autoclave Oxidation of Paper 6

Decentralized Preparation of Nuclear Science Abstracts Entries 7

2. Reactor Projects 7

Molten-Salt Reactor Experiment 7
Determination of Trivalent Uranium in MSRE Fuel Samples 7
Determination of Tritium in MSRE Gas Streams 8

Analytical Developments for Molten-Salt Breeder Reactors 9
Development of Reference Electrodes for Molten Fluoride Salts 9

In-Line Measurement of Trivalent Uranium in Molten Fluoride Salts 10
Spectrophotometric Studies of Actinide Ions in Molten Fluoride Salts 11
Studies of Unusual Oxidation States of Ions in Molten Fluoride Media 11
Analytical Developments for $NaBF_4$ Coolant Systems 11
Volatization of Some Chlorides of MSBR Fuel Constituents with Aluminum Chloride 12

Analysis of Natural Gas Samples 12

3. Analytical Biochemistry 14

Biological Macromolecular Separations Technology Project 14
Analysis of Nucleic Acids and Nucleic Acid Components 14
Analysis of Proteins and Enzymes 15

Molecular Anatomy (MAN) Program 16
Characterization of Compounds Isolated from Physiological Fluids 16
Protein Sequence Studies 18

Characterization and Purity of Biochemical Compounds 18

Separation of Oxypurines by Ligand-Exchange Chromatography 19

GeMSAEC Analyzer: Clinical Development Program 19

4. Nuclear and Radiochemistry 20

Trace Element Determinations in Biological and Environmental Samples 20
Mercury 20
Copper and Manganese 21
Other Elements 22

Cooperative Isotopes Program 22

Radioisotope Characteristics and Measurements 24
Nuclear Measurements 24
Decay Studies and Isotope Enrichment 24
Fission Product Release from Reactor Fuel Microspheres 25

Proton Reaction Analysis for the Ratios $^{13}C/^{12}C$ and $^{15}N/^{12}C$ in Biological Samples 25

Gamma-Ray Spectrometry and New Facilities 27
Low-Level Gamma-Ray Spectrometry 27
Fission Product Measurement in Nuclear Reactors by Remote Gamma Spectrometry 27
Compilation of Nuclear Data for Ge(Li) Gamma Spectrometry 28
Gamma-Ray Spectrometer Systems 28
High Flux Activation Analysis Laboratory 29
Photon and Fast-Neutron Activation Facility at the ORELA 29
Californium-252 29

Nuclear Safety Support Program 29
PWR Studies 29
Radiolytic Sulfur and CH_3I 30
BWR Studies 31

Effects of Radiation on Analytical Methods 32

Cerenkov and Phosphor Studies 32

5. Analytical Instrumentation 34

Instrumentation Research and Development 34
Q-2792 Polarograph and Q-2942 DME Drop-Time Controller 34

Dual Potentiostat 34
Cyclic Voltammeters 35
Q-5065 Differential Voltmeter 35
Q-1728A Potentiometric Titrator 36
Fabrication Information 36

Computer Analytical Systems 37
Programmable Calculator Course 37
PDP-8 Computer Programming Course 37
Voltammetric U(IV)/U(III) Ratio Determination 37
GeMSAEC: FOCAL Programs 37
GeMSAEC: Kinetic Methods of Analysis 38
GeMSAEC: Programs for Clinical Analyses 38
Differential Scanning Calorimeter 38
Linear Systems Analysis 39
Digital Polarography 39

6. Methods Development and Evaluation Laboratory 40

7. Mass Spectrometry 43

8. Electron Microscopy 45
Transmission and Scanning Electron Microscopy 46
Electron Spectroscopy 47
X-Ray Diffraction Studies 48
Electron Microprobe Analysis 49

Part B. Service Analyses 50

9. Spectrometry Services 51

10. Process Analyses 54
High-Level Alpha Radiation Laboratory 54
General Analyses Laboratory 54
General Hot-Analyses Laboratory 55
Radioisotopes-Radiochemistry Laboratories 56
Radiation Control and Safety 56
Quality Control 56
Inorganic Preparations 57

Part C. Activities Related to Education 58
Advisory Committee Members 58
Consultants 58
Great Lakes Colleges Educational Program 59
ORAU Research Participants 59
Graduate Thesis Research Program 59
ORNL Loanees 60

Summer Student Program 60
Project "Available Better Careers" (ABC) 60
ORNL Technical Improvement Program 60
Alien Guest in Residency 61

Part D. Extralaboratory Professional Activities 62

Part E. Presentation of Research Results 66
Publications 66
Contributions to Books 66
Articles 67
Theses 70
Reports 70
Oral Presentations 71
Fourteenth Conference on Analytical Chemistry in Nuclear Technology 71
At Meetings of Professional Societies, Conferences, and the Like 72
Patents 76
Articles Reviewed or Refereed for Periodicals 77
Organization Chart 79

Preface

The Analytical Chemistry Division has the responsibility of providing complete analytical support to the research programs at ORNL. This annual progress report includes examples of such support, which encompasses both research activities and direct methods development and service functions.

The Division has 162 members, a sizable decrease in number over the total of previous years. This decrease is largely due to the completion of the Molten-Salt Reactor Experiment and reductions in efforts in other research programs at ORNL. As a consequence of these lower budgets we have intensified our continuing efforts to increase efficiency of operation. The automation of data gathering and processing is an obvious approach to this objective, and we have made considerable advancement in this area in the past year. A sizable amount of our data operations is now handled by small dedicated computers. New facilities include computerized data processing, such as in the HFIR irradiation facility, and the fast analyzer system GeMSAEC for environmental-type analyses. We expect to apply computers as much as is feasible to all future operations.

We have increased our involvement in the environment through participation in the ORNL-NSF program on The Environment and Technological Assessment and through cooperation with the newly formed Ecological Sciences Division. The impact and relevance of analytical chemistry to the solution of environmental pollution problems are obviously significant and will grow more so as improved means of analysis are applied.

The Division's program on the characterization of cigarette tobacco smoke and condensate for the National Cancer Institute was expanded markedly. An essentially complete laboratory has been established for this purpose, and the efforts have been coordinated within the framework of the overall effort by the NIH to provide characteristics of safer smoking products. Through this program the Division has become proficient in organic analyses, thereby complementing the existing facilities for inorganic analyses. This is but the latest addition in the Division's overall program to broaden and extend its capabilities, a program that has led us into such diverse fields as analytical biochemistry, environmental studies, better high- and low-level radioactivity measurement, and complete automated analytical systems.

Summary

PART A. ANALYTICAL RESEARCH AND DEVELOPMENT

1. Analytical Methodology

The Analytical Methodology Group has worked conjointly this year with other groups, divisions, and educational institutions; this interaction continues to increase, due to involvement in environmental problems. Support is given a number of groups within ORNL, and a water laboratory is being established. Standard procedures for chemical and biochemical oxygen demands are operative, and a thermal analyzer for total organic carbon determination is on order. Preliminary results from a study of electrochemical monitoring devices for air and water pollutants are encouraging. Investigation of environmental applications of the GeMSAEC photometric analyzer continues to progress; one study has been completed, and a second is nearing completion. The investigation of the gas chromatography of aqueous solutions has begun, with determination of inorganic anions in waters being stressed. Development of a pyrolysis gas chromatographic system for determining P, N, S, and C in ecological samples is a joint effort between the Ecological Sciences Division and the Analytical Chemistry Division. Use of pyrolytic degradation in this system is not possible, so the pyrolyzer was replaced with an inlet system and a catalytic hydrogenation furnace; the modified system is being tested now. Active participation was maintained in the NSF-sponsored summer study, the initial phase of Project IDEA (i.e., *I*nter*d*isciplinary *E*nvironmental *A*ssessment).

The Tobacco Smoke Analysis Project, sponsored by the National Cancer Institute, National Institutes of Health, underwent a rather severe change in orientation this year; a request was received to set up facilities and methodology for analyzing a large number of cigarette and cigarette smoke condensates. (These comprise cigarette samples of 23 experimental cigarettes that are under study elsewhere.) Thus, research efforts were severely curtailed while equipment, facilities, procedures, and staff were acquired and made functional. The laboratory, now operative, has completed the analysis of samples of all 23 experimental cigarettes for "tar," nicotine alkaloid, water, and total particulate matter. The smokes have been analyzed for acetaldehyde and acrolein. A rather brief investigation was made into the use of sulfur-specific detection for gas chromatographic examination of sulfur-containing compounds in smokes. Profiling studies have continued, as has the examination of the chromatographic behavior of phenols, nitrogenous compounds, acids, and polynuclear aromatic hydrocarbons. The experience gained in this project should prove useful in future programs at ORNL.

Analytical support and analytical research within ORNL's Transuranium Research Laboratory continue. A complexometric method for determining curium was developed so that half-life measurements could be made; a new controlled-current coulometric titrator was used for this work, as well as for other applications during the past year. A study into the use of bathophenanthroline to prevent iron from interfering in the controlled-potential coulometric method for determining plutonium was completed. Tin oxide ("conducting glass") electrodes continue to look especially promising for electrochemical studies of the transuranium elements; these have been used with a number of techniques, and their characteristics are under study. Some preliminary experiments with thin-layer electrochemical techniques have been conducted, with promising results. An instrument for examining twin-electrode thin-layer electrochemical techniques has been acquired and tested briefly.

The study of decentralized abstracting and indexing of reports for *Nuclear Science Abstracts* was completed this year, and the results were reported and presented. Developmental work with the silicon-specific detector for gas chromatography was also completed this year. This device will be used in studies of the "on-column

silylation" technique when time permits. Gas chromatography continues to be a powerful tool in attacking many short-term problems; two examples are the qualitative examination of aqueous products from autoclaved paper wastes and the survey of animal organs for DDT content. Increased capabilities in liquid chromatography seem warranted in the Division, and efforts are under way in this direction.

2. Reactor Projects

Samples of radioactive MSRE fuel were analyzed for U(III) using two methods proposed for in-line analysis of the fuel of breeder reactors. Both the voltammetric and spectrophotometric methods, which have been demonstrated to provide accurate results on laboratory samples, gave U(III) concentrations substantially below those expected from reactor operating history. Because of sampling and transfer problems it was not certain that the samples analyzed were representative of the fuel in the reactor. For both types of samples it was possible to adjust U(III) concentrations while the samples were in the hot cell. The variation of measured U(III) concentrations on reductive and oxidative treatment of these samples paralleled that observed in previous experiments on nonradioactive melts. This indicated that the methods would be applicable to future in-line measurements. Spectral changes were also observed in these samples that correspond to the generation of U(III) via the radiolytic loss of F_2, a change predicted but not previously observed experimentally.

During the last runs of the MSRE, on-site equipment to measure the tritium content of gaseous reactor streams was set up. Dual-temperature oxidation of these streams was used to distinguish tritium combined as methane from the total tritium. Special sampling techniques were devised to measure the rate of diffusion of tritium into coolant stack air.

Electrochemical methods appear to offer one of the more practical approaches to the in-line analysis of reactor salt streams. Kinetic measurements were made on the Ni/Ni(II) couple in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ which show it to be a reversible couple suitable as a reference electrode. A new nickel reference electrode has been designed and fabricated for use in molten fluoride salts at reactor temperatures (650°C). This electrode, which is unaffected by reducing melts, incorporates a single crystal of LaF_3 as an ionic conductor between the reference electrode melt and the experimental melt. It is planned to use a PDP-8/I computer to control the voltammetric determination of U(IV)/U(III) ratios in the simulated MSRE fuel salt of a thermal convection loop.

Spectrochemical methods are also promising for the in-line analysis of molten-salt streams. Certain actinides are of considerable interest in the operation of molten-salt breeder reactors, and spectral studies of Pa(IV), Pa(V), Pu(III), and Cm(III) in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ have been made. Americium(III) impurity was identified in the curium solution.

The present phase of the electrochemical generation and spectral characterization of unusual oxidation states of solute species in molten fluoride salts has been concluded. This work was performed to survey the utility of this technique as a preparative and investigational tool.

The operation of an $NaBF_4$ circulating test loop by the Reactor Division is part of the investigation of $NaBF_4 \cdot NaF$ (92-98%) as a heat transfer medium for reactors. Two contaminants in the off-gas (BF_3 in helium) from this test loop were trapped and identified. A study of the removal of the hydrolysis products from the off-gas prior to recovery of its constituents for recycle is under way, and an on-line analysis system for BF_3 in helium-BF_3 gas mixtures has been constructed. Preliminary studies of the volatilization of the chlorides of certain constituents of reactor fuel have shown that lithium may be separated from the rare-earth chlorides as $LiAlCl_4$.

The apparatus for the analysis of natural gas samples from wells stimulated by underground nuclear explosions has been completed and calibrated. Agreement within ±1% was obtained in the activities of fractions separated from repeated analysis of a "Gasbuggy" sample furnished by LRL. This equipment will be used for the separation and determination of long-lived radionuclides in the natural gas from the Rulison Project.

3. Analytical Biochemistry

Analytical assistance has continued to the Biology and Chemical Technology Divisions in support of the Biological Macromolecular Separations Technology Project and to the Molecular Anatomy (MAN) Program. In the analysis of transfer ribonucleic acids (tRNA's), assay conditions were optimized for arginine-, aspartic acid-, glutamic acid-, and isoleucine-accepting tRNA's from *E. coli* by statistically designed experiments, bringing to ten the number of optimized assays. The assay of mammalian tRNA's, mainly from bovine liver, has been studied, and enzyme preparation procedures and assay conditions which are adequate at this stage

have been developed. A rapid method for checking the specific activity of the ^{14}C-labeled amino acids used in the tRNA assays was developed. The terminal nucleoside and base ratios in both tRNA and ribosomal RNA (rRNA) have been determined by anion and cation exchange procedures. Work on the gas chromatographic analysis of nucleic acid components as their trimethylsilyl (TMS) derivatives has been extended to nucleotides and a modified derivatization procedure developed for cytidine and related compounds. The Chemical Technology Division is studying two protein separation techniques: separation of histones by column chromatography and concentration of enzymes by ultrafiltration. In support of these studies methods are being developed for the analysis of histones and polyacrylamide gel electrophoresis on a 15% gel in an acidic medium, and standard methods have been tested for the assay of the enzymes chymotrypsin and aldolase.

Constituents of body fluids isolated by high-pressure chromatographic techniques by the Biochemical Separations Systems Development Group of the MAN Program are continuing to be identified. Overall, 60 different ultraviolet-absorbing compounds and 11 carbohydrates have been found, mainly by a combination of gas chromatography and mass spectrometry. A gas chromatographic method for the analysis of common anions was also developed. A gel electrophoresis laboratory which will not only develop analytical electrophoresis methods but will also study the problems of measuring and recording data and long-term storage and retrieval of data is being established to serve the MAN Program. As part of an effort to improve the performance of automated protein sequenators by modifying the chemistry, 22 amino acid derivatives with methylthiohydantoin (MTH's) and thiobenzoylthioacetic acid (PTA's) were prepared and attempts made to analyze mixtures of MTH amino acids. All but MTH cysteine could be separated and determined by gas chromatography. Attempts to separate the PTA derivatives have so far been unsuccessful.

Assistance to NAS-NRC committees to establish specifications and criteria for the purity of biochemical compounds has continued, and the purity of 58 nucleic acid derivatives has been evaluated, mainly by paper chromatography, gas chromatography, and ultraviolet spectrophotometry, on behalf of the Subcommittee on Nucleotides and Related Compounds. For the Committee on Specifications for Adenine in Anticoagulant Solutions, six adenine samples were exhaustively tested, and specifications based on these data will be written. Differential scanning calorimetry as a means of determining absolute purity is under evaluation, but at present precision is poor.

Ligand-exchange chromatography has been used to separate and determine various oxypurines in physiological samples, pharmaceutical preparations, and common beverages.

A computerized GeMSAEC analyzer was installed in the Health Division; evaluation of the system includes comparison of results obtained here and at various hospital laboratories using different automated instruments and methods.

4. Nuclear and Radiochemistry

Mercury in environmental samples has been determined by reactor neutron activation analysis, by isotope exchange, and by use of ^{252}Cf. Sensitivity for the nondestructive neutron activation determination of copper and manganese in biological tissue has been improved, 15 trace elements have been determined in an air filter, and a method to determine arsenic in foliage samples by use of a ^{241}Am source and x-ray fluorescence was developed. The cooperative isotopes program continued, with an improved quality control program; a large-scale survey, "National Uses and Needs for Standard Radioactive Materials," conducted for the National Research Council was completed. Half-lives for ^{153}Gd, ^{85m}Sr, ^{87m}Sr, ^{88}Y, and ^{137}Cs were redetermined. Attempts to confirm effects observed elsewhere of chemical and physical environment on half-lives of radionuclides gave negative results. Systematic study of nuclear decay structure in the rare-earth region continued, and the photofission of iron has been shown to yield nuclides of mass <35. Attempts to enrich actinide elements through use of Szilard-Chalmers reaction with metal-phthalocyanine complexes were unsuccessful. Fission product release from irradiated fuel microspheres was studied, and a new method for the determination of strontium was developed. The method of proton irradiation for $^{13}C/^{12}C$ and $^{15}N/^{12}C$ ratios in biological samples was demonstrated to be reproducible and sensitive. Additional results have been obtained on induced activities in returned Apollo 11 and Apollo 12 samples. A small low-level spectrometer system has been calibrated for environmental radioactivity survey purposes. Remote gamma spectrometry with a Ge(Li) detector was used to measure fission product deposition in the MSRE, and a table of accurate gamma energies and branching ratios was compiled to aid in nuclide identification. Two new gamma-ray spectrometer systems employing PDP 15/20 computers have been developed, but delivery of one of

them to the HFIR Activation Analysis Laboratory awaits final approval. The photon and fast neutron activation facility at the ORELA, however, was put into operation.

The Nuclear Safety Support Program for pressurized water reactors (PWR) continued; an encouraging finding was that $NaVO_3$ in base borate decreases $G(H_2)$ by a factor of 10. Studies continued on radiolytic sulfur and CH_3I, and studies similar to those for the PWR were begun for boiling-water reactors. Tartrate and formate ions were found to give good protection for certain colorimetric reagents. ^6Li has been used to study the effects of radiation on analytical methods; neutron irradiation of this nuclide yields tritons and alpha particles whose effects can be studied without the hazard of handling large amounts of alpha emitters. Improved wave shifters have been recommended for use in Cerenkov counting, and the exposure of certain phosphors to alpha radiation was shown to limit their usefulness. Use of phosphor screens for short-term information storage was also studied.

5. Analytical Instrumentation

Four trends have been observed in design of instrumentation: use of theory in circuit design, use of theory in analytical measurement, optimal mixing of all elements, and development of computer interrelated systems; these have been put into practice. A new polarograph and a drop-time controller were fabricated and performance checked; results were excellent. A dual potentiostat capable of controlling the potentials of two electrodes simultaneously and independently was designed and put in use, and the controlled-potential and current cyclic voltammeter was modified. A high-impedance, ultra-low-drift differential voltmeter was designed for molten-salt applications, and the remote titrant delivery units of two potentiometric titrators in the TRU facility were replaced. Three CAPE packages were prepared, and other detailed drawings and check-out procedures were supplied to interested parties. Two programming courses have been instituted: one using a Hewlett-Packard programmable desk calculator, the other using a PDP-8 computer. The latter computer was programmed to make unattended measurement of U(IV)/U(III) ratios in molten fluoride salts. The PDP-8 has also been applied to GeMSAEC, and the FOCAL capabilities of the computer were considerably extended. GeMSAEC is also being used to investigate a kinetic technique for metallic ions and in a program for clinical analyses; programs have been written to assist in both these projects. The PDP-8 has also been interfaced to a Perkin-Elmer differential scanning calorimeter, programmed, and the system used for purity measurements in the Analytical Biochemistry Group. The PDP-8 has been programmed to perform linear systems analysis for use in circuit design, and the computer is being interfaced to a simple cell transducer to obtain information for design and operation of polarographic systems.

6. Methods Development and Evaluation

The activities of the Methods Development and Evaluation Laboratory were directed primarily to three general areas: LMFBR reactor fuel analysis, the transuranium program, and MSRE fuel analyses. Work was performed conjointly with the Chemical Technology, Reactor Chemistry, and Metals and Ceramics Divisions on the production and characterization of the U, Pu nitride, carbide, and carbonitride fuels, irradiation studies of these materials, and methods for the separation, purification, and determination of the actinide rare-earth elements. In addition, analytical support and assistance were given to all groups within the Service Laboratories as well as to other divisions.

7. Mass Spectrometry

The study of the thermal ionization behavior of the actinides has been continued with measurements of desorption energies and mean residence times of ions and neutrals. The first ionization potential of curium was measured as 6.18 ± 0.09 eV. A new sample wheel carrying ten filaments has been designed and constructed, and design calculations have been made for improved configurations of double-focusing mass spectrometers. The interfacing for the 1130 computing system was accepted and permits direct transfer of data from outside sources into the computer at rates up to 10,000 words/sec.

A combined gas-chromatograph–mass-spectrometer system was put into routine operation. Most of the samples handled during the year were from the Body Fluids Analysis Program. A series of trimethylsilyl derivatives of inorganic ions were studied with the GC-MS. Collaborative work with Snyder and Blank at ORAU assisted the study of the biosynthesis of the ether bond in glycerolipids. A large number of organometallic complexes were studied for Laubereau and coworkers in the Chemistry Division of ORNL.

Studies of gases in various minerals and of the isotopic compositions of uranium and lead from biotite containing "anomalous" pleochroic halos were done as assistance to R. V. Gentry in the Chemistry Division.

Searches were made to high mass (up to 350) by thermal and spark ionization looking for "superheavy" elements.

8. Electron Microscopy

Transmission electron microscopy has been used for examination with high resolution (10 to 20 Å) of powders, thin sections of metallurgical specimens, and surfaces of solids that are too thick for transmission of electrons. An example of the examination of the surfaces of solids, which requires replication, is featured. The installation of a scanning electron microscope, which will greatly facilitate the examination of solid surfaces, is under way. The electron microprobe technique has been used for elemental analysis of very small particles and for the determination of homogeneity in the elemental composition of solids; gradients in the concentration of elements at the surfaces of solids have been measured. X-ray diffraction has been used for compound identification and the measurement of variations in lattice parameters of solid solutions as a function of composition. A routine service for estimating crystallite size from the breadth of lines diffracted from UO_2 and ThO_2 in aqueous suspension has been developed. Photoelectron spectroscopy has been found to be a very useful analytical tool with many applications. Pollution problems and biological compounds have been studied, and a contribution to the characterization of a newly synthesized compound, $KBrO_4$, has been made with this technique. A facility for analytical service in photoelectron spectroscopy is being constructed.

PART B. SERVICE ANALYSES

9. Spectrometry Services

Relative sensitivity values, K_r, were established for certain rare-earth and actinide elements with respect to erbium by solution and spark-source mass spectrographic techniques. The relative sensitivity values for the rare-earth elements were near unity, and for the actinide elements the range was from 1.61 to 2.65. A reproducibility of about 4% over a concentration range of 1 to 250 indicated that the K_r constants were independent of concentration.

For 2-μg-sized samples of the actinide elements the spectrum intensity was composed of 77% single, 20% double, and 1% triply charged metal ion lines and 2% complex ions of the type MC_2^+ and MO^+. The relative sensitivity values for the actinide elements are compared with the temperatures observed for thermal ion emission from a hot rhenium filament.

The output of the two spark-source mass spectrometers increased 55% over the previous year. Thorium concentrations in a series of zirconium-thorium alloys were determined by the isotopic dilution spark-source mass spectrographic technique. For the preparation of plutonium-uranium oxide microsphere samples for spark-source mass spectrographic analysis, a 25-ton ring press was installed in a glove box.

The Mass Spectrometry Service Laboratory measured the relative isotopic abundances of over 1000 stable isotope samples of 40 elements. Over 600 cylinders of A, He, and N_2 were certified for ORNL and the Y-12 plant.

The Transuranium Mass Spectrometry Laboratory continued to supply isotopic analyses of radioactive elements for a diverse group of customers. All elements from thorium through einsteinium are done routinely, and other elements are done when requested.

The Spectrochemistry Laboratory reported 49,000 results. Environmental samples from the Health Division constituted the largest number of results. Large numbers of metal, alloy, and salt samples were analyzed employing the Paschen direct-reading spectrometer for Inspection Engineering, Metals and Ceramics, Reactor Chemistry, and the Reactor Divisions. The number of results for the Y-12 plant more than doubled.

Nuclear magnetic resonance (NMR) spectrometry was used in the study of the effects of curing agents on resins and to check on the efficiency of polymer separation by molecular distillation. Biology Division personnel were aided in the study of enol-keto and thiol-thio structures of several pyrimidines by recording the NMR spectra of both the parent and its mercury derivative.

The Infrared Spectrometry Laboratory completed the reference spectra file on solid biological compounds. Because of the cost and scarcity of some of these biological compounds, a semi-micro mulling technique was developed and exclusively used. The accuracy of the Karl Fischer determination of water in 2-ethyl hexanol was checked by IR.

10. Process Analyses

The process laboratories performed some 165,000 analyses during the past year. This was a 19% decrease from last year with a decrease of 18.5% in personnel.

The High-Level Alpha Radiation Laboratory was remodeled and new equipment installed. Several methods were revised to give more precise analyses.

The General Analyses Laboratory adapted new methods for determining O/M ratios in substoichiometric UO_2; nitrogen in UN; BF_3 in $NaF{\cdot}BF_3$; NaF in mixtures of NaF and $NaBF_4$; and Ce, Gd, and Dy in MSRE salt. Equipment for measurement of helium and hydrogen and density of irradiated alloys and graphite was constructed. Atomic absorption was used in the analysis of water samples for alkali and alkaline earths.

The General Hot-Analyses Laboratory decreased its hot-cell work with the shutdown of the MSRE. New equipment and methods were installed to handle the analysis of samples from the LMFBR program.

The Radioisotopes-Radiochemistry Laboratory has shifted its work from radiochemical separation of MSRE samples to more of the environmental and nondestructive type of radiometric analyses. The half-life of ^{10}Be was determined to be about 1.6×10^6 years. A new Ge(Li) detector with an active volume of 54 cm^3 was put into service.

The Radiation Control and Safety Officer made several inspections during the year. Approvals were given various investigations for safe operations. Windows in the two "hot" cell areas were flushed and cleaned.

The number of control samples included in the Statistical Quality Control Program decreased 34.0%; the overall quality level increased from 91 to 93%.

Work in inorganic preparations has greatly decreased because of deemphasis of fused-salt programs. The reduced work load is concerned mainly with the heat treatment and preparation of alloys and the preparation of ferrites. Because of the increased use of isotopes in preparations, considerable time is now spent in salvage operations.

Part A. Analytical Research and Development

1. Analytical Methodology

W. D. Shults, Group Leader

M. R. Guerin, D. R. Matthews[2], J. R. Stokely
A. D. Horton[1], C. A. Pritchard, H. W. Wright
C. A. Horton, R. B. Quincy, G. Olerich

R. L. Coleman[3], J. R. Kuempel[4], J. E. McCracken[5], J. L. Robinson[6]

ENVIRONMENTAL ACTIVITIES

During the past year, we have continued to support the Laboratory's environmental programs and have expanded our capabilities via new facilities and new research efforts.

Water Laboratory. We are establishing a laboratory that is oriented to analyses required in studies related to water and water quality. The Technicon AutoAnalyzer is located there, for phosphate and nitrate analyses. Approximately 2000 water samples were analyzed for phosphate this year by the Technicon (phosphomolybdate) method. Because of the need for extreme sensitivity in this analysis, a rather thorough investigation of the Technicon procedure and equipment was made. We were able to improve performance considerably: our detection limit is now 5 ppb (P); previously it was 100 ppb (P).

We continue to have requests for dissolved oxygen analyses and for chemical oxygen demand (COD) determinations. Biochemical oxygen demand (BOD) is now being requested frequently. Standard procedures have been set up for these determinations. We have also purchased a Carle thermal analyzer for total organic carbon (TOC) measurements of aqueous samples of all types. When this instrument is operative, both conventional and modern facilities for performing these common analyses will be operational, and we will be in an excellent position to study the real meaning of these procedures.

Applications of the GeMSAEC Photometric Analyzer. A program of study into environmental applications of the GeMSAEC analyzer was initiated this year. Our GeMSAEC system was built for this type of work: it incorporates UV and visible sources, quartz optics, and monochromated light, and it is interfaced with a PDP-8/I computer. The determination of phosphate (phosphomolybdate) was studied first because it is a well characterized and frequently used procedure. We wanted to learn the idiosyncrasies and unique features of the GeMSAEC system during this initial study and to develop versatile and reliable software. The results were excellent. Precision and accuracy compare favorably with conventional methods. External calibration was found to be feasible, that is, a single calibration run can be used for successive runs provided procedural details are not altered. We also studied the time dependency of

[1] Reactor Projects Group.

[2] General Analyses Laboratory.

[3] ORAU Predoctoral Fellow from The University of Tennessee, Knoxville.

[4] Summer research participant from DePauw University, Greencastle, Ind.

[5] ORAU Predoctoral Fellow from the University of Missouri, Columbia.

[6] Summer research participant from Southeastern State College, Durant, Okla.

this procedure and learned that nonequilibrium reactions can be utilized under some conditions in the GeMSAEC analyzer. Parabolic regression was found to be superior to linear regression for reducing data, especially when nonequilibrium reactions are used. A paper describing this work has been submitted for publication.

We are presently studying two turbidimetric methods for determining sulfate using the GeMSAEC system. One method is based upon the classical barium chloride procedure, which, in the GeMSAEC system, is applicable to sulfate concentrations ranging up to 40 ppm. The other method utilizes 4-amino-4′-chlorodiphenyl as turbidant; it is the more sensitive method but is limited to sulfate concentrations less than 20 ppm. The prime advantage of the GeMSAEC analyzer here is that samples and calibration standards are treated exactly alike. Lack of such control is the inherent weakness in all turbidimetric methods. The real questions that must be answered concern the behavior of fine particles within the centrifugal field: Are they sufficiently stable for measurement and is there a significant time dependency? Our results indicate that the GeMSAEC analyzer provides great advantage for turbidimetric analyses. Indeed, we believe that the GeMSAEC approach offers considerable potential in environmental analysis.

Pyrolysis–GC System for Determining P, N, S, and C. The development of an analytical system for determining trace P, N, and S in diverse ecologically important materials is a joint undertaking between the Analytical Chemistry and Ecological Sciences Divisions. The system is based upon pyrolytic degradation of the sample, gas chromatographic separation of the degradation products, and selective detection and quantitation of the P, N, and S in the separated products. Simple pyrolytic degradation has been found to give low and erratic yields. Catalytic hydrogenation to form P, N, and S hydrides is promising. We have purchased a Dohrmann pyrolyzer and solid sample inlet system and incorporated them into our GC equipment. Preliminary testing of the modified system has just begun.

Gas Chromatography of Aqueous Solutions: Inorganic Anions. The formation and chromatographability of trimethysilyl (TMS) derivatives of several inorganic anions has been reported.[7] We are examining this technique in some detail, with the aim of applying it to the determination of anions in aqueous systems. Efforts to date have been restricted to phosphate and sulfate and to the use of TMS derivatives. These derivatives can be observed with a flame ionization detector; we have also studied the use of P- and S-selective flame photometric detection. With this type of detection and a 6-ft by ¼-in.-OD glass column containing 3% OV-17 on Gas Chrom Q (90/100), as little as 10 ng of PO_4 and 800 ng of SO_4 can be determined. Since sensitivity would be expected for SO_4, we suspect loss within the column itself. Several other columns have been examined, however, with little difference in performance.

These studies have involved derivatization of a small portion of the aqueous solution directly. Since water consumes derivatization reagent and because some concentration is needed, we are considering anion exchange and solvent extraction schemes that are compatible with the GC procedure. Phosphate and sulfate can be extracted satisfactorily into an organic solution of a tertiary amine or quaternary ammonium salt, but we have not yet been able to derivatize the extracted anionic species. This work will continue. Our goal is to develop a simple, rapid means for determining several anions in a single aliquot of an aqueous sample.

Participation in the ORNL-NSF Project IDEA. The initial phase of a program of *I*nter*d*isciplinary *E*nvironmental *A*ssessment (IDEA), sponsored by the National Science Foundation, consisted of a summer study of several broadly defined problem areas of environmental significance. The study was conducted by six interdisciplinary groups, each having representatives from appropriate ORNL divisions. We were engaged in the study of Environmental Indices. This study was directed at conceptualization of both general and specific indices of environmental quality. Very little analytical chemistry, as such, was involved at this early stage of the project. However, it is clear that much analytical chemistry will be required if the concepts developed in this study are to be tested and put to use.

CIGARETTE TOBACCO SMOKE ANALYSIS PROGRAM

We are establishing a facility for the extensive chemical analysis of the smoke of a series of experimental cigarettes. The results of these analyses will eventually be correlated with the results of biological tests of the same cigarettes. Cigarette production, procedure authorization, and final data correlation are the responsibility of the Tobacco Working Group of the

[7] W. C. Butts, *Anal. Lett.* "Gas Chromatography of Trimethylsilyl Derivatives of Common Anions", 3(1), 29–34 (1970).

National Cancer Institute. The availability of carefully defined chemical and biological data on the smokes of highly characterized cigarettes should allow confident assessments of the relationship between cigarette characteristics and experimental tobacco carcinogenicity.

Facilities. The special facilities and equipment necessary to study the chemistry of cigarette smoke are now operational. A four-channel version of the Philip Morris 20-channel automated smoking machine has been used to smoke in excess of 1600 cigarettes in various studies of the tar-nicotine deliveries of cigarettes. We have modified a Filamatic vial-filler and fabricated a four-port smoking machine to provide two smoke generation systems for analysis of whole smoke and the gas phase of smoke. Recently a commercial smoking machine was received from Germany for the production of condensate. We have also fabricated an apparatus for the measurement of the "resistance-to-draw" of an unlighted cigarette and an apparatus to test Cambridge filter holders for leaks. A laboratory maintained at 75° and 60% relative humidity and illuminated with yellow light tubes is in use for all cigarette conditioning and smoking operations. Storage facilities and techniques necessary to store and handle more than 23,000 cigarettes have been established.

Specialty analytical equipment is also on hand. A Griffith steam distillation apparatus has performed excellently in over 400 distillations of smoke particulate matter. A cryothermal gas chromatograph and a routine analytical gas chromatograph are in constant use in analyses of the particulate matter, condensate, and gas phase of smokes. A fluorescence spectrophotometer is in use in studies of the analysis of polycyclic aromatic hydrocarbons of smokes. Arrangements have been made for use of the Division's liquid scintillation counting facilities for studies of ^{14}C-labeled carcinogens. Ion-selective electrodes, polarographs, potentiometric titrators, and pH meters are in use in several research and routine operations. Cary model 14, Beckman model B, and Beckman model DBG spectrophotometers are in use in several spectrophotometric procedures. A research gas chromatograph equipped with element-specific detectors is finding extensive use in methods development and research operations.

Results and Methodology. We have completed determinations of the total particulate matter, water, nicotine alkaloid, and "tar" deliveries of the full series of 23 experimental cigarettes. Cigarettes were smoked under high and low draft conditions, and our results indicate that low draft conditions are preferable for interlaboratory comparisons of the data. Extensive statistical and comparative treatments of the data allow us to conclude that the generation and analysis of smoke particulate matter at ORNL produce results of a quality comparable with those generated by the highly experienced laboratories of the tobacco industry.

We have achieved excellent precision in the analyses of the gas phases of the 23 experimental cigarettes for acetaldehyde and acrolein using a state-of-the-art analytical system designed and fabricated by this group. Parts of the system are applicable for use in other analyses of the gas phase of smokes. The complete system, involving a smoking machine, a valve interface, and a cryothermal gas chromatograph, affords many unique opportunities for the study of the gas phase of smokes.

Spectrophotometric techniques are presently being applied to determine the hydrogen cyanide and formaldehyde deliveries of the experimental cigarettes. We are preparing for studies of the carbon monoxide, carbon dioxide, and oxides of nitrogen deliveries of the cigarettes. An apparatus designed to measure the pH of whole smoke has been applied to studies of the gas phase of smokes. Substantial research may be required to establish the significance of the response of a pH meter to the gas phase of smoke.

We are preparing to carry out a series of analyses of cigarette smoke condensate. A procedure for the determination of the water and acetone contents of condensate preparations has been developed and verified. A gas chromatographic system for the simultaneous determination of nicotine and nornicotine has proved useful for the determination of nicotine but requires a study of the quantitative significance of the data generated for nornicotine. Tracer techniques, extraction procedures, and gas chromatographic conditions have been determined for the quantitative assay of the phenol and cresol contents of condensates.

Research Activities. Research activities in various aspects of the analytical chemistry of cigarette smokes have been maintained. A brief study of the polarographic properties of *N*-nitrosamines has suggested this as a possible technique for their determination. We have developed a gas chromatographic procedure that allows a quantitative visualization of at least 40 of the major components of smoke condensate in less than 1 hr. Such chromatograms – profiles of the components of the given samples – can also be conveniently generated for samples of the gas phase of smokes. The direct application of porous polymer column gas chromatography coupled with flame photometric detection provides an excellent means of studying the distribution of sulfur-containing compounds of smokes. The gas

chromatographic characteristics of phenols, nitrogen compounds, carboxylic acids, and polycyclic aromatic hydrocarbons have been studied to various degrees. An analytical liquid chromatograph has been tested in a preliminary way for its utility in the analyses of condensates for polycyclic aromatic hydrocarbons.

A detailed progress report describing the facilities, procedures, and results of this program as of September 1, 1970, is in preparation.

ANALYTICAL RESEARCH AND SUPPORT ACTIVITIES IN THE TRANSURANIUM RESEARCH LABORATORY

We are engaged in analytical research and support activities in the Transuranium Research Laboratory (TRL). Research activities are aimed at application and development of new techniques for analyzing and studying the properties of the transuranium elements. Support activities involve application of diverse analytical techniques which require the use of TRL facilities.

Complexometric Titration of Curium: Half-Life Measurement. An absolute method for chemical analysis of curium has been developed. The method was developed for determination of the half-lives of ^{246}Cm and ^{248}Cm by specific activity measurements and to provide a method for accurate chemical analysis of long-lived curium isotopes in the future. The procedure consists in addition of a known excess of ethylenediaminetetraacetic acid (EDTA) to the curium and determination of the excess EDTA by complexometric titration with mercury(II). Since only small quantities (*ca.* 0.5 micromole) of curium were available, mercury(II) for the back titration was generated electrolytically by anodic dissolution of a mercury pool electrode. The end point in the titration was determined potentiometrically with a gold amalgam electrode. These coulometric titrations were made with the controlled-current coulometric titrator described below. The accuracy and precision of this procedure were evaluated with neodymium. The relative standard deviation was 1.5%, and the relative error was less than 1% when 100 μg of neodymium was titrated. Similar precision was obtained in the titration of curium for the half-life measurements. Nuclear data for these measurements were obtained by C. E. Bemis of the Chemistry Division. Chemical purification of curium was performed by R. D. Baybarz of the Chemical Technology Division. The results of this work are being prepared for publication.

Potentiostatic Coulometry of Plutonium in the Presence of Iron. For many years we have needed a means for circumventing the interference of iron in the potentiostatic coulometric method for determining plutonium. We have completed a study of the use of batho-phenanthroline sulfonic acid (BPSA) in this method. Addition of BPSA to the medium alters the formal potential of the iron couple and allows plutonium to be determined without iron interference. This work has been submitted for publication.

Applications of Conducting Glass Electrodes. Conducting glass is a semiconducting film of antimony and tin oxides which is fired on a Pyrex glass surface. We believe electrodes of this type will be applicable in our studies with the transuranium elements and for electrochemical work in general. Conducting glass electrodes (CGE) have been used in voltammetric, coulometric, and thin-layer electrochemical cells during the past year.

A promising application of the CGE in coulometry is the determination of uranium and plutonium in a single aliquot. Conventionally, separate electrodes and coulometric cells are required for uranium (mercury electrode) and for plutonium (platinum electrode) analysis. Successive titration of these elements in a single cell would greatly simplify the procedures and provide less chance of error. We fabricated a coulometric cell that has a large-area conducting glass electrode and studied the titration of uranium and plutonium mixtures. Although encouraging results were obtained, two practical problems have not been solved. One is that the electrolyses are slow; we need to design a cell with a maximum electrode-area-to-solution-volume ratio. Second, there is a rather high blank correction associated with the uranium titration. Studies into electrode design (discussed below) are aimed at understanding and solving this problem.

We also investigated the use of the CGE for determining berkelium. The large oxygen overvoltage of the CGE, plus exploratory work with cerium(III) as a "stand-in" for berkelium(III), suggested that berkelium could be determined by coulometric oxidation to berkelium(IV). The titration did not prove to be feasible because of direct (or possibly indirect) oxidation of radiolysis products along with berkelium(III). Similar behavior was observed in several media. Unique behavior was observed in sodium carbonate medium. In this medium, we observed oxidation of berkelium(III)

by radiolysis or radiolysis products. Normally, in acid media, radiolysis due to ^{249}Bk results in the reduction of berkelium(IV). This behavior in carbonate medium was observed initially in our electrochemical work, and it has now been confirmed independently by spectral studies. The magnitudes of the autooxidation and autoreduction rates are comparable.

Analytical Support in TRL. We continue to provide analytical support for TRL programs. Carbon, hydrogen, and nitrogen analyses are provided frequently, and a special facility has been installed for this purpose. It has been described in a special report.[8] Some typical sample types and our results for them are published.[9]

The Gaseous Diffusion Plant at Paducah asked us to perform several oxidation state analyses on samples that contained cobalt, plutonium, and uranium fluorides. Considerable development work was involved. Procedures based upon selective dissolution and coulometric analysis of the resulting solutions were discussed and utilized.

ELECTROCHEMICAL RESEARCH

Controlled-Current Coulometric Titrator. A new approach to coulometric titrimetry is being studied in which the electrolysis current is controlled in such a manner that the chemical system is maintained closer to equilibrium during a titration than heretofore possible. The titration curve of indicator electrode potential vs integrator output potential is plotted continuously by an *X-Y* recorder. The controlled-current coulometric titrator (Coulotrator) was built and tested at the University of Missouri, Columbia, and was brought to ORNL for evaluation and application. Improvements in circuitry and cell design have been made at ORNL. The instrument has been evaluated with four types of titrations: those involving redox, precipitation, acid-base, and complexometric reactions. Specific methods have been developed for (1) the precise and accurate determination of milligram quantities of iron, uranium, and vanadium, singly and in mixtures; (2) the precise and accurate argentometric determination of chloride, bromide, and iodide, singly and in mixtures; (3) the determination of micromolar amounts of strong and weak acids and strong bases; and (4) the microdetermination of curium and neodymium. This approach to coulometric titrimetry offers good precision, accuracy, and versatility; it should be valuable for both research and routine work. Manuscripts that describe the instrument and its applications are being prepared.

Electrochemical Properties of Stannic Oxide Electrodes. We have initiated a study into the properties of tin oxide (conducting glass) electrodes so that applications of electrodes of this material can be made in coulometry, voltammetry, and thin-layer electrochemistry. Properties that are of interest are the specific resistance of the conducting layer, anodic and cathodic limits of electrodes in aqueous solutions, reversibility, and adsorption phenomena at the electrode surface.

A number of electrodes of different composition were prepared by spraying the (hot) glass surface with tin-antimony solution. Tin-to-antimony ratios in the spray solution were varied between 99.0 and 90.0 wt %. The electrodes were then cleaned (in different ways) and tested for electrochemical performance. The properties of electrodes prepared with a given tin-to-antimony ratio were quite similar, except that specific resistance is determined by layer thickness. Anodic and cathodic limits were 1.6 and −0.4 V vs S.C.E., respectively, in 1 *M* H_2SO_4. We observed voltammetric peaks upon both anodic and cathodic scan in 1 *M* H_2SO_4, the peak heights being dependent upon the electrode itself. The peaks are diminished or removed by a water rinse. We also observed that electrodes having a high antimony content are permanently altered by polarization at approximately −0.4 V vs S.C.E. These features are being studied further.

The reversibility of four couples – Fe^{2+}, Fe^{3+}; U^{5+}, U^{6+}; Ce^{3+}, Ce^{4+}; and $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ – was examined with each electrode that we studied. Increasing irreversibility was observed with decreasing antimony content in the conducting layer. Electrodes prepared with 1 wt % Sb exhibited peak potential shifts of 200 to 400 mV, and those prepared with 10 wt % Sb exhibited shifts of only 50 mV. These shifts are somewhat dependent upon scan rate, but cannot be attributed entirely to uncompensated resistance. We expect to be able to optimize electrode design upon completion of this study.

[8] J. R. Stokely, *Installation and Performance of a Perkin-Elmer Model 240 Elemental Analyzer in a Glove Box*, ORNL TM-2825 (Oct. 13, 1970).

[9] M. D. Danford, *et al.*, "Preparation and Properties of Some Rare Earth and Americium Chelates", *Inorg. Chem.* 9, 1953 (1970).

New Instrumentation. Four instruments were acquired during the past year for our electrochemistry work. An ORNL model Q-2792 polarograph-voltammeter and a model Q-2942 drop-time controller were procured. An electronic integrator was built for the polarograph to allow us to do scanning and controlled-potential coulometry with conventional and thin-layer electrochemical cells. T. R. Mueller of the Analytical Instrumentation Group designed an instrument for electrochemical studies with dual working electrodes. It has been fabricated and tested preliminarily. This instrument provides independent potential control of two working electrodes with the capability of scanning either or both electrodes.

GAS CHROMATOGRAPHY

We have been engaged in several short-term projects this year, several of which involved gas chromatography. They are reported here.

Survey of Pesticides in Animal Organs. We were asked by researchers at ORAU to survey extracts of the brain, liver, and fat of pigeons that had been experimentally exposed to large doses of DDT. Hydrogen flame-ionization gas chromatography proved inapplicable because of the large quantities of nonpesticides in the extracts, but we were able to use our ^{63}Ni electron capture detector for this survey. Although the sensitivity of the detector was not optimized, it was possible to conveniently detect nanogram quantities of DDT. Under the conditions used, 40 pg of DDT was the approximate detection limit. The extracts were found to contain both *p,p'*-DDT and *o,p*-DDT as well as what appeared to be DDE. At least 8 other electron-capturing species were noted in most extracts. Extracts of the fat contained the largest amount of pesticide, while liver extracts contained less, and the brain extracts contained the least amount.

Liver and muscle extracts of South American marmosets were also surveyed. These animals had died soon after captivity. Although the marmosets were not experimentally exposed to pesticides, thin-layer chromatographic work carried out at ORAU suggested the presence of DDT or a similar unknown pesticide. Electron-capture gas chromatography revealed the presence of small amounts of what may be DDT in both muscle and liver extracts. A relatively large quantity of an electron capturing species that is not DDT or DDE was found to be present in the liver extract. A preliminary study of the marmoset tissue extracts using the flame photometric detector indicated that sulfur-and-phosphorus-containing pesticides were not present.

Examination of the Aqueous Products of the Autoclave Oxidation of Paper. The Housing and Urban Development Group at ORNL has been studying wet oxidation at elevated temperature and pressure as a means for treating waste paper. We have continued to provide analytical support for these studies, as mentioned in last year's report. During the past year, we examined a number of aqueous products and head-space samples by gas chromatography, attempting to establish the general composition of the organic materials that were present. Portions of the samples were analyzed directly for major low-molecular-weight components in solution and in the head-space vapor. The remainder of each sample was separated into acidic, neutral, and basic fractions. These fractions were concentrated and analyzed by methylsilicone column programmed-temperature gas chromatography.

The head space was found to contain at least six components possibly including *n*-propanol, acetic acid, and acetone. The aqueous liquid was found to contain at least ten components possibly including methanol, formaldehyde, ethanol, acetone, *n*-propanol, and acetic acid. Less than ten components, all relatively low boiling and present in small amounts, were observed by programmed-temperature gas chromatography of the basic fraction of the organic extract. Silylation did not significantly increase the number of peaks attributable to basic compounds. The neutral fraction was found to contain in excess of 35 compounds, approximately one-half of which are present in significant quantities. All but a few of the more minor compounds cannot include the hydroxyl moiety as evidenced by zero retention shift upon silylation. A regularly spaced distribution of peaks at the high-temperature end of the chromatogram suggests the presence of a homologous series. The retention positions of nine of these peaks agree very well with those for the C_{23}, C_{24}, C_{25}, C_{26}, C_{27}, C_{28}, C_{29}, C_{30}, and C_{31} *n*-alkanes.

The acid fraction was found to contain at least 40 compounds, approximately one-half of which are present in significant quantities. Most of the 40 compounds visualized appear to be carboxylic acids. One compound, suggested by gas chromatography and mass spectroscopy to be benzoic acid, greatly predomi-

nates. Some evidence for the presence of simple phenols was also found.

DECENTRALIZED PREPARATION OF *NUCLEAR SCIENCE ABSTRACTS* ENTRIES

The work reported last year on the decentralized preparation of documentation, abstracts, and indices by two systems using ORNL reports for input material continued during this year. The results[10-12] indicate it is feasible for the International Nuclear Information Service to use decentralized inputs of nuclear information for their information center. The various time factors of the centralized system and the ORNL decentralized system were similar, and the indexing had at least an adequate quality and consistency with indexing that was done centrally. Authors rated a portion of the indexing as equal in quality for the two types of operation.

[10]C. A. Horton, *ORNL Decentralized NUCLEAR SCIENCE ABSTRACTS Preparation,* First Semiannual Report, Period Ending July 1, 1969, ORNL-TM-2653 (Oct. 22, 1969).

[11]C. A. Horton, *ORNL Decentralized NUCLEAR SCIENCE ABSTRACTS Preparation,* Second Report, Period July 1969 to June 1970, ORNL-TM-3026 (1970), in press.

[12]C. A. Horton, *A Study of Decentralized Nuclear Science Indexing,* ORNL-TM report, in press, 1970.

2. Reactor Projects

A. S. Meyer, Group Leader

J. M. Dale, Assistant Group Leader

R. F. Apple
C. M. Boyd
G. Goldberg
D. L. Manning
A. L. Travaglini
J. P. Young

F. R. Clayton[1] J. D. Lodmel[1] G. Mamantov[2]

MOLTEN-SALT REACTOR EXPERIMENT

Determination of Trivalent Uranium in MSRE Fuel Samples. The Molten-Salt Reactor Experiment, which was shut down December 12, 1969, has provided us with a number of challenging problems. For example, the determination of the redox condition of the molten fuel was one of the most important objectives of our program for the in-line analysis of MSRP salt streams. This measurement provides an index of the corrosiveness of the fuel. An evaluation of variations in the concentration of the chromium in the MSRE fuel[3] has indicated that the rate of corrosion is essentially nil when the fuel is maintained at a reducing level estimated to correspond to about 0.5% of the uranium in the trivalent state. As we had acquired the equipment and experience needed to apply two of the proposed methods for the in-line determination of U(III) to highly radioactive molten salts, we performed several analyses on fuel samples taken during the latter runs of the reactor. These analyses were made in an attempt to confirm the U(III) concentrations calculated from material balances of the reductants added to the fuel[3] and to determine whether future in-line applications would be affected by the high radiation levels of the fuel.

We have used the equipment and method described in the last annual report[4] for the voltammetric determination of U(III)/U(IV) ratios in three MSRE fuel

[1]Student Guest, University of Tennessee, Knoxville.

[2]Consultant, Associate Professor of Chemistry, Department of Chemistry, University of Tennessee, Knoxville.

[3]R. E. Thoma, "Relationship of the Distribution of ^{95}Nb in the MSRE to the Presence of Uranium Trifluoride in the Fuel Salt," *MSR Program Semiann. Progr. Rept. Feb. 28, 1970,* ORNL-4548, p. 97.

[4]J. M. Dale and R. F. Apple, "Voltammetric Determination of U(IV)/U(III) Ratios in MSRE Fuels," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969,* ORNL-4466, p. 29.

samples taken during run 19 of the reactor. During a period of approximately one month, two beryllium additions were made to the fuel salt. The amount of beryllium which dissolved with the first addition was calculated to be equivalent to the formation of 0.4% U(III) in the fuel salt, and the second addition gave an increase to 1.16% U(III). The results of the voltammetric U(III) determinations after the first addition showed the presence of 0.13% U(III), and after the second, about 0.05%. These results indicated that either the beryllium was reducing something other than U(IV) or the samples, after transfer to the hot-cell apparatus, were not representative of the fuel salt. During run 20 an amount of beryllium equivalent to 2.9% U(III) was dissolved in the fuel salt,[3] but the analysis results showed the presence of only 0.20%. After run 20, shutdown of the MSRE prevented further investigations into these discrepancies through direct analyses of the fuel salt. In order to test the method with significant quantities of U(III) present in a radioactive sample, we reduced the samples by sparging them with hydrogen. Following reduction, U(III) concentrations of 1.0 and 2.4% were measured, approximately in agreement with that predicted for the hydrogenation operation [control of hydrogenation conditions within the hot cell was not adequate for precise computation of U(III) generation]. At 650°C the measurements were reproducible to a few tenths of a percent, and when the temperature was reduced to 500°C, the observed U(III) concentrations decreased to about 0.29 and 0.32%, respectively, in excellent agreement with the concentration predicted from the shift in equilibrium of the reaction

$$2U(III) + Cr(II) \rightleftharpoons 2U(IV) + Cr^0 .$$

Our interpretation of these experiments is that they are entirely consistent with the method providing accurate analyses in radioactive molten salts. The discrepancies, if real, reflect the problems associated with the transfer of a representative sample of the fuel to the hot-cell apparatus.

Three samples of MSRE fuel were also taken during run 20 of the reactor for the determination of the U(III) concentration by molten-salt spectrophotometry. The hot-cell spectrophotometer and apparatus for preforming this determination have been described earlier.[5] Because of a change in the operating schedule of the MSRE, the samples, ~300 mg each, were withdrawn from the reactor in modified copper windowless cells, transferred, and stored under inert atmosphere for a period of one to two months. The samples were maintained at a temperature of 250°C to prevent the formation of radiolytic F_2. After storage, the first two samples could not be transferred to the spectral furnace for melting without exposing the samples to the atmosphere. The failure in both cases was the inability to open a sealed, threaded plug immediately under the sample container. These plugs were in a high radiation field and were heated for over a month at 250°C. The third sample container, under the same storage conditions, opened without problem and was successfully transferred without exposure to air. The first two samples when melted under a helium atmosphere were visibly turbid; the spectra of the resultant melt showed no evidence of U(III) or U(IV). It would appear that the dissolved uranium obviously present in the reactor fuel had come out of solution in sampling, storage, or remelting of these samples in the spectral furnace.

The third sample, when melted, yielded spectral evidence of U(IV) but not U(III). At the time this sample was taken, the estimated concentration of U(III) in the reactor was 2.9%. Because of the small quantity of U(III) present in a 300-mg sample, this apparent loss may have been caused by oxidants desorbed from the walls of the transport container during the extended storage at 250°C.

After the analytical measurements were completed, we froze the sample and allowed it to stand at room temperature for several days. An increase in the absorbance at 360 nm was observed in the remelted sample. This corresponded to a small increase in U(III) concentration, as we expected from the loss of radiolytic fluorine. An approximately proportional increase was observed following a second period of room-temperature storage. Further, we demonstrated that U(III) could be generated or removed (oxidized) in this sample by the addition of uranium metal or FeF_2 respectively. As with the electroanalytical studies, our experiments indicated no evidence of radiation interference with the proposed method. Rather, they serve to emphasize the ultimate need for in-line analytical methods, particularly for such fragile constituents as U(III).

Determination of Tritium in MSRE Gas Streams. Tritium was produced in the MSRE by neutron reactions with lithium in the fuel salt. It was of interest, therefore, to measure the concentrations of tritium in the effluent off-gases from the reactor to determine what action would be needed to capture and confine

[5] J. P. Young, "Facility for Spectrophotometric Studies of Radioactive Material," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969*, ORNL-4466, p. 34.

the tritium in future MSBR power reactors. During the operation of the MSRE in the latter part of run 19, we set up analytical equipment in the sample station at the MSRE vent house to measure the concentration of tritium in the various reactor effluent gas streams. A fractional part of the gas stream being analyzed was passed over a bed of hot copper oxide to convert the tritium to water. In general two copper oxide temperatures were used, one at ~340°C and the other at ~800°C. The higher temperature allows the oxidation of methane, while the lower temperature does not. After oxidation the gas stream was passed through a bubbler tube which contained a few milliliters of water and then through an empty trap which was cooled to about −80°C. Two sets of traps were used to ensure that all of the tritium was being collected. Sample streams were controlled at about 100 cm^3/min, to which 3 cm^3/min of natural hydrogen was added as a carrier for the tritium. We determined the amount of tritium collected for a specified period by a liquid scintillation technique.

The system was checked with a standard gas of known hydrogen and methane concentrations. It was determined by both gas chromatographic and mass spectrographic analyses of the standard effluent from the copper oxide at 800°C that the hydrogen and methane were completely oxidized. The results of the analyses made during run 19 indicated that the total tritium effluent from the fuel off-gas, the coolant off-gas, and the reactor containment cell were 22.7, 0.62, and 0.003 Ci/day respectively.

About three weeks after the end of run 19, two samples were taken from the fuel off-gas system. At this time the pump bowl was empty of salt, and the helium flow through the system had been dropped from 4.2 to 2.4 liters/min. The results obtained from the low- and high-temperature analyses were 3.15 and 7.44 Ci/day, respectively, an appreciable amount compared with that found when the reactor was at full power. These results indicated that there was some part of the reactor that was capable of adsorbing tritium during power operation until a dynamic equilibrium condition was established. After about two weeks into run 20, the total tritium from the fuel off-gas had increased to 15.0 Ci/day, still short of the maximum value found in run 19.

We also attempted during run 19 to determine the concentration of tritium in the coolant stack air with the existing analytical setup. This was precluded by the residual amount of tritium in the analytical system and sampling lines from previous analyses. Although the amount of tritium found in these samples was comparatively small (microcuries), the large air flow in the stack greatly magnified any sampling errors. For this reason a new sampling system was installed during the shutdown period between run 19 and run 20 so that a more concentrated sample could be taken. A sheath was installed on a 2-ft section of a radiator tube and was fitted with tubing so that relatively low air flows could be drawn through the sheath for sampling. These analyses indicated that about 0.5 Ci/day was going up the radiator coolant stack during power operation. Another approach was taken to determine the amount of tritium being expelled through the radiator tubes. This involved taking 1-liter cooling air stack samples into evacuated bulbs which contained about 1 ml of water. The gas samples were allowed to equilibrate with the water, and the tritium was counted. These analyses indicated that about 4.5 Ci/day was being expelled. The only apparent explanation for the difference between the results of the two methods is that the sampling was not equivalent.

ANALYTICAL DEVELOPMENTS FOR MOLTEN-SALT BREEDER REACTORS

Development of Reference Electrodes for Molten Fluoride Salts. Electrochemical methods provide a useful technique for basic research on the chemistry of molten fluoride salts and appear to offer one of the more practical approaches to the in-line analyses of reactor salt streams. A stable and rugged reference electrode would be very useful both for fundamental studies and for fuel analyses, such as the potentiometric determination of U(III) in MSRP fuels. Our earlier work has indicated that the Ni/Ni(II) couple may be used for a practical reference electrode for fluoride melts. We have made additional kinetic measurements on the Ni/Ni(II) couple in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ at 500°C by the voltage step method and the potential step integral method to test its reversibility. Our previous results[6] on the heterogeneous rate constant (k) and the transfer coefficient (α) were obtained at a nickel electrode for the voltage step experiments and at platinum and pyrolytic graphite electrodes for the potential step integral data. To compare the results obtained from the two methods relative to the same electrode material (nickel), the potential step integral experiments were repeated at a nickel electrode. Kinetic constants from

[6] D. L. Manning, H. W. Jenkins, and G. Mamantov, "Electroanalytical Studies of the Ni/Ni(II) Couple in Molten Fluorides," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969*, ORNL-4466, p. 33.

the potential step data obtained in molten $LiF\text{-}BeF_2\text{-}ZrF_4$ were also reevaluated from log exchange current vs log nickel concentration plots after fitting the data by the method of least squares. Average values obtained for k and α utilizing the voltage step method and the potential step integral method are $\sim 2 \times 10^{-3}$ and 4×10^{-3} cm/sec and 0.34 and 0.43 respectively. The measurements of k and α by the two methods are in reasonable agreement. A rate constant in the range determined for the Ni/Ni(II) couple in this study (2 to 4×10^{-3} cm/sec) may be considered to correspond to a reversible (or quasi-reversible) process, although it is considerably lower than the rate constant of ~0.1 cm/sec reported for the same couple in LiCl-KCl at 450°C.[7]

We have demonstrated that a nickel–nickel fluoride reference electrode (contained in thin-walled boron nitride) was suitable for use in molten fluoride at a working temperature of ~500 to 550°C. At reactor temperatures (~650°C) the BN deteriorates rapidly. In view of these limitations, studies were initiated on a somewhat different concept for a reference electrode. The new approach involves the use of a single crystal of lanthanum trifluoride (LaF_3) as the ionic conductor separating the half-cells. The designers (D. L. Manning and H. R. Bronstein, Chemistry Division) independently followed similar paths in this study, and only details from the most promising electrode system which evolved from combining individual experiences are reported here. At high temperatures, single-crystal LaF_3 has sufficient ionic conductance, almost completely supplied by the mobile fluoride ions, so that any liquid junction potential would tend to be minimal if the melts on either side of the crystal were essentially the same. Two models of the electrode are being tested. One model is similar to Egan's electrode[8] in which the Ni/NiF_2 reference couple exists in the solid phase as a pressed pellet. In our electrode the Ni/NiF_2 pellet is press fitted with a nickel electrode against one face of the LaF_3 crystal (3/8 in. diam × ~1/4 in. thick). The other face of the crystal fits against a fine porosity (<5 μ) nickel frit welded into the bottom of a nickel sheath. The electrode assembly is contained inside the nickel sheath (some are copper) but insulated from the walls with boron nitride. The purpose of the fine porosity nickel frit (3/8 in. diam × 1/4 in. thick) is to protect the single-crystal LaF_3 as much as possible from undue etching by the molten fluoride. The other model of the electrode is similar, except the LaF_3 crystal is in the form of a small cup which contains the same molten fluoride as the test melt but is saturated with NiF_2. Contact to the melt in the cup is achieved with a small nickel electrode. Initial experiments are encouraging. The electrode exhibits good electrical characteristics, and the potential appears stable and reproducible. The resistance of the electrode is of the order of 300 kilohms. The fine porosity frit appears effective in protecting the crystal from attack by the melt. The most severe case so far was a 5% weight loss after approximately 40 days in $LiF\text{-}BeF_2\text{-}ZrF_4$ at 500°C. The "junction" potential, or potential across the crystal which separates the two half-cells, appears to be lower in molten $LiF\text{-}BeF_2$ than in $LiF\text{-}BeF_2\text{-}ZrF_4$. In the latter melt this potential is of the order of 50 to 100 mV, but stable. The source of this potential is yet to be resolved. Preliminary results of emf measurements on the Be/Be(II) couple in molten $LiF\text{-}BeF_2$(66-34 mole %) and the Zr(IV) couple in $LiF\text{-}BeF_2\text{-}ZrF_4$ (65-30-5 mole %) vs the $Ni/NiF_2(LaF_3)$ reference electrode are reported elsewhere.[9] We have also shown that the potential of the reference electrode does not appear to be affected by reducing melts, that is, a melt in which the U(III)/U(IV) ratio may be as high as 1:10. Since the free energy of NiF_2 is well established, an electrode of this type should provide a standard as well as a constant potential for electrochemical measurements in molten fluorides.

In-Line Measurement of Trivalent Uranium in Molten Fluoride Salts. A PDP-8/I digital computer purchased for application to in-line analytical methods for molten salts was received by the Reactor Projects Group. We plan to make the first application of the computer to the control of voltammetric determinations of U(IV)/U(III) ratios in simulated MSRE fuel salt in a thermal convection loop. This project will be carried out in cooperation with members of the Metals and Ceramics Division who designed and are in the process of constructing the salt loop. A new, more versatile voltammeter is also being fabricated for use on this project. Besides providing information on the effect of U(III) concentrations on fuel salt characteristics, this project will allow practical knowledge to be obtained

[7] H. A. Laitinen, R. P. Tischer, and D. K. Roe, "Exchange Current Measurements in KCl-LiCl Eutectic Melt," *J. Electrochem. Soc.* 1, 760 (1964).

[8] *Electromotive Force Measurements in High Temperature Systems*, p. 91 ff, ed. by C. G. Alcock, Grosvernor Press, Portsmouth, England, 1968.

[9] H. R. Bronstein, "A Reference Electrode System for Use in Fluoride Melts," *Chem. Div. Ann. Progr. Rept. May 20, 1970*, ORNL-4581, p. 119.

for application to automated in-line analyses of fuel salts by other analytical techniques.

Spectrophotometric Studies of Actinide Ions in Molten Fluoride Salts. In addition to uranium, certain actinides, for example, protactinium and plutonium, are of considerable economical importance in the operation of molten-salt breeder reactors. The disposition of other actinides in the reprocessing system and their possible effect on in-line spectrophotometric measurements is of analytical interest. Accordingly, when the MSRE samples were completed, we used the hot-cell spectrophotometric facility to start a program to measure the spectra of actinide ions in molten fluoride salts. The Reactor Chemistry Division supplied solidified samples and cooperated in some of these studies. Spectral studies of Pa(IV), Pa(V), Pu(III), and Cm(III) in molten $LiF\text{-}BeF_2\text{-}ThF_4$ have been carried out. Americium(III) impurity was seen in the curium solution. The spectral observation of Pa(IV) is believed to be the first for protactinium in a molten salt. *F-f* transitions of Pa(IV) near 5460 cm^{-1} have also been observed. Although these transitions have been seen in the solid state, this is the first such solution spectrum. This again points out the fact that molten-salt solvents exhibit a wider spectral range than do the more conventional solvents. The spectra of Pu(III), Cm(III), and Am(III) are similar to the spectra seen for these ions in aqueous media.

Studies of Unusual Oxidation States of Ions in Molten Fluoride Media. The present phase of the electrochemical generation and spectral characterization of unusual oxidation states of solute species in molten fluoride salts has been concluded. The solvent system used in this study has been mainly, but not exclusively, LiF-NaF-KF. The work was carried out to survey the utility of this technique as a preparative and investigational tool. Our original assignment of the absorption spectrum of superoxide, O_2^-, in molten LiF-NaF-KF has proven to be in error. Superoxide does exist in this melt; it exhibits an ultraviolet absorption peak at 234 nm and a Raman spectral peak at 1107 cm^{-1}. The yellow solution obtained by the addition of NaO_2 to the melt, however, is due to the oxidation of chromium impurities (<10 ppm) to CrO_4^{2-}. It has been reported that O_2^- dissolved in liquid NH_3 also forms a yellow solution with an absorption peak near 360 nm. It was not possible to confirm this; rather, the addition of NaO_2 to liquid NH_3 yielded a colorless solution with an absorption peak at 252 nm. In other results of this work, we found it was possible to generate electrolytically Mn(III), Cu(II), U(III), and CrO_4^{2-} and to obtain their spectra in the melt. Although Co(II) could be oxidized electrolytically in the melts studied, the product, probably Co(III), was not stable under the experimental conditions of the study, and no spectrum could be obtained. A method for removing dissolved chromium and other reducible metal ions to less than ppm amounts in molten LiF-NaF-KF was developed. Likewise, the generation and spectral measurement of CrO_4^{2-} can be used for the spectral determination of chromium to less than 1 ppm in amenable fluoride melts. This complete study has been summarized in the Ph.D. thesis of F. L. Whiting.

Analytical Developments for $NaBF_4$ Coolant Systems. A molten-salt eutectic $NaBF_4 \cdot NaF$ (92-8%) is under investigation as an economical heat transfer medium for reactors. In the operation of a large $NaBF_4$ circulating test loop, two objectionable contaminants have been found in the off-gas (BF_3 in helium). One of these contaminants, particulate solids shown by analysis to be of similar composition to the salt in the loop, can be largely removed mechanically. The second contaminant, a corrosive liquid, tentatively identified as hydrolysis products of BF_3, has been found to collect in part in downstream sections of the off-gas system such as control valves and thus to interfere with the operation of the system. With members of the Reactor Division we performed development studies to further characterize this liquid, to see if its concentration in the off-gas could be measured, and to determine if such measurement might be used to detect steam leaks into the coolant. For these studies an ice-cooled weighable trap and a metallic filter were installed in the off-gas system. A dark oily liquid collected in the ice trap during extended loop operations and was found by infrared analysis to contain heavily bonded OH and less intense bands corresponding to C-F, B-F, and SiO structures. The silicon probably originates from the reaction of the fluorides with the borosilicate trap. Titrations with Karl Fischer reagent of a portion of the off-gas, sampled at a point upstream of the traps, corresponded to about 50 ppm of "water" in this stream. No measurable increase in this titration was observed when 10 g of water was injected about 3 in. below the salt level in the pump bowl, although calculations indicated that titrations several times the background level would be expected. Approximately 3 g of the liquid contaminant, collected during the 24-hr period following water injection, was found to contain approximately 880 mg of water, a value corresponding to a mixture of $BF_3 \cdot H_2O$ and $BF_3 \cdot 2H_2O$.

To simulate a condition postulated to explain the retention of the BF_3 hydrates in the off-gas system, mixtures of BF_3 and helium were passed through a fluorothene trap containing water. When the water

became "saturated" with BF_3, the titration of water in the off-gas approached the background imposed by the fading of the Karl Fischer reagent. When the trap and connecting lines were heated to 50°C, measurable titrations were obtained. These titrations increased with temperature to exceed our maximum titration rate at 100°C. These studies point out the need for a high-temperature in-line monitor for the cover gas of the MSBR coolant. We are considering several approaches to this problem.

The above apparatus is now being used to study methods for the removal of the hydrolysis product from the off-gas prior to recovery of its constituents for recycle. Various molecular sieves have been found to be less than 100% effective at the temperatures necessary to maintain the contaminant in the vapor phase. A corrosive gas chromatograph equipped with a gas density detector to permit more effective screening of potential adsorbents is being set up.

In cooperation with S. Cantor and W. T. Ward (Reactor Chemistry Division) we have constructed a system to permit on-line analysis of BF_3 in the effluent gas from solubility studies of BF_3 in molten fluoride salts. A thermal conductivity cell was installed downstream from the melt, and a system for the dynamic preparation of BF_3 mixtures for standardization was fabricated. To date, two saturation/stripping studies have shown that about 5 hr is required to remove BF_3 from $LiF\text{-}BeF_2$. The maximum concentration of BF_3 in the carrier gas that can be measured by the cell is now being determined. During standardization it was found that when the flow is restricted by a capillary, BF_3 does not behave as an ideal gas over the range of pressures investigated. This anomaly is receiving further attention.

Volatization of Some Chlorides of MSBR Fuel Constituents with Aluminum Chloride. We have made preliminary studies of the volatization of the chlorides of certain constituents of reactor fuel. At the time of these studies, significant problems existed in proposed reprocessing schemes for the separation of rare-earth fission products from the major fuel constituents. Volatization experiments were carried out to determine whether complexes such as $NdCl_3 \cdot (Al_2Cl_6)_n$[10] could be used to separate the fission products from chloride streams (essentially rare-earth chlorides in molten LiCl) that could be generated by the Chemical Technology Division's Metal Transfer Process.

[10]D. M. Gruen and H. A. Oye, "Vapor Complex of Neodymium Chloride with Aluminum Chloride," *Inorg. Nucl. Chem. Letters* 3, 453 (1967).

The volatization tests were made in a quartz tube that contained weighed quantities of chlorides ($NdCl_3$, $EuCl_3$, and LiCl) in a platinum or quartz boat. These chlorides were exposed to a stream of helium (~100 cm^3/min) that had been contacted with $AlCl_3$ near its sublimation temperature. Because of plugging problems the concentration of $AlCl_3$ in the helium carrier was limited to about 10%. The chlorides were exposed to the gas stream for periods of about 1 hr at temperatures up to 750°C. We were unable to distill significant quantities of either $NdCl_3$ or $EuCl_3$; however, it was found that LiCl volatized (apparently as a 1:1 complex with an estimated partial pressure of 10 mm) at 600°C. Effective separation of LiCl from mixtures with rare-earth chlorides was demonstrated. On the basis of these results, we proposed that a reprocessing system incorporating $AlCl_3$ distillation be considered for breeder reactor systems. An evaluation by the Chemical Technology Division indicated that the application of this process to the main reprocessing stream of the reactor would require the distillation of prohibitive quantities of salt. Accordingly, further study of these complexes has been assigned a low priority. These studies will be made as time permits to determine the properties of the $LiAlCl_4$ complex, evaluate its possible use for smaller reactor streams, and investigate analytical applications of this inorganic complexing agent.

ANALYSIS OF NATURAL GAS SAMPLES

The apparatus for the analysis of natural gas samples from wells stimulated by underground nuclear explosions has been completed and subjected to various calibration analyses. This apparatus, which was designed to be functionally similar but more compact than that used by the Lawrence Radiation Laboratory at Livermore (LRL), will be used to carry out separations of the various chemical components of natural gas samples from test wells, for example, the Rulison Project, so that the distribution of long-lived radionuclides (^3H, ^{14}C, and ^{85}Kr) among these constituents can be measured.

A few minor changes in the original design and procedure were found necessary to achieve convenient operations and adequate separations. These modifications include some additional interconnections between sections and a reduced eluent flow through trap-column assemblies that have been redesigned to provide longer flow paths. With this modified procedure we have obtained agreement to within ±1% in the activities of fractions separated from repeated analyses of a "Gasbuggy" sample furnished by LRL. In the course of

calibration of counting equipment, results obtained by the LRL absolute proportional method were compared with those from the ORNL combustion liquid scintillation technique. The two methods were found to agree to within about 1.5%. As limits of ±1% are assigned by the Bureau of Standards to the activity of the standard used to calibrate the scintillation apparatus, this agreement appears excellent. In these measurements internal proportional counters specially designed by R. Zedler (Instrumentation and Controls Division) were used; the end-effect corrections on these counters were only about 0.1%. We are finding a somewhat higher concentration of ^{85}Kr (~10%) in a Gasbuggy sample than that reported by LRL. This measurement requires the empirical calibration of end-window counting cells with a known quantity of ^{85}Kr. For this calibration a mass-spectrographically-analyzed dilution of ^{85}Kr in normal Kr (~0.6% ^{85}Kr) as a primary standard was used, whereas LRL uses ^{85}Kr extracted from a sample of irradiated uranium alloy. The dilution required (~10^5 to 10^6) of our primary standard is a possible source of error. A series of attenuating masks has been prepared which permits the comparison of the radiation of the primary standard with that of the sequential dilutions. These counting measurements indicate that the error in the combined dilution steps is less than 2%. We hope to have these differences resolved before samples are received.

We have developed a modified procedure for the determination of the total activity in gas samples. The combustion-scintillation counting procedure yields an accurate measurement of the total tritium content of the samples but does not provide for ^{85}Kr determination. The combustion of the samples yields a product containing H_2O, CO_2, and noncondensables (N_2 and traces of O_2). In the new procedure, krypton carrier is added before the combustion, and the krypton is separated from the combustion products for counting. After the water is collected by trapping at −80°C, the remaining constituents are collected on a molecular sieve trap at liquid nitrogen temperatures. The sieve is warmed to room temperature, and the krypton is transferred to a liquid-nitrogen-cooled receiver and the noncondensables removed by brief periods of pumping. A trace of CO_2 accompanies the krypton but is removed by a second adsorption-desorption step on a freshly regenerated sieve trap. We have tested this procedure with synthetic samples and found that the specific activity of the recovered krypton is within 1% of that added. This indicates a quantitative removal of the other constituents of the oxidized sample. A substantial fraction (up to 25%) of the krypton is lost during the procedure, largely during the removal of noncondensables. We are now testing cryogenic desorption methods to obtain quantitative recovery of the krypton fraction. If this procedure is successful, the sensitivity of the ^{85}Kr measurements can be multiplied by repeated use of the same krypton carrier for burns of successive test portions of a gas sample.

3. Analytical Biochemistry

Gerald Goldstein, Group Leader

J. E. Attrill D. W. Hatcher[1]
W. C. Butts H. Kubota
J. E. Caton M. L. Moss[2]
I. B. Rubin

J. C. Wolford[3] W. B. Cottrell[4]

BIOLOGICAL MACROMOLECULAR SEPARATIONS TECHNOLOGY PROJECT

Analysis of Nucleic Acids and Nucleic Acid Components. Development studies on the isolation and purification of specific transfer ribonucleic acids (tRNA's) from the bacterium *Escherichia coli* have continued under the Laboratory's Macromolecular Separations Program. As these tRNA's are prepared, it is necessary for us to establish the optimum conditions for their determination. The general conditions for the determination of any tRNA includes 11 quantitative and qualitative variables, and the object of an optimization study is to find the combination of these variables to yield the most complete reaction for a fixed quantity of tRNA. Last year, we began studies to establish the optimum conditions for the assay of arginine- and glutamic acid-accepting tRNA's. We have completed studies on these two tRNA's and have virtually completed studies on aspartic acid- and isoleucine-accepting tRNA's. This makes 10 amino acid-accepting tRNA's for which we have optimized the assay conditions. In these recent studies, we used statistically designed and evaluated experiments which have been variations of two-level factorial designs. For example, in an initial experiment we can test all 11 variables together, at two levels of each of the quantitative variables and in the presence and absence of each of the qualitative variables. We then use simpler designs in succeeding experiments as the effects of the variables become evident. The results are evaluated by a relatively simple arithmetical procedure. However, as the optima for the quantitative variables are approached, we use designs which involve fitting a second-order equation, and the results are evaluated by means of a computer program. We have carried out from six to nine experiments on each of these four optimization studies, and each series of experiments required from 350 to 500 individual assays.

As a transitional stage between isolation and purification of specific transfer ribonucleic acids (tRNA's) from bacterial and from human cells, the Macromolecular Separations Program is studying the processing of mammalian liver, mainly bovine, tRNA's. It has therefore been necessary for us to prepare the corresponding mammalian liver aminoacyl-tRNA synthetases, or activating enzymes, and to test both the tRNA products and the synthetase preparations for the various aminoacyl-tRNA activities. We have processed and tested six bovine and one porcine liver enzyme preparations. These preparations were processed by two different procedures, although there were some batch-to-batch variations within each procedure. In both methods, we homogenized the tissue in the same medium, centrifuged the homogenate at a moderate speed and then centrifuged it at 105,000 × *g*. In one method, the supernate was chromatographed on diethylamino-ethylcellulose, while in the other method the supernate was treated with ammonium sulfate. The product from the ammonium sulfate treatment had a lower specific activity for most of the aminoacyl-tRNA synthetase activities but catalyzed greater total aminoacylation of the tRNA's, because of the greater quantity of enzyme present. A number of tRNA products were tested. These included rat liver and mouse tumor tRNA's from the Biology Division of ORNL and bovine liver tRNA from the National Institutes of Health. Enzyme preparations from those sources were also tested. In general, our bovine liver enzyme preparation compared favorably with those from other sources, except for the mouse tumor enzyme, which was much more active. Since the mammalian liver project has not progressed to the point at which partially purified tRNA's are available, no optimization studies were carried out except to find near-optimum enzyme concentrations

[1] Present address, Saint Mary's Hospital, Knoxville, Tenn.

[2] Special assignment.

[3] Predoctoral student guest from the Graduate School of Chemistry, The University of Tennessee, Knoxville.

[4] ORAU student trainee from The University of Tennessee, Knoxville.

and incubation times. For the tRNA assays, we used the same conditions as used for *E. coli* tRNA assays. We found these conditions to give results equal to or better than other suggested conditions.

The Bioanalytical Service Group uses large quantities of ^{14}C-labeled amino acids in the determination of specific tRNA's for the Macromolecular Separations Program. We have occasionally found gross errors in these analyses which could be traced to an incorrect value for the specific activity of the labeled amino acid given by the vendor. As a quality control measure, we have adapted the aminoacylation–isotope dilution method for the determination of unlabeled amino acids[5] to the determination of specific activity of labeled amino acids. The total quantity of amino acid in the test solution can be calculated from the isotope dilution experiment. The only additional step needed is to spot an aliquot of the test solution on a filter paper disk, dry it, and count it in order to get a measure of the total activity present in the test solution. The specific activity can be calculated from these data. Compared with values of specific activity given by the vendors, this procedure has a negative bias of about 5%. Precision for the aminoacylation–isotope dilution procedure is about 5%.

Our UV analyzer model Mark-II, equipped with an anion exchange column, has been used for the separation and quantitative analysis of nucleotides in alkaline hydrolysates of ribosomal ribonucleic acids (rRNA). The molecular weight and base ratios of 16S rRNA calculated from nucleotide analyses were in good agreement with other results reported for this RNA. In addition, we have set up a high-resolution cation exchange column and a high-sensitivity UV monitoring apparatus for the separation and determination of purine and pyrimidine bases and nucleosides based on the work of Uziel *et al.*[6] in the Biology Division. This apparatus is currently being used for terminal nucleoside assay and analysis of nucleosides in enzymatic hydrolysates of rRNA's.

As part of our analytical support for the Macromolecular Separations Program we have been investigating procedures for the analysis of nucleic acid components by gas chromatography of their trimethylsilyl (TMS) derivatives. Last year we reported on some nucleosides and nucleic acid bases. This work has now been extended to the nucleotides, and a modified derivatization procedure has been developed for cytidine and related compounds[7] which chromatograph poorly as TMS derivatives. The new derivatization procedure involves reaction of the compound with methoxylamine hydrochloride, converting the NH_2 group on carbon 4 to the $= N{-}OCH_3$ derivative, followed by silylation with bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS). The resulting TMS-methoxime derivative elutes earlier and with better peak symmetry than the simple TMS derivative. Figure 3.1 shows a summary of our work with nucleic acid components.

Analysis of Proteins and Enzymes. The histones are a family of small, basic proteins usually found in the cell nucleus associated with the DNA and appear to be involved in the process by which gene activity is turned on and off. The Chemical Technology Division intends to study large-scale separation methods for these molecules by reversed-phase column chromatography, and consequently we are developing appropriate analytical methods. Our work to date indicates that polyacrylamide gel electrophoresis on a small pore-size gel in an acidic medium is the preferred method. The conditions tentatively established are:

Gel	15% polyacrylamide, 2.5% cross-linked
Gel buffer	2 *M* urea, 0.9 *M* acetic acid
Electrode buffer	0.9 *M* acetic acid
Current	1–2 mA per sample
Voltage	90–100 V
Sample size	20–40 μg
Stain	0.1% aniline blue black in 20% ethanol

In addition, we found that bands are sharper if the prepared gels are preelectrophoresed under the same conditions for 1 hr. Using these conditions, a calf thymus histone sample has been separated into three major components and several minor ones.

The Unit Operations Section of the Chemical Technology Division is studying the use of ultrafiltration as a means of concentrating solutions of biological macromolecules. For one phase of this study, we have been requested to develop procedures for the assay of various enzymes and then to teach these procedures to the Chemical Technology personnel. We have tested procedures for the assay of two enzymes thus far. For the assay of the first of these, chymotrypsin (E.C.3.4.4.5),

[5] I. B. Rubin and Gerald Goldstein, "An Ultrasensitive Isotope Dilution Method for the Determination of L-Amino Acids," *Anal. Biochem.* 33, 244 (1970).

[6] M. Uziel, C. K. Koh, and W. E. Cohn, "Rapid Ion Exchange Chromatographic Microanalysis of Ultraviolet-Absorbing Materials and Its Application to Nucleosides," *Anal. Biochem.* 25, 77 (1968).

[7] W. C. Butts, "Gas Chromatographic Separation of Trimethylsilyl (TMS)-Nucleotides: TMS-Methoxime Derivatives of Cytidine and Deoxycytidine," *J. Chromatog. Sci.* 8, 474 (1970).

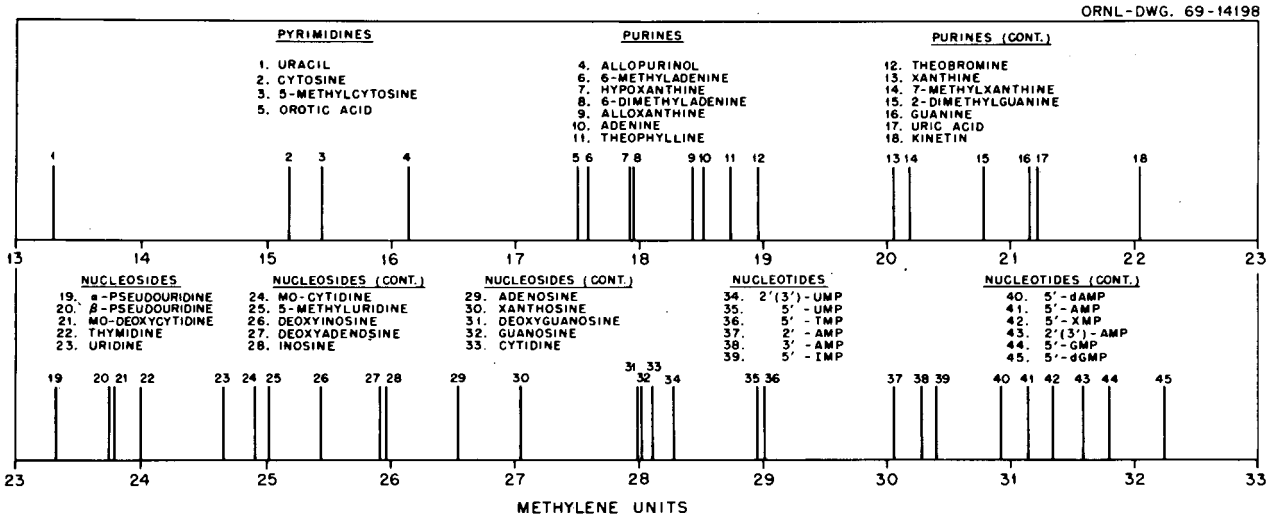

Fig. 3.1. Gas Chromatographic Elution Positions of TMS Derivatives of Nucleic Acid Components from a 5% SE-30 on HP-Chromosorb W Column.

we found the method as published by the manufacturer, Worthington Biochemical Corporation, to be satisfactory. It is simple and rapid and gives a linear calibration curve with good precision. For the assay of the second enzyme, aldolase (E.C.4.1.2.7), we found it desirable to make modifications which decreased the time for a single assay from 20 to 10 min and which resulted in a linear calibration curve. In the manufacturer's published method, the calibration curve was not linear. In this modification, the reaction rate of the substrate-hydrazine reaction is first established. Then the test solution of the enzyme is added simultaneously with the substrate, instead of 10 min later as in the original method, and the overall reaction rate is measured after an initial delay of 3 to 4 min.

MOLECULAR ANATOMY (MAN) PROGRAM

Characterization of Compounds Isolated from Physiological Fluids. The Biochemical Separations Systems Development Group (formerly the Body Fluids Analysis Group) of the MAN Program is currently involved in the development of two high-pressure anion exchange systems for application to UV-absorbing constituents (UV-analyzer) and carbohydrates (carbohydrate-analyzer) of physiologic fluids. The Analytical Chemistry Division is actively supporting this work in the identification of the components resolved from urine and other body fluids. Sixty compounds (42 within the past year) have been identified in fractions collected from the UV-analyzer (Table 3.1), and 11 carbohydrates have been identified. Although the carbohydrates were identified primarily by the use of gas chromatography,[8] gas chromatography, mass spectrometry, UV-spectral data, and elution position from the UV-analyzer were used in the identification of the UV-absorbing fractions.[9]

Approximately one-half of the components identified have been found in normal urines and the remainder in urines from subjects with pathologies such as alkaptonuria, phenylketonuria (PKU), hyperuremia, Lesch-Nyhan syndrome, and schizophrenia. In addition to components of apparent pathologic significance, several drug metabolites have been identified, including four metabolites of nicotinic acid and nicotinamide.

A new gas chromatographic (GC) technique for the analysis of anions was developed[10] that has potential application in many areas, particularly for such purposes as the determination of sulfate, phosphate, and other anions in body fluids or environmental samples. The ammonium salts of ten anions have been reacted with bis-(trimethylsilyl)-trifluoroacetamide to form volatile trimethylsilyl (TMS) derivatives of the anions. Figure 3.2 shows the GC separation of seven of these anions; borate and arsenite have been chromatographed

[8] W. C. Butts and R. L. Jolley, "Gas-Chromatographic Identification of Urinary Carbohydrates Isolated by Anion-Exchange Chromatography," *Clin. Chem.* **16**, 722 (1970).

[9] J. E. Mrochek *et al.*, "The Separation and Identification of Urinary Constituents Using Multiple Analytical Techniques," *Clin. Chem.* (in press).

[10] W. C. Butts, "Gas Chromatography of Trimethylsilyl Derivatives of Common Anions," *Anal. Letters* **3**, 29 (1970).

Table 3.1. Identified Urinary Constituents

5-Acetylamino-6-amino-3-methyluracil	Indole-3-carboxylic acid
4-Acetylaminobenzoic acid	Kynurenic acid
4-Acetylaminobenzoylglycine	Mannoheptulose
Allopurinol	3-Methoxy-4-hydroxyacetanilide
2-Amino-3-hydroxybenzoylglycine	3-Methoxy-4-glucuronosidoacetanilide
Benzoic acid	3-Methoxy-4-glucuronosidobenzoic acid
Citric acid	3-Methoxy-4-hydroxybenzoic acid
Creatinine	3-Methoxy-4-hydroxybenzoylglycine
p-Cresol	3-Methoxy-4-hydroxymandelic acid
2,5-Dihydroxyphenylacetic acid	3-Methoxy-4-hydroxyphenylacetic acid
1,7-Dimethylxanthine	3-Methoxy-4-hydroxyphenyllactic acid
3,7-Dimethylxanthine	*N'*-Methyl-2-pyridone-5-carboxamide
3-Ethoxy-4-glucuronosidobenzoic acid	*N'*-Methyl-4-pyridone-3-carboxamide
3-Ethoxy-4-hydroxybenzoylglycine	1-Methylxanthine
4-Glucuronosidoacetanilide	3-Methylxanthine
Glyoxylic acid	7-Methylxanthine
Hippuric acid	Nicotinamide
4-Hydroxyacetanilide	Nicotinamide, *N*-oxide
2-Hydroxybenzoic acid	Orotic acid
4-Hydroxybenzoic acid	Orotidine
2-Hydroxyhippuric acid	Oxipurinol
3-Hydroxyhippuric acid	Phenylacetylglutamine
4-Hydroxyhippuric acid	Phenyllactic acid
4-Hydroxymandelic acid	β-Pseudouridine
2-Hydroxyphenylacetic acid	Sulfanilamide
4-Hydroxyphenylacetic acid	Trigonelline
4-Hydroxyphenyllactic acid	Uracil
Hypoxanthine	Urea
Indoleacetic acid	Uric Acid
Indoleacetylglycine	Xanthine

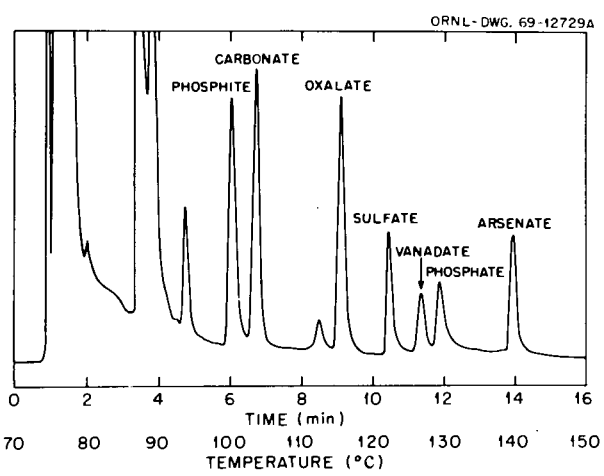

Fig. 3.2. Gas Chromatogram of Trimethylsilyl Derivatives of Seven Anions.

in addition to those shown, and sulfite yields the same derivative as sulfate. Each of the anion derivatives has been identified by combined gas chromatography—mass spectrometry.[11]

We are in the process of equipping an analytical gel electrophoresis laboratory to serve the needs of the various groups in the MAN Program. The objective of this electrophoresis program is: (1) to develop the ability to accurately measure and record electrophoretic data, (2) to preserve these data in some significant form over a long period of time by good cataloging procedures for data from both samples and standards, and (3) to test a variety of techniques for the gel electrophoresis of proteins of different types. This laboratory has the necessary equipment to perform analytical gel

[11] W. C. Butts and W. T. Rainey, Jr., "Gas Chromatography and Mass Spectrometry of Trimethylsilyl Derivatives of Common Anions," presented at 160th ACS National Meeting, Chicago, September, 1970.

electrophoresis by either slab or disk techniques utilizing constant current, constant voltage, or constant pulsed power sources. After the electrophoresed gel has been stained, a photograph of the gel may be obtained in less than 5 min using Polaroid type 55 P/N film. Such photographs are convenient for the rapid communication of results to interested co-workers. In addition to photography, quantitative data can be obtained from gels by scanning the gel with a microdensitometer. Our microdensitometer system is capable of automatically integrating peak areas and printing the results and can also record band migration distances to an accuracy of ±0.02 mm on a strip chart. In order to improve characterization of the distribution of bands on a developed gel, an expression for resolution in gel electrophoresis was developed. This expression was based on the following definition: The resolution of two bands on a developed gel is equal to the distance separating their maxima divided by the sum of the adjacent half-widths of the two bands. This expression, with appropriate modification, will enable one to preserve much of the important data from a gel scan by cataloging and storing only four quantities for each band on the scan. A tentative electrophoretic standard consisting of human serum, myoglobin, ovalbumin, and cytochrome-C was studied extensively. This standard was chosen for two major reasons: (1) it contains the best-characterized human body fluid and (2) the proteins in the serum along with the other added proteins provide a wide range of molecular weights and electrophoretic mobilities. Techniques which have been studied so far include electrophoresis of large proteins, which are relatively insoluble, on gels containing urea or sodium dodecyl sulfate, and the determination of molecular weight by gel electrophoresis.

Protein Sequence Studies. In connection with the development of an automatic protein sequenator being made at ORNL, based on the original design by Edman and Begg,[12] a study was made of two additional reagents which react with peptides and might improve some features of the Edman procedure and provide alternative systems of analysis. In one series of experiments, each of 22 amino acids was reacted with methylisothiocyanate at pH 9.0 to 9.2, and the products were then treated with aqueous HCl to form the methylthiohydantoin (MTH) amino acid. Various solvents were then utilized in attempts to prepare each of the compounds in a high state of purity, the progress of the preparations being monitored by melting point determinations and mass spectrometry. An attempt to separate mixtures of these MTH amino acids by paper and thin-layer chromatography was not successful, but 16 of them could be separated and determined by gas chromatography using a two-column system. Five additional compounds could be separated as their TMS derivative following silylation. Data for MTH cysteine were inconclusive. The results of the above study have been published.[13] A similar study was made with thiobenzoyl derivatives. The reactant (thiobenzoylthioacetic acid) was condensed with an amino acid or peptide to form an intermediate which then undergoes an intramolecular rearrangement to produce an $n - 1$ peptide and a cyclized derivative (the phenyl thiazol-5-one or PTA) of the N terminal amino acid residue of the peptide. In contrast to the Edman reaction (using phenyl or methyl isothiocyanate), the phenyl thiazolinones do not convert to a linear molecule but remain in the cyclized state in the absence of oxygen or moisture. Some 15 of these compounds were prepared and purified, but attempts to separate them by paper, thin-layer, or gas chromatography have been unsuccessful. The advantages that we hope to realize with one or both of these methods over the classical Edman procedure using phenylisothiocyanate include: greater reactivity in the condensation step; better wetting of the protein or polypeptide chain by the reagents; easier separation of the amino acid derivatives formed and greater volatility of the derivatives being analyzed and reagents being used, thus extending the capability of automatic sequencing.

CHARACTERIZATION AND PURITY OF BIOCHEMICAL COMPOUNDS

We have evaluated the purity of 58 commercially available nucleotides and related compounds by paper chromatography in four different solvents and by ultraviolet spectrophotometry at three pH values. In addition, we have obtained infrared, NMR, mass and emission spectra, and gas chromatograms of many of the compounds. This work is sponsored by the National Academy of Sciences–National Research Council, Committee on Biological Chemistry, Subcommittee on Nucleotides and Related Compounds, as part of an effort to improve the quality of chemicals available for biomedical research by establishing criteria, standards, and specifications with regard to purity. If a compound shows no impurities on paper chromatograms, and its

[12] P. Edman and G. Begg, "A Protein Sequenator," *Eur. J. Biochem.* 1, 80 (1967).

[13] J. E. Attrill *et al.*, "Gas Chromatography of Methyl Thiohydantoins of Amino Acids," *Anal. Letters* 3, 59 (1970).

molar absorptivity agrees to within ±3% with a molar absorptivity value judged by the Subcommittee to be the best available, then it may be specified by the manufacturer as NRC grade. Of the 58 compounds tested, 15 met these specifications. The results of these tests will be published by the NAS-NRC, with support from the National Institutes of Health, in *Specifications and Criteria for Biochemical Compounds,* Third Edition, scheduled for publication in 1971. This is a continuing program. At least 50 additional compounds will be tested, and some of the testing procedures will be modified.

On behalf of the NAS-NRC Committee on Specifications for Adenine in Anticoagulant Solutions, we have evaluated the purity of four commercial samples of adenine and two special preparations. In addition, we have spiked adenine samples with compounds considered to be the most likely impurities, determined the best way to separate them from adenine, and ascertained the lowest level at which they can be detected. A combination of tests including anion and cation exchange chromatography, gas chromatography or trimethylsilyl derivatives, paper chromatography in three solvents, and ultraviolet spectrophotometry are necessary to detect organic impurities and emission spectroscopy to detect inorganic impurities. We will write specifications based on these tests. This work is of considerable practical importance because it has been found that whole blood with adenine added can be routinely stored in blood banks for 35 to 42 days compared with the currently permissible 21 days.

We are currently investigating a technique for the determination of the absolute purity of organic compounds by differential scanning calorimetry.[14] The differential scanning calorimeter (DSC) quantitatively measures the heat input as a function of temperature as the sample passes through its melting point transition. From these data, the fraction of the sample that is melted as a function of temperature, and the heat of fusion are calculated. From the van't Hoff equation which relates the melting point depression to the amount of impurity,

$$T = T_0 - \frac{RT_0^2 X}{\Delta H_f} \frac{1}{F},$$

where T is the instantaneous temperature, T_0 the melting point of the pure compound, and F is the fraction melted at temperature T; the mole fraction of impurity (X) can be calculated by plotting $1/F$ vs T. Our experience to date has indicated some difficulty with the reproducibility of the experimental data and with the evaluation of corrections to the data for thermal lag, heat capacity changes, and other effects. At present we can determine from 0.1 to 3 mole % of impurity with a standard deviation of 10 to 20%. The DSC is interfaced to a PDP-8/I computer providing digital data which are punched on cards and processed on the IBM System 360 computer. Ultimately, all the calculations will be done by the PDP computer.

SEPARATION OF OXYPURINES BY LIGAND-EXCHANGE CHROMATOGRAPHY[15]

We have previously reported on the separation of nucleosides, nucleic acid bases, and sulfur-containing compounds by ligand-exchange chromatography on a copper-loaded chelating resin eluting with aqueous ammonia and have now tested the oxypurines. The oxypurines are of interest because the group includes numerous physiologically active compounds used medically, as well as compounds normally present in the body. Some of the more significant separations achieved include the separation of the nucleic acid purines (guanine and adenine) and their metabolic products (hypoxanthine, xanthine, and uric acid), and the separation of the methylated xanthines from each other. Caffeine, in particular, was rapidly separated from and quantitatively determined in pharmaceutical preparations containing salicylates, barbiturates, and antibiotics, and in coffee, tea, and cola beverages.

GeMSAEC ANALYZER: CLINICAL DEVELOPMENT PROGRAM

We have completed installation of a computerized GeMSAEC[16] in the ORNL Health Division, including training of laboratory personnel in the use of various procedures for blood serum analysis. Methods for glucose, cholesterol, total protein, albumin, albumin/globulin ratios, and several enzymes are being evaluated. This evaluation includes analysis of numerous patient samples from hospitals where alternative methods and equipment are used.

[14] *Thermal Analysis Newsletter,* Nos. 5, 6, Perkin-Elmer Corp., Norwalk, Conn.

[15] This work is part of a Ph.D. thesis submitted by J. C. Wolford to The University of Tennessee.

[16] N. G. Anderson, "Analytical Techniques for Cell Fractions. XII. A Multiple-Cuvet Rotor for a New Microanalytical System," *Anal. Biochem.* 28, 545 (1969).

This work represents a critical phase of the GeMSAEC development program inasmuch as it is the first experience obtained in a clinical setting, and commercial versions of the instrument have not yet reached the point where availability of a satisfactory system is assured. As a result of this program, methodology will be available for detailed biochemical health surveillance of ORNL employees. The work will also provide an opportunity for ORNL to influence the outcome of the present crisis in delivery of health care if GeMSAEC technology successfully anticipates the needs of large hospital laboratories and screening centers.

Although our results indicate that most of the usual blood chemistries will be adaptable to the GeMSAEC, the basic operation of adding one or two reagent solutions to a blood sample and measuring a change in light absorption requires reactions of very high specificity. We have not yet found it necessary to perform preliminary separations or other manipulations off the instrument except for sample measurement and dilution.

Relative standard deviations for glucose by the hexokinase method are about 1% within runs, and 2 to 5% from day to day, depending on the experience of the operator. Differences between our results and those obtained in one of the hospital laboratories amount to 10 to 15% in some cases, as would be expected because of the entirely different chemical methods used in the two instruments.

For an enzyme determination, such as alkaline phosphatase, in which stability of specimens, operating conditions, and the actual concentration levels influence precision, day-to-day reproducibility to within 5 or 6% is considered satisfactory at this time.

Efforts have been successful in reducing the manipulative skill required by the operator through development of an automatic reagent dispenser, more systematic manual operations, and improvements in the procedures. Mechanization of the instrument startup and rinsing cycles, and installation of a monochromator to extend the linear portion of the working range, all of which will contribute to higher precision, have been planned. These improvements will also increase the present output of 60 tests per hour for a 15-place rotor by a factor of 2 or more.

4. Nuclear and Radiochemistry

W. S. Lyon, Group Leader

H. H. Ross, Assistant Group Leader

L. C. Bate
F. F. Dyer
J. S. Eldridge
J. F. Emery
T. H. Handley
H. Kubota[1]
S. B. Lupica
S. A. Reynolds
E. Ricci
J. E. Strain
H. E. Zittel
K. J. Northcutt[2]

TRACE ELEMENT DETERMINATIONS IN BIOLOGICAL AND ENVIRONMENTAL SAMPLES

Mercury. Because of the recent interest in mercury as an environmental pollutant, we have begun a number of studies aimed toward a better understanding of the problems in the determination of this element.

In our opinion the main uncertainty in the determination of mercury arises prior to the analysis, that is, in sampling, storing, and resampling for analysis. Mercury is a most difficult element to keep in solution in trace quantities; it is known to plate out on the walls of sample containers and pass through plastic. Mercury in aqueous solutions or sludges or silts could be adhering to the solid, bound to it, in the aqueous phase as mercury or ionic mercury, or complexed in an organic form. Any sample of natural water will contain dissolved, colloidal, and suspended matter, and a mercury determination to be meaningful must sample and measure all three of these phases. Additionally, should one be interested in assessing the relative amounts of

[1] Analytical Biochemistry.

[2] Radioisotopes-Radiochemistry.

mercury present in each of these phases, a method should be available to do this. We have begun to study these problems primarily by use of neutron activation analysis (NAA). NAA produces a highly specific and sensitive method for the determination of mercury, and by use of it we are able to determine mercury in all forms in all phases of a sample. In a sample relatively free from gross amounts of contaminants (natural water, for example) one may sample, seal the bottle, irradiate, and determine mercury nondestructively by measuring the induced radioactive mercury. We are using this technique in sampling and analyzing water at ORNL and are attempting to compare the results with those obtained on samples taken at the same time and analyzed by conventional techniques. We can determine a few tenths of a nanogram of mercury by this technique, and there should be no uncertainties with sealed samples. The problem with mercury determinations comes when a concentration step is required, when because of contamination chemical separation must follow irradiation, or when irradiation longer than a few minutes is required. These are discussed below.

Our ORR pneumatic facility cannot handle samples larger than about 500 mg and because of heating liquids cannot be irradiated longer than a few minutes. We use the reaction $^{196}Hg(n,\gamma)^{197}Hg$ (65 hr). Obviously, sensitivity could be improved with longer irradiations or by concentrating the sample prior to irradiation. Our tests show, however, that mercury is lost from solution during evaporation, and until we can solve this problem we will be limited to short irradiations of unconcentrated samples.

We have been interested in the determination of mercury in fish flesh and specific organs. Here we have irradiated for 5 min in the ORR and dissolved the sample in an H_2SO_4-HNO_3 mixture containing mercury carrier. A chemical separation of mercury is made, and we count the induced 65-hr ^{197}Hg. Any losses should be correctable by yield calculation. So far we have analyzed only small fish, and some of the organs are so small as to push our sensitivity to its limit. We find that mercury content varies from fish to fish, but in general the mercury content decreases by organ: brain > liver > flesh > GI tract > kidney > heart. The flesh of bream raised in White Oak Lake ranges from 0.43 to 0.25 μg per gram of tissue on a wet-weight basis. If we can assure ourselves that no mercury is lost in a drying process, we can then dry the sample and make a longer irradiation as well as irradiate more sample.

There would also be an advantage to longer irradiations (say in the Bulk Shielding Reactor) to use the reaction $^{202}Hg(n,\gamma)^{203}Hg$ (46 day). We could then wait until short-lived contaminants such as ^{24}Na had decayed out and perhaps make determinations nondestructively. So we are using tracer techniques as well as activation studies in an effort to establish reliable methods of sample concentrations and drying.

Within the Analytical Methodology Group an apparatus has been assembled for the determination of mercury in water solutions by the cold-vapor atomic absorption method. By using a long absorption path (92 cm) and optimizing gas flow rates and surge tank conditions, a detection limit of 0.04 ppb of mercury (2 ng in 50 ml) can be obtained. Further reduction of the detection limit is possible, but it is not worth pursuing at present because it is not needed and because cross-contamination problems are already formidable at the present level. We are now directing attention toward finding effective methods for minimizing these problems and for analyzing natural waters and tissue samples.

We also have an isotope exchange method for determination of mercury. We have determined mercury in surface water by isotopic exchange with 203-mercuric di-*n*-butyl phosphorothianate in an extraction system. Synthetic samples as low as 2 ppb of mercury were determined by this method. However, we do not know exactly what effect trace complexers found in natural waters will have on complete exchange, and organically bound mercury would probably not exchange.

Finally, we have begun an experiment to use ^{252}Cf to determine mercury in water. A 4-ft^3 plastic tank was built and was filled with water. A 10-μg ^{252}Cf source is placed in the center of the tank, and mercury is added to the water. At the beginning we are using mercury solutions in plastic containers dropped into the tank. We are attempting to determine mercury through the measurement of capture gamma rays from the (n,γ) reaction using a Ge(Li) detector and a multichannel analyzer. O. L. Keller of the Chemistry Division and V. A. DeCarlo of the Chemical Technology Division are assisting in this project.

Copper and Manganese. In a continuing effort to determine 0.02- to 0.1-μg amounts of copper and manganese nondestructively in biological tissue, we have enlisted the assistance of A. R. Brosi (Chemistry Division). Using his Ge(Li) detector and analyzer system we are able to measure the ^{56}Mn radioactivity in the irradiated tissue samples despite the intense radioactivity of ^{24}Na.

The analyzer system allows the setting of several single-channel "windows" containing only the photopeaks of interest. A window was set at 0.51 MeV for

annihilation gamma of the positrons of ^{64}Cu, and another window was set at 0.85 MeV for the ^{56}Mn gamma ray.

For the first time we were able to determine manganese nondestructively with good precision and accuracy at the ppm level, but annihilation gamma rays produced by pair production induced by 2.76-MeV gamma rays of ^{24}Na interfered in the determination of copper.

We also attempted to analyze these samples for copper by measuring the *K* x rays from electron capture in ^{64}Cu using an Si(Li) x-ray detector system. We had difficulty here because of absorption of *K* x rays in the sample matrix. Absorption corrections were calculated for each sample using its weight dimensions. These corrections were uncertain and ranged from 20 to 40%.

Other Elements. We have also analyzed an air filter obtained from the St. Louis area by neutron activation analysis for 15 elements. The sample was originally obtained to see if activation with a ~0.3-mg ^{252}Cf source would yield any measurable activities; nothing above background was seen. Portions of one air filter were then irradiated in the ORR. Sb, Co, Cr, Au, Sc, Se, and Ta were in the range of 0.1 to 1.0 μg, while Al, Br, Cl, Mn, and Na were in the range of 10 to 300 μg. Ca, Fe, and Zn were ~1 mg. The quantities of these elements on the filter correspond to 10% of the total particulate matter.

Dr. Michael Newton of Oregon State University School of Forestry wanted to determine the fate of arsenic (cacodylic acid) in foliage. Traditional methods of arsenic analysis were unsatisfactory for field monitoring of pesticide residue. Therefore an x-ray fluorescence method using a ^{241}Am source was developed. We found the method useful for concentrations $\geqslant$100 ppm; however, below that level secondary scattering and/or background prevented accurate analysis. The results were found to fit kinetic theory, and it was concluded that the method has substantial utility in arsenic monitoring at levels $\geqslant$100 ppm.

COOPERATIVE ISOTOPES PROGRAM

A joint program of the Isotopes and Analytical Chemistry Divisions, now in its sixth year, is concerned with analysis and characterization of isotopes. The great variety of uses of isotopes and their radiations in medicine, environmental sciences, industry, and other fields makes our program both locally and nationally significant. Technical assistance includes preparation and reviews of papers and reports and consultation on problems of characterization and analysis of isotopes, both in-house and external. Many of the recent activities of the Isotopes Division were reported elsewhere.[3] *The Isotope User's Guide*[4] has fulfilled its promise of usefulness as information source and teaching aid.

American Nuclear Society personnel used our data on properties of radioisotopes and licensing requirements in the *Radioisotope Directory,*[5] which is intended to supersede the *Isotope Index.* ASTM Committee E-10 obtained a copy of the *Guide* for each of its 173 members and affiliates as a source of standardized data. The Japan Atomic Industrial Forum requested and received permission to translate it and publish it for use in that country.

The analysis of routine and special radioisotope products is broken down into assay and quality control. The former refers to content of the desired radionuclide and involves standards and calibration techniques, while the latter includes purity and chemical characteristics. It is apparent that ORNL products must be assayed as accurately as is feasible, because some users accept the stated concentration of a shipment without verifying it, and others attempt to confirm the measured concentration and protest if they cannot. Further, the products must obviously be reasonably free of impurities, equaling or exceeding catalog specifications of purity. This work must in general be of an ad hoc nature, responding to locally detected deviations of assay or purity or to inquiries or complaints of users. Methods and instrumental techniques are reviewed on occasion, new ones are recommended or developed, and special analyses are sometimes done.

A significant quality-control study was initiated in an attempt to explain the deformations of some ^{137}Cs sources.[6] The usual analyses were performed: ^{137}Cs assay and chloride, sulfate, carbon, rubidium, and spectrographic examination. Because NH_4Cl is isomorphous with CsCl and presumably would vaporize on heating, possibly causing swelling of CsCl sources, ammonium determinations were made. Microscopic examinations and determinations of water-insoluble

---

[3] AEC Division of Isotopes Development, Washington, D.C., *Division of Isotopes Development Research and Development Projects: 1969,* TID-25372 (February 1970).

[4] F. E. McKinney, S. A. Reynolds, and P. S. Baker, *Isotope User's Guide,* ORNL-IIC-19 (September 1969).

[5] *Radioisotope Directory, Nuclear News* 12(12) (December 1969).

[6] N. C. Bradley and C. L. Ottinger, *Investigation of Deformation in Rectangular Cesium-137 Sources,* ORNL-TM-3069 (August 1970).

solids were also done, including carbon determinations on the solids. The carbon values were anomalous on some samples; attempts to determine the form of the carbon were not successful. Analyses for atmospheric gases in inactive CsCl were done by vacuum fusion, with measurement of pressure of evolved gas. Although the amounts of gas found were small, generally less than 0.1 cc at STP per gram of CsCl, precision was adequate for the purpose. The analytical program did not furnish an explanation of the deformations, which were avoided by changes in encapsulating procedures.

To determine chlorine in elemental ^{14}C, thermal-neutron activation analysis was recommended, because the technique is adequately sensitive, simple, and nondestructive.

An essential part of the quality control program with respect to assay is concerned with standards. Some are prepared locally, and others are purchased from reputable suppliers, submitted as "unknowns" to the control laboratory (Radioisotopes-Radiochemistry Group), and the results compared with the suppliers' certifications. The purpose is triple: to confirm local calibrations, to evaluate suppliers' calibrations, and to anticipate user inquiries about assay, which may involve standards obtained from the same suppliers. Two standards were received from the National Bureau of Standards, and our value on ^{85}Kr was 1.7% higher than theirs, which was certified to 6%. On ^{36}Cl the local value was 0.8% higher than the NBS one, which was certified to 2%. Standards of ^{35}S were obtained from three commercial suppliers. The efficiencies for the liquid-scintillation technique were 62.0, 66.3, and 69.2%, compared with our established value of 62.6%. Although not particularly satisfactory, the results agree with the average within the suppliers' stated accuracies of 5 to 10%. The National Research Council Subcommittee on Use of Radioactivity Standards recently sponsored a round-robin involving preparations of often-used radioisotopes. The very satisfactory results by our routine laboratory were 1.7% higher than the average on ^{57}Co and 1.3% lower than the average on ^{125}I. In two facilities of the Radioisotopes-Radiochemistry Group, measurements were made of a set of eight IAEA standards. Agreement with the IAEA calibrations was satisfactory.

A survey has been completed for the Ad Hoc Panel on National Uses and Needs for Standard Radioactive Materials of the National Research Council. A draft of the Panel's report has been prepared here and sent to the members for their final revisions. This report contains information on uses for standard radioactive materials in various fields and on the present status of such materials in the United States. There are many suppliers, and their calibrations are in most cases unrelated; there is no regulation of this activity. The report is largely concerned with the results of a survey to determine present and future needs. Several hundred people actively engaged in work requiring standards were queried by questionnaire and personal interview. Major attention was given the biomedical and environmental sciences. The panel members are specialists in a variety of disciplines who also have knowledge of radioactivity measurements and standards. The National Bureau of Standards (NBS), as the statutory source of calibrations for the nation, is the focal point of these considerations. It is recommended that NBS exercise leadership in improving the quality of standards and calibrations through extension of its Interlaboratory Testing Program to radionuclides. Because of the small volume of sales of radioactivity standards, it is not feasible for commercial suppliers, competent as they may be, to do unaided the extensive research and tedious measurements required for primary standardization. Since interest is growing among professional societies and other organizations, it is recommended that an office be set up at NBS or another appropriate site to gather information and coordinate activities. Fourteen nuclides, including ^{133}Xe, ^{99m}Tc, and ^{75}Se, were found to be of immediate importance, and NBS is requested to give priority to preparation of standards of those materials. All suppliers are urged to intensify quality-control efforts and to supply complete information about their products to permit intelligent use.

The survey resulted in the collection of a large amount of information obviously useful in answering inquiries about availability and quality of standards; it has been used to advise the National Bureau of Standards on needs for standards of three nuclides, including names of individuals and institutions indicating such needs.

A dilute alloy of cobalt in aluminum has long been used for monitoring thermal-neutron flux in reactors. The National Bureau of Standards has recently issued SRM 953, *Neutron Flux Monitor Wire,* with the cobalt content certified as 0.116% with an uncertainty of 0.002%. This value was confirmed within the stated uncertainty by using activation analysis with ORNL standards. It was necessary to allow 2.7-day ^{198}Au to decay before measurement; this nuclide is formed from an impurity, 4.5 ppm of gold in the alloy.

RADIOISOTOPE CHARACTERISTICS AND MEASUREMENTS

Nuclear Measurements. Such properties of radionuclides as half-lives, gamma energies and percentages, and beta and alpha heat outputs must be known to permit handling, analysis, and application. We must often select values, because compilation and adoption by information groups necessarily lag several years behind availability of that information. In other cases information of sufficient quality is simply not available and must be determined. Our measurement of the half-life of ^{153}Gd by gamma ionization chamber has been completed. The value is 240.9 ± 0.6 days. Determination by scintillation counter is continuing. Using experimental products of ^{85m}Sr, a medically important nuclide, we have determined its half-life and that of by-product ^{87m}Sr. By well-type scintillation counter, we find the values were 67.66 ± 0.07 min and 2.81 ± 0.02 hr. For ^{85m}Sr the confirming result by gamma ionization chamber was 67.92 ± 0.25 min. The values for both nuclides agree with recently published ones. The half-life of ^{88}Y was estimated by remeasuring the activity of an IAEA standard 2.5 years after the original local measurement. Ascribing an error of 3% to the ratio of the two measurements, the half-life was calculated to be 106.1 ± 0.4 days, in essential agreement with values of 106.5 and 106.6 from the National Bureau of Standards. Decay will be followed to substantiate the estimate. After 10.5 years of measurements of gamma decay of four sources of ^{137}Cs, the final half-life value is 30.18 ± 0.10 years, in good agreement with a weighted average of published data, 30.13.[7] No significant difference is found in our result by treating data separately from the first half and second half of the decay period.

It is well known that the half-lives of nuclides which decay by electron capture and by converted isomeric transition can be altered slightly by the environment in which the radioatoms find themselves. A European author has recently published several papers showing substantial effects on half-lives of beta emitters, for which there is neither prior experimental nor theoretical support. After an exchange of letters, we decided to attempt to confirm his experimental work on ^{64}Cu and ^{131}I. G. I. Gleason of ORAU irradiated copper foil, verified purity of ^{64}Cu by Ge(Li) spectrometry, and followed decay of copper metal and $Cu(NO_3)_2$ solution by means of an NaI(Tl) spectrometer. The results were: metal 12.723 ± 0.015 and 12.730 ± 0.022, $Cu(NO_3)_2$ 12.700 ± 0.22 hr. There are no significant differences among these values, and they are in agreement with that of Emery, 12.71 ± 0.01 (solution and solid samples), reported previously.

The ^{131}I half-life values (in days) are tabulated below. Emery used a well-type scintillation counter and Gleason an NaI(Tl) spectrometer.

Chemical Form	Emery	Gleason
Solution	8.0403 ± 0.002	8.028 ± 0.007
I_2 in CCl_4	8.041 ± 0.002	
LiI solid	8.042 ± 0.002	
KI solid	8.043 ± 0.002	8.030 ± 0.007
AgI solid	8.036 ± 0.002	8.019 ± 0.006

Again it appears that there are no significant differences. These findings were reported to the European investigator, and he was told that they will be included in our next paper on half-lives. Hopefully this study will eliminate the temporary confusion about chemical effects on half-lives.

Decay Studies and Isotope Enrichment. We have continued to cooperate with members of the Electronuclear Research Division in the systematic study of nuclear decay structure in the rare-earth region. Isotopically enriched rare earths such as ^{155}Gd are irradiated in the ORIC, and the induced activity is isolated by ion exchange techniques. A weightless source is prepared by electrodeposition, and the spectrum is recorded on film in the permanent magnet spectrographs; several spectrographs of varying magnetic field strength are used. New experimental evidence on low-lying states excited in ^{153}Tb and ^{155}Tb has been obtained. It is known that a marked change in nuclear structure occurs between neutron numbers 88 (^{153}Tb) and 90 (^{155}Tb). By combining the conversion results with complementary data from independent photon studies, partial decay schemes are constructed from energy sums, multipolarities, and intensities of the transitions.

We have completed a more extensive study of previously reported evidence for photofission of iron. Thin foils of iron were bombarded with electrons either at the Stanford Linear Accelerator or the Cambridge Electron Accelerator. Radiochemical and gamma-ray spectroscopy were used to measure yields of radionuclides produced in the targets. The experimental evidence obtained in this series of experiments indicates that nuclides of mass <35 produced in the iron targets are the result of a fissionlike process. We have submitted a paper entitled "Photonuclear Reactions in Iron

[7] G. Harbottle, "The Half-Lives of Two Long-Lived Nuclear Isomers, ^{108m}Ag and ^{192m2}Ir, and of ^{137}Cs and ^{204}Tl," *Radiochim. Acta* 13, 132 (1970).

and Aluminum Bombarded with High-Energy Electrons" to the *Physical Review*. This is a cooperative effort of ORNL, the University of Tennessee, Stanford Linear Accelerator, and Cambridge Electron Accelerator.

The Szilard-Chalmers process has been used with metal-phthalocyanine complexes to prepare enriched nuclides. An effort was made to use this technique to enrich actinide isotopes; however, lanthanide phthalocyanines were used as models of the actinide compounds. The La, Eu, Gd, and Y phthalocyanines were prepared (1) by fusion reaction of phthalonitrile with the metal chloride and (2) preparation of lithium phthalocyanine and its reaction with the anhydrous metal chloride. The two methods produced compounds with different properties. However, each preparation was tested for use as an isotope enrichment agent by neutron bombardment. Low enrichment factors were obtained in every experiment. We interpret these results to mean that the lanthanide phthalocyanine complexes are not sufficiently stable for use as isotope enrichment agents by the Szilard-Chalmers method; therefore, further work was discontinued.

Fission Product Release from Reactor Fuel Microspheres. The study of fission product release from reactor fuel microspheres is a cooperative program with the Reactor Chemistry Division. We measure the rate of release of ^{137}Cs and ^{89}Sr-^{90}Sr from the irradiated microspheres heated in the induction heater apparatus at various temperatures ranging from 1700 to 2200°C. We find that the higher the temperature, the higher the release rate. The time lag from starting the heating at a given temperature until the release of ^{137}Cs and ^{89}Sr-^{90}Sr is decreased as the temperature is raised, and at 2100°C the ^{137}Cs release can be measured after 30 min heating time. The released ^{137}Cs is collected and measured on the furnace tube and the graphite crucible. The ^{89}Sr-^{90}Sr is removed from the furnace tube, and the graphite crucible is dissolved prior to chemical separation and measurement.

We have begun release studies on bonded bed microspheres for ^{137}Cs and ^{89}Sr-^{90}Sr; the first run was completed after 2500 hr at a temperature of 1250°C. The run was stopped several times to measure the ^{137}Cs on the furnace tubes. We will measure ^{89}Sr-^{90}Sr after we have removed it from the furnace tube.

We have developed a rapid method for the separation of strontium from fission products using ^{85}Sr for yield correction.[8] The sample with carrier is made basic in the presence of dichromate, which removes many of the interfering radioactivities including Ba, Y, and La by precipitation as the chromate or hydroxide. The strontium is then precipitated with Na_2CO_3 from the radioactivities remaining in the solution. The sample can be counted after the decay of the ^{137m}Ba daughter of ^{137}Cs, about 30 min. The complete separation procedure takes about 20 min.

[8] L. C. Bate, "Rapid Radiochemical Strontium Separation," *Radiochem. Radioanal. Letters* 4, 385 (1970).

PROTON REACTION ANALYSIS FOR THE RATIOS ^{13}C/^{12}C AND ^{15}N/^{12}C IN BIOLOGICAL SAMPLES

A mathematical treatment was developed for the determination of nuclide ratios in biological samples by proton reaction analysis (proton microprobe) that greatly simplifies its interpretation. On the basis of this treatment we ran a new series of experiments at the 3-MV Van de Graaff accelerator that provided new conclusions about the method.

The reactions and resonance energies of interest are ^{12}C$(p,\gamma)^{13}$N, 0.450 MeV; ^{13}C$(p,\gamma)^{14}$N, 0.554 MeV; and ^{15}N$(p,\alpha\gamma)^{12}$C, 0.429 and 0.898 MeV. When a thick target is bombarded with charged particles, the prompt-gamma-ray count rate resulting from a given nuclear reaction may be expressed by

$$r = \frac{cfeN_0 I}{W} \int_{E_0}^{0} \frac{\sigma(E)}{S(E)} dE \,, \qquad (1)$$

where f is the fractional abundance of the reacting nuclide, c and W are the concentration in the target material and the atomic weight, respectively, of the corresponding element, e is the counting efficiency, I and E_0 are the beam intensity and kinetic energy, respectively, N_0 is Avogadro's number, $\sigma(E)$ is the reaction excitation function, and $S(E)$ is the stopping power of the target material. Equation (1) would give, for example, the prompt count rate for the ^{13}C reaction; if the ratio ^{13}C/^{12}C were desired, however, this equation would be divided by that for ^{12}C to obtain the ratio of the rates, r. Moreover, as a standard would generally be used for comparison, its own ratio should, in turn, be combined with the above one. A complex equation would then result, involving four integrals as the one in Eq. (1); the same would be true for the determination of the ratio ^{15}N/^{12}C.

Fortunately, we have observed that for any two organic targets, chosen among a large variety, the ratio of their proton stopping powers is reasonably constant for each of the above energies. This fact results in a drastic simplification of the mathematical treatment.

Indeed, the integral factors mentioned above cancel, and the complex equation reduces to

$$\frac{R_x}{R_s} = \frac{F_x}{F_s}, \qquad (2)$$

where the F's are ratios of nuclide abundances f (e.g., $^{13}C/^{12}C$ or $^{15}N/^{12}C$) and the R's are ratios of corresponding prompt gamma-ray count rates (r) measured for the sample x and for the standard s.

The new series of experiments comprised bombardments of freeze-dried samples of human brain and lung and *E. coli* with 0.7-MeV protons. Attempts were made to improve sample cooling both by compressing the samples into 2.5-cm-diam, 2-mm-thick disks and by providing the target holder with an aluminum finger submerged in acetone–dry-ice mixture (−78.5°C). Unfortunately, however, though proton currents of ~0.5 μA could now be accepted, the samples still carbonized after 15 to 30 min irradiation. Gamma-ray spectra were obtained simultaneously with two 5- × 5-in. NaI(Tl) detectors facing each other at 90° with respect to the proton beam and with a 30 cm^3 Ge(Li) detector to compare the sensitivity and resolution of both counting systems. Urea, benzamide, and graphite standards were used, according to the approximations leading to Eq. (2); yield curves were also determined with these standards for the reactions of interest.

A total of 122 spectra were obtained, and it was clear early in these experiments that the efficiency of Ge(Li) detectors was generally too small to yield acceptable sensitivities. Some results are presented in Table 4.1.

It may be observed that the precision for these determinations is approximately 5 to 9%, while the absolute error (accuracy) is generally below that value, as expected. Spectrum smoothing by the computer program GAMMA BASIC 3D (E. Schonfeld), used for handling of the data, resulted in some improvement of the precisions and accuracies of Table 4.1.

Yield curves were determined with graphite and urea targets for the reactions of interest by bombarding with protons of 0.7 to 1.8 MeV. The yield for the ^{12}C reaction stays constant at 75.8 cpm/μA per unit percent nuclide (^{12}C), while that for ^{13}C doubles from 582 (analogous units) at 0.7 MeV to 1090 at 1.2 MeV. Above the latter proton energy, high interference from other reactions prevents reliable determinations. Contrastingly, the ^{15}N yield increases smoothly from 6970 at 0.7 MeV to 1.66 × 10^8 at 1.8 MeV without interferences being apparent.

The biological samples were also subjected to long proton bombardments to observe any possible time variation of the ratios $^{13}C/^{12}C$ and $^{15}N/^{12}C$. The irradiations were carried out with 0.4- to 0.5-μA beams of 0.7-MeV protons and lasted a total of 2 hr in each case. Determinations of the ratios were made every 30 min. To discover any deviation from constancy we fitted these results (represented by R_x) by the least-squares method to a straight line for each sample,

$$R_x = a + bt,$$

in terms of bombardment time, t. Results for the ratio $^{13}C/^{12}C$ can be fitted with relatively small error to a horizontal line; that is, the ratio remains constant throughout the bombardment, as was indeed expected, because this ratio is independent of chemical composition. A less-expected though analogous result was obtained for the ratio $^{15}N/^{12}C$. The constancy of this value – equivalent to the ratio N/C *dependent* on composition – implies that no significant chemical change occurs in the area of the biological target exposed to the beam during bombardment in the above conditions.

Two papers for publication in the open literature are being prepared to report and discuss in full the method and results briefly summarized here.

Table 4.1. Precision and Accuracy of ^{13}C Abundance Determinations by 0.7-MeV Proton Microprobe

Sample	Standard	Number of Determinations	Average ^{13}C Abundance (%)	Standard Deviation (%)	Absolute Error[a] (%)
Human lung	Graphite	4	1.18 ± 0.11	9.4	+6.3
	Benzamide	4	1.21 ± 0.11	9.4	+9.6
Human brain	Graphite	4	1.15 ± 0.05	4.6	+3.8
	Benzamide	4	1.18 ± 0.05	4.6	+7.0
E. coli	Graphite	4	1.10 ± 0.07	6.5	−0.7
	Benzamide	4	1.13 ± 0.07	6.5	+2.3

[a]All samples had the natural abundance of ^{13}C, that is, 1.108%.

GAMMA-RAY SPECTROMETRY AND NEW FACILITIES

Low-Level Gamma-Ray Spectrometry. Two similar gamma-ray spectrometer systems capable of measuring cosmogenic and primordial radionuclides at levels of 100 dpm/kg and less have been used for analyzing returned lunar samples of igneous rocks, breccias, and "fines" from the Apollo 12 mission.[9] Most of the whole-rock analyses were performed in the Low Level Radiation Counting Facility at the Lunar Receiving Laboratory, Houston, Texas. Following the 50-day quarantine period, samples were then sent to other laboratories including ORNL for specialized measurements. At ORNL, studies were performed on small sections from two of the Apollo 12 igneous rocks by measuring radionuclide content as a function of depth in the rock. Four- to ten-gram sections cut from vertical slices of the rocks were used for the measurements. Analysis of the data showed that solar proton activation is an important source of the induced radioactivity in lunar surface materials and that detailed radioactivity measurements can provide orientation information on such samples.

Primordial ^{40}K measurements coupled with ^{40}Ar determinations from rare-gas experiments yielded gas-retention age values that showed the Apollo 12 materials to be about one billion years younger than those of Apollo 11. This information verified the observations of crater density ages at the two sites, and the large age difference indicates that the lunar mare had a prolonged period of filling.

We tested the accuracy of the overall analytical scheme for the Houston spectrometer by making up a replica test mixture of Apollo 11 rock 17 (a massive 971-g igneous rock). The replica was made by dispersing known amounts of four cosmogenic and three primordial radionuclides in a replica shell that had the same size and shape as the actual lunar sample. Concentrations of the radionuclides were at the levels measured during the preliminary examination period. This eight-component sample was then measured for 1035 min, a time similar to that for the lunar sample itself. Results of the analysis of this test mixture are shown in Table 4.2. As can be seen the dual-parameter analyzer system is a powerful tool for measurement of low levels of gamma-emitting nuclides, and it is capable of 5% accuracy in complicated mixtures.

[9] *Proc. Apollo 11 Lunar Science Conf.*, vol. 2, *Geochim. Cosmochim. Acta Suppl. 1*, pp. 1407–23 (1970).

Table 4.2. Analysis of Lunar Sample Synthetic Mixture by Use of Exact Library (1035-min Counting Interval)

Nuclide	Added	Found[a]	Difference (%)
K	2270 ppm	2220 ± 50	−2.2
Th	2.85 ppm	2.82 ± 0.07	−1.1
U	0.70 ppm	0.71 ± 0.03	+1.4
^{22}Na	101 dpm/kg	103 ± 6	+2.0
^{26}Al	125 dpm/kg	126 ±6	+0.8
^{46}Sc	115 dpm/kg	118 ± 5	+2.6
^{54}Mn	106 dpm/kg	111 ± 6	+4.7
^{56}Co	101 dpm/kg	106 ± 8	+5.0

[a]Errors stated are those due to counting statistics only.

Computer programs are being written for data processing of the dual-parameter spectrometer at ORNL (a hard-wired 4096 channel analyzer) in a manner similar to that employed in the PDP-9 computer-based system at Houston. In addition a 14% efficient, 2.3-keV-resolution Ge(Li) detector has been ordered for use in the ORNL low-level laboratory. We will use this device for specialized measurements on a variety of geochemical and lunar samples.

We are studying meteorite specimens (Lost City and Murchison) using the ORNL spectrometer. These are the first of a series of such studies aimed at categorizing meteorite type with radionuclide content.

A smaller low-level gamma-ray spectrometer system at ORNL has been calibrated for environmental radioactivity survey purposes. This spectrometer is an auxiliary device to the lunar sample analysis program and was formerly used for material surveys during the developmental stage of the larger spectrometer systems. Detection limits and efficiencies were determined for several radionuclides in the system containing two 5- X 4-in. NaI(Tl) detectors in a lead shield of 5-in. wall thickness. Measurements were made for 10- and 760-g samples. The system is suited to measurements of larger samples as well as in vivo whole-body determinations of animals, birds, and fishes. The system was applied to the analysis of some special plates from a Plowshare program and provided answers unavailable from more conventional detectors.

This is a cooperative project between G. D. O'Kelley of the Chemistry Division, Ernest Schonfeld of NASA-MSC, Houston, Texas, and the Analytical Chemistry Division.

Fission Product Measurement in Nuclear Reactors by Remote Gamma Spectrometry. We have continued to develop and apply remote gamma spectrometry for

fission product measurement in nuclear reactor components. For such studies we use a high-quality Ge(Li) detector in a collimated shield that permits only those gamma rays from a small section of a remotely located reactor component to reach the detector. The technique has been applied extensively in the molten-salt reactor experiment to measure highly radioactive materials at distances of 15 ft or more. At the present time we are considering using similar procedures to monitor low-level concentrations of fission products in high-temperature gas-cooled reactors (HTGR).

In a joint effort with the Reactor Division we completed a thorough examination of the fuel salt circulation and off-gas systems of the MSRE. Almost 1400 gamma spectra were accumulated during shutdown and at several power levels. The complex gamma spectra (some containing several hundred photopeaks) were resolved using a version of GAMANAL, a computer code developed at Livermore and translated to FORTRAN IV at Argonne National Laboratory. Quantitative information was obtained on the behavior of nearly all the gamma-emitting isotopes of Kr, Rb, Nb, Mo, Tc, Ru, Rh, Sb, Te, I, Xe, Cs, Ba, La, and Ce with half-lives longer than about 10 sec. We discovered that antimony isotopes plate out on metal surfaces contacted by the circulating fuel salt. It was already known that ^{95}Nb, ^{103,106}Ru, ^{99,101}Mo, and tellurium isotopes plate out on metal surfaces. We believe that this study has contributed significantly to knowledge of fission product behavior in molten-salt reactors and may materially aid in design of future reactors.

We are assisting the ORNL HTGR nuclear safety project (coordinated by H. J. de Nordwall of the Reactor Chemistry Division) in a program to assess fission product transport in HTGR coolant circuits. Specifically, we intend to determine the types and amounts of fission products transported, where and to what extent they deposit in the circuit, and the mechanisms (whether on dust, as free atoms or molecules, etc.) of transport.

We plan to begin experimental measurements on the Peach Bottom HTGR and have begun discussions with Philadelphia Electric Corporation (owner and operator of the reactor) and Gulf General Atomic (designer) concerning the measurements. Initially we plan to measure the short-lived gases, extend the presently used methods of aerosol collection and examination, and determine directly the amounts of gamma-emitting fission products on several coolant-circuit components by gamma spectrometry. In addition we hope to be able to obtain and examine sample deposits from surfaces within the primary coolant circuit.

Compilation of Nuclear Data for Ge(Li) Gamma Spectrometry. To facilitate data reduction of gamma spectra produced with high-resolution Ge(Li) detectors, we have compiled a table of accurate gamma energies and branching ratios. Most of the data were taken from references published within the past three years. References were chosen whose authors had used special care in determining both gamma energies and branching ratios. We believe that most energy values tabulated are uncertain by about 0.5 keV or less. The data survey was initially undertaken to aid in resolving and identifying photopeaks of some very complex fission product spectra obtained in remote gamma spectrometry of MSRE components. Although especially valuable for its entries of short-lived fission products, the table now contains data for 369 radionuclides produced by fission, neutron, and charged-particle reactions as well as some that occur naturally.

The data are kept on punched cards that are processed by a computer code to give a listing or to produce a magnetic tape data file. The listing presently consists of two sections, one arranged by increasing atomic number, the other by increasing gamma energy. The latter arrangement is especially useful for photopeak identifications in complex Ge(Li) spectra. We plan to distribute the data to interested persons through the ORNL Radiation Shielding Information Center.

Gamma-Ray Spectrometer Systems. We have recently acquired two 4096-channel gamma-ray spectrometer systems. They consist of a basic 4096-channel Nuclear Data Analyzer interfaced to a PDP-15/20 computer. The computer has an 8192 18-bit word memory with hard-wired multiply and divide. The input-output peripherals are: a KSR-35 Teletype, a high speed paper tape reader and punch, and two Digital Equipment Corporation magnetic tape transports. Each transport provides bidirectional reading and writing on 3-in.-diam tape reels. The tape holds 166,000 18-bit words.

In addition to the usual hard-wired analyzer commands, which are also available through software control, there are software commands for data manipulation such as a 5-point coefficient, smooth, log conversion, calculation of the coefficients for a linear equation relating channel number to energy, locating the centroid of peaks, and then calculating the energy of these peaks. Through software control the system is capable of a 4096 X 4096 resolution using magnetic tape as buffer storage for addresses.

These systems give us the capability of acquiring high-resolution, full-energy Ge(Li) gamma-ray spectra in a single counting period. These systems will be used for

gamma-ray spectral analysis in neutron activation analysis, radioisotope analysis, and decay scheme studies.

High Flux Activation Analysis Laboratory. Although the construction that was initially planned for the High Flux Activation Analysis Laboratory was completed, safety considerations raised by the Reactor Experiment Review Committee (RERC) caused insertion of the in-vessel section of the pneumatic tube to be postponed. The RERC reviewed the experiment twice: on February 11 and August 13, 1970; following these reviews modifications were made to the system, and it is now approved. We hope to install the pneumatic tube during a HFIR shutdown about the end of 1970.

Photon and Fast-Neutron Activation Facility at the ORELA. The photon activation pneumatic facility at the Oak Ridge Electron Linear Accelerator (ORELA) was finally completed. The performance of the "rabbit" was thoroughly tested, and the first irradiations are scheduled for October 1970.

Despite our hopes, the pressure of urgent physics work at the ORELA prevented access to the target room for a long period of time after ORNL took possession of the accelerator in mid 1969. Thus only in early August 1970 was the Analytical Chemistry photon activation facility completed. Figure 4.1 shows the location of the two aluminum irradiation chambers in the target room of the ORELA. On the left is the completed facility, in the electron forward direction, for bremsstrahlung photon bombardment; on the right, where the photon flux is minimum, is the fast-neutron facility. The latter should be completed in the near future, because its irradiation chamber is already finished and awaiting installation in the target room; most of the external pipeline is also in place and being currently used with the photon facility.

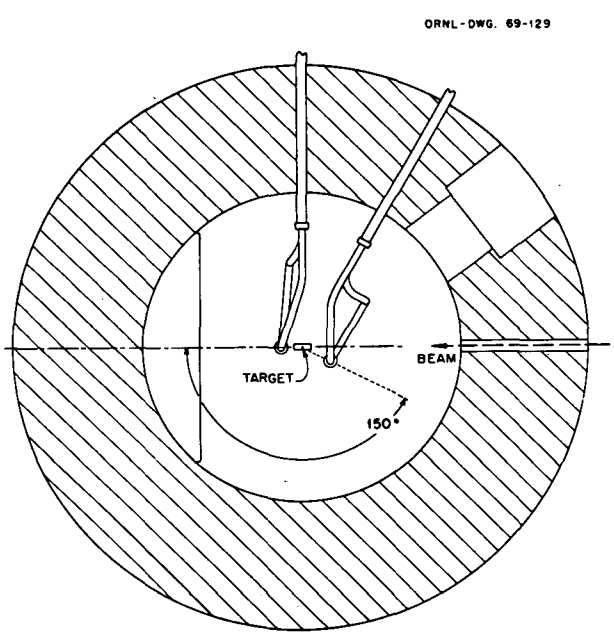

Fig. 4.1. ORELA's Target Room Showing Location of Photon Activation (Left) and Fast-Neutron Activation (Right) Irradiation Chambers.

As mentioned before, during bombardment the rabbit – an aluminum sphere containing up to four samples or standards – spins and precesses, supported by an upward air current, which so insures irradiation homogeneity and provides cooling. By using a transparent mockup the height of the spinning sphere with respect to the electron beam was calibrated vs air flow to guarantee maximum photon flux. The operation of the pneumatic system was also tested innumerable times and proved reliable. Basic counting equipment including a 3- X 3-in. NaI(Tl) detector and a 400-channel analyzer is presently being assembled at the loading-receiving station – furnished also with two hoods – to support our first photon bombardments shortly. These preliminary experiments will be with bremsstrahlung from 140-MeV electrons and will concern studies on rabbit cooling efficiency, sample bombardment homogeneity, and rough determinations of analytical sensitivities for a few elements of interest, such as mercury, lead, and some light nuclides.

Californium-252. We have begun a program to utilize ^{252}Cf neutron sources as an analytical tool that is directed toward exploiting the unique properties of ^{252}Cf: small size and portability. In the first phase we plan to determine the practical sensitivity for determination of an element in a very large sample of water by measurement of the prompt gamma rays produced in neutron capture. This is a promising approach, because water will act as the moderator. This first experiment will probably require only a small ^{252}Cf source. For the second phase we plan to build a portable source of ~100 mg. Specific areas of application for the portable source are (1) monitoring for fissionable material, (2) geological survey, (3) examination of environmental pollution, (4) ecological studies, and (5) process analysis.

We expect the first phase to get under way immediately; however, the second phase is still in the planning stage.

NUCLEAR SAFETY SUPPORT PROGRAM

PWR Studies. The work carried out in the past year on the above program is a continuing effort in support

of the Spray and Absorption Technology Program being coordinated by ORNL for the AEC. It is proposed that the pressure reduction sprays in pressurized water reactors (PWR) be used to reduce the fission product concentration in the reactor containment building following a loss-of-coolant accident (LOCA). Since these sprays will be exposed to extremes of temperature (ambient to 135°C) and radiation ($\sim 3 \times 10^8$ rads), it is important that the stability of the various proposed spray solutions be established under these conditions. Our work in the past on various proposed solutions has eliminated all but two from consideration for usage by the reactor vendors. The two still under consideration are the base borate (0.15 *M* NaOH–3000 ppm B) and base borated thiosulfate (1 wt % $Na_2S_2O_3$–0.15 *M* NaOH–3000 ppm B). Our work has established that, from a chemical viewpoint, both solutions are sufficiently stable under expected accident conditions to be used as safety sprays.

In previous studies all our work had been carried out in a static, that is, capsule, manner. This work indicated strongly that radiolytic H_2 might be a problem in an LOCA. There remained some doubt as to the applicability of capsule data to a dynamic system such as would be operative in an LOCA. Therefore in the past year we fabricated and set up several circulatory gamma radiation loops. These loops are of such a nature that any condition of gas-liquid ratio, pumping speed, temperature, and cover gas which could be expected to obtain in the real use can be simulated.

Using these dynamic loops we carried out studies on the radiolytic behavior of the two spray solutions. Emphasis was largely on the problem of radiolytic gas generation. The results of these studies are largely confirmatory of the results obtained in earlier capsule tests. It was established that in a dynamic system $G(H_2) \cong 0.4$ for both solutions. No "steady state" is established at radiolytic gas pressures expected in the accident case. We studied the effect of flow rate, gas-liquid ratio, and temperature on both rate of radiolytic H_2 production and "steady-state" concentration under conditions approximating those in the accident case; reasonable variations in these parameters show little effect. It is true, however, that the radiolytic gas "steady-state" concentration is affected by temperature, that is, the higher the temperature the lower the "steady-state" concentration. However, even under the more ideal conditions – ideal in the sense that a low radiolytic H_2 concentration is desirable – the radiolytic gas concentrations build up to well over 1 atm gauge pressure with little evidence of a "steady state." Our work has proven that radiolytic gas concentrations may well be a safety hazard in the LOCA; that is, sufficient radiolytic H_2 may build up to reach explosive limits. Therefore we initiated a search for possible remedies. The various reactor vendors have proposed several answers to the problem, none of which seems highly acceptable. The notion of purging the reactor containment after radiolytic H_2 reaches a danger limit leaves much to be desired from a safety viewpoint. Another proposal is a flame recombiner to burn off the H_2 as it is formed. This too is probably unacceptable. It has been known for some time that various metals such as copper work well as radiolytic gas recombiners – but only in fairly strong acid media. The idea of such an "internal" recombiner struck us as much more desirable than the ideas proposed by the vendors. It also seemed logical that perhaps the oxygenated anions of the Group V and VI metals would be active in causing recombination of the radiolytic gases. Therefore the effect of a group of these ions, all soluble in basic medium, on both radiolytic H_2 production and "steady-state" concentration was investigated. Among the compounds tested in the base borate solution were Na_2CrO_4, Na_2HAsO_4, Na_3MoO_4, $VOSO_4$, and $NaVO_3$. All the above show some effect in lowering $G(H_2)$. However sodium metavanadate, $NaVO_3$, seemed to be the most effective. The data obtained indicate that $NaVO_3$ in base borate medium decreases $G(H_2)$ by a factor of ~ 10; that is, when no $NaVO_3$ is present, $G(H_2) \cong 0.4$, whereas when 1×10^{-3} *M* $NaVO_3$ is present, $G(H_2) \cong 0.044$. The data also showed that an increase in $NaVO_3$ concentration above 1×10^{-3} *M* has no added effect, while a decrease does increase $G(H_2)$.

Since the addition of $NaVO_3$ seemed to be so successful in decreasing $G(H_2)$ in the base borate medium, we then tested it in the base borated thiosulfate medium. The effect on $G(H_2)$ was negligible or even worse – the $G(H_2)$ with $NaVO_3$ present shows a slight increase. Apparently the $NaVO_3$ is a strong enough oxidizing agent, even in this alkaline medium, to react with the $Na_2S_2O_3$ which is present in large excess. Because of these negative results we tested the other compounds mentioned previously as well as various organic compounds well known as hydrated electron scavengers. Among these were quinone, ascorbic acid, nitrobenzene, picric acid, and orthonitrophenol. None of these showed positive results. To date we have found no compound which acts as a recombiner for radiolytic H_2 in the base borated thiosulfate medium.

Radiolytic Sulfur and CH_3I. Even though our previous work had indicated no problem with the chemical stability of the base borated thiosulfate solution, there

was still some speculation that this spray might generate copious amounts of radiolytic sulfur under the extreme conditions of radiation and temperature expected in the accident case. Therefore we carried out a definitive study in the dynamic loop facility on this point. The data obtained enabled us to establish the following: at various gas-liquid ratios of from 10 to 0.1, at temperatures up to 125°C, and at radiation doses up to 5×10^8 rads radiolytic sulfur should present no problem in the accident case. We further found that the pH of the spray solution must be kept above 8.5 and the H_2 overpressure kept at some reasonable level (<2 atm) if essentially no radiolytic sulfur is to be formed. These recommendations have been incorporated into the spray solution design requirement.

Since it is considered that ~10% of the ^{131}I present in the accident case will be there as CH_3I, it is necessary to consider ways of coping with it, since the spray solutions do not adequately degrade it. Therefore we carried out a series of studies on the effect of radiation on CH_3I both in the gaseous and spray solution form. It was hoped that CH_3I would show sufficient sensitivity to radiation so that it could be shown not to be a real problem. The CH_3I in both forms did prove to be sensitive to radiation, but unfortunately the degree of degradation did not prove sufficient to eliminate the CH_3I problem.

BWR Studies. Our work carried out on the proposed spray solutions in PWR systems indicated that radiolytic gas generation in the accident case could be great enough to require serious design considerations. While boiling water reactors (BWR) are not designed to utilize the same concept of containment sprays, it was recognized that a similar problem could arise in a BWR LOCA. Accordingly we, in conjunction with General Electric Company, initiated a program to establish the extent to which water radiolysis could prove a hazard in a BWR.

The objective was to determine the effect of various parameters (temperature, flow rate, gas-liquid ratio, composition of cover gas) on the rate of generation of radiolytic H_2 and O_2 from distilled water under simulated accident conditions for a BWR. The rate-of-generation study also entailed determination of the "steady-state" concentrations of the radiolytic gases under varying conditions of the experiments. All experiments were carried out in the dynamic loop radiation facility. The results of the experiments may be summarized in short:

1. The "steady-state" radiolytic gas concentration is a function of pumping rate, that is, turbulence. In every case studied, the higher pumping rate resulted in higher "steady-state" gas concentration.
2. The temperature has a definite effect on the "steady-state" concentration. This effect is much more noticeable at the higher pumping rates. In each case as the temperature increases from 65 to 95°C, the radiolytic gas concentration decreases. As the temperature is increased to 125°C (boiling) the effect of temperature is largely negated, apparently by the increased turbulence due to boiling. The gas solubility also decreases, which may be a contributing factor to the decreased change brought about by the higher temperature.
3. The gas-liquid ratio is shown to have some effect, although less than the other parameters. In general as the gas-liquid ratio increases, a slight increase in "steady-state" equilibrium gas concentration is noted. However, for all practical purposes this effect is negligible in comparison with the effects shown by variation of the other two parameters.
4. The use of a partially inerted atmosphere (95% N_2, 5% O_2) rather than an air cover is shown to have an effect on the radiolytic gas concentration. The effect is not highly pronounced, but it is in the direction of decreasing "steady-state" concentrations.
5. The data do not indicate that $G(H_2)$ drops to some low multiple of the commonly accepted value (0.45). It should be pointed out that the $G(H_2)$ values found in this study can be said to vary from ~0.3 to 0.0. That is, if $G(H_2)$ is accepted as the slope of the radiation dose-gas pressure curve, any $G(H_2)$ may be arrived at, since a "steady-state" is reached. However, the important $G(H_2)$ value is that obtained initially. Realistically the G values for H_2 vary between ~0.1 and 0.3. This point must be emphasized: $G(H_2)$ governs the rate of approach to a "steady-state" condition and decreases as the "steady state" is approached.
6. The data show quite clearly that the volume of radiolytic hydrogen generated in each case is very close to twice the volume of radiolytic oxygen generated. If $G(H_2) = 0.3$, then $G(O_2) = 0.15$.
7. The variation of the parameters within the limits studied would indicate that the lower limit for "steady-state" radiolytic hydrogen concentration is between ~3 and 4 vol %.

EFFECTS OF RADIATION ON ANALYTICAL METHODS

The need to apply analytical methods to highly radioactive materials remains a vital part of the Analytical Chemistry Division's effort. Because many methods are adversely affected by intense radiation, a program was begun several years ago to investigate and understand the nature, and devise ways to reduce the effects, of radiation on analytical methods. We have continued the work with a study of chemical protection of reagents from radiolysis. We have also begun an investigation of the effects of alpha radiation.

Analytical reagents in water are affected greatly by the radiolytic products of water but little by direct interaction with the radiation itself. There are, however, considerable differences between the rates at which different solute species are attacked by the radiolytic products of water. We therefore expected that this fact might be used as a basis to protect analytical reagents from radiolytic destruction. Protection would occur if a chemical agent which would react faster with the radiolytic products than the chemical reactants were added to the system. This idea was evaluated by testing the ability of several additives to protect the color reagents arsenazo(III) and xylenol orange. Complete protection was found when 0.1 *M* solutions of thiosulfate, tetrathionate, and nitrite at pH 12 were exposed to 10^4 rads of gamma radiation. Iodide and organic anions, for example, tartrate and formate, give good protection up to about 5000 rads and at pH values down to 7. Although nitrite and tetrathionate are useful to pH 3, no additive was found that would give significant protection in more acid media.

As part of the study on the effects of alpha radiation on analytical methods, we are investigating reactor irradiations of ^{6}Li solutions. The reaction of thermal neutrons with ^{6}Li yields triton and alpha particles with a total energy of 4.78 MeV. Irradiations are being made in the heavy-water tank of the Bulk Shielding Reactor (BSR). Two irradiation holes with gamma dose rates of 10^4 R/min and thermal neutron fluxes of $\sim 10^{12}$ exist in this facility. Samples can be placed in and taken from these holes during reactor operation. Essentially no fast neutrons are present. Calculations show that solutions containing 1 mg/ml of ^{6}Li, when exposed to this neutron flux, would receive about 4×10^5 R/min from the triton and alpha particles of the ^{6}Li reactions. This charged-particle dose rate is comparable to the alpha-particle dose rate received by solutions containing 1 mg/ml of ^{242}Cm. Therefore we believe that ^{6}Li irradiations can be used to simulate the radiolytic effects found in solutions of intense alpha-emitting transuranium solutions.

Thus far we have briefly studied the effects of irradiations using ^{6}Li with the $Ce(SO_4)_2$ (0.02 *M*) dosimeter system and NaCNS (5×10^{-4} *M*) nitric acid solutions. Irradiations were made for 5 min using 1-ml solution volumes. The concentration of ^{6}Li was varied from about 1 to 0.05 mg/ml. At the higher ^{6}Li levels extensive reduction of Cd(IV) and decomposition of the CNS ion occurred. The extent of reaction in each system appeared to be dependent on dose rate. The decomposition of the CNS ion increased with nitric acid concentration.

Although these experiments are preliminary, they seem to confirm the expected usefulness of the ^{6}Li irradiation system. Compared with conventional alpha emitters for radiolytic sources, the ^{6}Li system is more convenient, requires much less provision for radiation safety measures, and can be "turned on and off" merely by placing the sample in and out of the reactor. A study of the radiolysis of several analytical color reagents is planned.

CERENKOV AND PHOSPHOR STUDIES

In 1964 it was suggested that Cerenkov counting, already well established in the area of high-energy measurements, could be used to assay ^{32}P in a standard liquid scintillation counter. Since that time there has been virtually an exponential increase in the application of Cerenkov techniques to the routine assay of a variety of radionuclides. The method has many potential advantages, among which is the extreme simplicity of sample preparation.

The major portion of the photon emission from Cerenkov events occurs in the ultraviolet spectral region. Since many phototubes exhibit a sharp drop in sensitivity in this region, it is often desirable to incorporate a waveshifting compound into the counting mixture. A search of the literature indicated that a number of compounds had been studied as waveshifting agents. However, no systematic study had ever been made to compare the relative merit of these materials, nor were the conditions for their use adequately described. Because of the growing interest in Cerenkov techniques, we elected to initiate such a study. Thirteen fluorescent compounds were selected as possible waveshifters. The parameters investigated included the isotropy of emission, concentration effects, residual phosphorescence, pH, beta energy, stability, and counting efficiency. The results indicate that many desirable benefits can be realized by using a waveshifter. For

low-energy beta emitters, the counting efficiency can be increased by a factor of 5; the counting efficiency of energetic emitters (^{32}P) can be almost doubled. Also, the change in the directional properties of Cerenkov emission caused by waveshifters is important in coincidence counting systems.

Our experiments indicated that many of the compounds recommended as waveshifters had severe limitations, while others, less well known, were often superior. As a result of this study, we recommend as an "overall best" waveshifter the compound 4-methylumbelliferone. It appears to be an outstanding choice in every respect, and it is the one we have selected for all of our routine Cerenkov counting.

For some time, we have been investigating the problems of using a light-emitting phosphor as the primary conversion element in small electrical power systems. In such a system radioisotope decay energy is converted by the phosphor to light, which is subsequently changed to electrical energy by a secondary element – a solar cell. Our previous work with beta excitation of phosphors showed that even with high-efficiency photoelectric converters, the overall electrical yield was very small. The major problem proved to be the low efficiency of the phosphor at the isotope loading levels used.

In the past year we have directed our attention to the use of alpha radiation as the primary excitation source. Although light output/unit excitation was the most important parameter, our preliminary tests were designed to also evaluate the radiation damage of the selected phosphors and their spectral emission characteristics. All of this work was carried out in a glovebox facility located in Building 2026. A unique feature of these experiments was that the scanning spectral radiometer (specially designed for these tests) was located in the glovebox, and all measurements were made without removing active sources from the box.

The general procedure consisted in preparing known mixtures of $^{241}Am_2O_3$ powder and selected inorganic phosphors. The mixtures were transferred to an emission cell and permanently sealed. These samples were periodically measured for total light output and spectral distribution; the results were most discouraging. All of the phosphors tested showed a marked degree of radiation damage and reduced light output with relatively low total dose rates.

For example, the sulfide phosphors (ZnS:Cu, ZnCdS:Cu, CdS:Ag) degraded to half their original intensity level at a total alpha dose of about 4×10^8 rads (three days). The rare-earth phosphor, YVO_4:Eu, proved significantly more resistant; a dose of 1.3×10^{10} rads was needed to reduce the original emission to half. The spectral characteristics of all the tested phosphors were essentially unaffected by radiation damage. However, the reflectivity of the phosphors was often changed, and this effect caused small spectral shifts.

As the result of this investigation, we feel that the dual conversion process suggested above is not technically suitable for use in a small power system. We have terminated all work on this project and have submitted our results and recommendations to an interested government agency.

Another aspect of our phosphor program was concerned with the development of phosphor screens for short-term information storage. Here, the results were much more promising. The basic problem involves the activation of phosphorescent materials by light of specific wavelengths. The activation takes place by variation in both the geometrical and time domains. The purpose of the phosphor screen is to store the individual information bits and, after activation, allow an instant readout of the composite activation mosaic. This type of screen would have applications in multiplexed optical transmissions, visual signal averaging, investigation of short-term optical phenomena, and several possible medical uses.

Our specific studies were designed to determine if such a storage screen is feasible and also to measure the important operating parameters such as resolution, visual sensitivity, decay characteristics, spectral activation response, and film construction. The initial tests were used to examine a large number of phosphors for their activation and decay characteristics. From this group we found several that were likely candidates for the application. Activation occurred in the proper spectral region, and usable decay periods were found. We selected a special formulation of ZnS:Cu for further study. We attempted to fabricate self-supporting films of the phosphor using a variety of techniques. However, all of these attempts were deficient in one or more of the important physical or optical characteristics. A supported film has proved to be superior in every respect. The film is prepared by coating the phosphor on a TiO_2-loaded plastic sheet. The phosphor is then covered with a thin transparent plastic. Preliminary tests with this type of film have shown that it can be used to store intensity information for over 4 hr when activated by light at 540 nm. Also, the resolution is sufficiently high but somewhat limited by the phosphor thickness and light scattering by the TiO_2 reflective backing. Samples of this film are now being tested under the conditions of the proposed application for further evaluation.

5. Analytical Instrumentation

D. J. Fisher, Group Leader

R. W. Stelzner, Assistant Group Leader

M. T. Kelley[1] W. L. Belew[2] W. L. Maddox T. R. Mueller

We see four basic present trends in the factors and principles for the design of analytical instrumentation. Two concern uses of theory for the mathematical modeling of instrumentation circuits and measurement systems. The first is the use of matrix and transform theory or Boolean algebra and logic theory in a mathematical approach to both the analysis and the synthesis of circuits in analog or digital domains, that is, to the prediction and to the optimization of a desired linear or nonlinear system response. The second is the concurrent use of theory to obtain more meaningful information in analytical measurements through a more exact interpretation of complex circuit-transducer-chemistry interactions. A number of versatile elements for design have become available: The development of operational amplifiers and their sustained improvement makes analog functions and analog modules increasingly useful; the development of integrated circuit digital devices makes digital functions, digital modules, and digital computers very accessible. Thus the third trend is the use of an optimum mix of all of these elements in instrumentation systems, consistent with the state of the art and tempered by reasoned reconciliations and choices among the inevitable performance trade-offs. Finally, we observe a burgeoning development of computer-assisted, -automated, and -controlled interactive measurement systems, with the digital computer included literally and functionally as an integral part, and with the user directly involved.

Our work has been directed toward following these four trends and contributing to their development.

INSTRUMENTATION RESEARCH AND DEVELOPMENT

Q-2792 Polarograph and Q-2942 DME Drop-Time Controller. One each of our model Q-2792 polarographs[3,4] and model Q-2942 drop-time controllers[5] were required for electrochemical research and methods development by the Methodology Group for the Transuranium Laboratory. After these instruments had been fabricated by the Instrumentation and Controls Division, in cooperation with J. R. Stokely of the Methodology Group we evaluated their performance by means of both electrical and electrochemical tests.[6] It was necessary for us to make these tests because the performance of electroanalytical instrumentation cannot be adequately defined and measured in the absence of a cell, electrodes, and electrochemical reaction(s) of known characteristics.[6] This work has demonstrated and ensured that the quality of performance delivered by this instrumentation is consistent with the standards that were set by its design. Also, an addition was made to the Q-2792 check-out procedure that takes into account the use of an improved operational amplifier (higher gain); copies of the revised page have been sent to those on record as having a copy of the method.

Dual Potentiostat. A potentiostat capable of controlling the potentials of two electrodes simultaneously and independently was designed. The request for this device originated with the Analytical Chemistry Division's Methodology Group. That group has initiated studies using thin- (solution) layer electrochemical cells. Because of the very small distances between electrodes, species reacted at one electrode can arrive at the other electrode within a fairly short time. By considering electrode spacing and the potential of each electrode with respect to a reference electrode and by measuring the desired currents as functions of time or potential, the experimenter has a technique at his disposal with

[1] Part time.

[2] Present address: Technicon Corporation, Tarrytown, N.Y. 10591.

[3] H. C. Jones, W. L. Belew, R. W. Stelzner, T. R. Meuller, and D. J. Fisher, "A Solid-State Controlled-Potential DC Polarograph with Cyclic Scanning and Calibrated First- and Second-Derivative Scales," *Anal. Chem.* **41**, 772 (1969).

[4] R. W. Stelzner, "The Design of Measuring Circuits for a DC Polarograph," *Chem. Instr.* **2**, 213 (1969).

[5] W. L. Belew, D. J. Fisher, H. C. Jones, and M. T. Kelley, "Apparatus for Precision Control of Drop Time of Dropping Mercury Electrode in Polarography," *Anal. Chem.* **41**, 779 (1969).

[6] D. J. Fisher, W. L. Belew, and M. T. Kelley, "Electrical and Electrochemical Tests of Performance of Polarographs: I. Needs and Methods; II. Diagnostic Criteria for Establishing the Degree to Which Recorded Polarograms Are Adversely Affected by Circuit Performance," *Chem. Instr.* **1**, 225 (1968).

which to study transient, steady-state, or combinations of transient and steady-state phenomena. The potentiostat required for this application must be capable of controlling the potentials of both electrodes against a single reference electrode. Provision must also be made for varying the electrode potentials according to a desired function of time. The instantaneous current flowing at each electrode must be made available for recording as a function of time or potential. Instruments have been described to accomplish these ends.[7,8] We believe that the manner in which we have provided for the requirements represents a unique approach in terms of ease and versatility of operation of the potentiostat. For instance, with our instrument the operator can select directly the potential of each electrode, whereas with other designs the potential of one electrode is selected, and the potential of the other electrode is established as a "delta E" between electrodes. Our instrument also presents the option of sweeping one or both electrode potentials as a linear function of time. The basic circuit is very flexible with respect to the addition of other than linear potential scan. The potential sweep at the two electrodes need not start simultaneously. With only minor changes the circuit could be adapted to control the current rather than the potential. In fact, the instrument need not be used exclusively for thin-layer work. The instrument was loaned to Professor J. Q. Chambers of the Department of Chemistry, University of Tennessee (Knoxville). He has used it to control the potential of ring and disk in ring-disk electrode studies. He reports that useful experimental data were obtained with it and that it has aided him in designing an instrument for his work. We do not plan extensive development of the instrument at this time. The prototype instrument is our first attempt to design an instrument with integrated circuit amplifiers throughout, and we intend to follow its performance in order to assess the feasibility of incorporating similar amplifiers in future designs.

Cyclic Voltammeters. Our prototype controlled-potential and -current cyclic voltammeter[9] has been in use since December 1966 for electrochemical investigations in molten-salt systems. To meet the need at the Chemical Development Laboratory, Y-12 Plant, for a cyclic voltammeter for studies in aqueous solvent systems, we have modified the design of a Q-2943 NIM version of the instrument. Long-term voltage and current drifts of the amplifiers selected for the new design were lower by an order of magnitude in most cases. Specifications for some amplifiers were met at considerably reduced cost. We also relocated some of the leads carrying high-level signals between modules so that pickup by low-level circuits is minimized. This second Q-2943 NIM design has about half as much noise as the previous instrument and is the result of our cooperative efforts with W. T. Hutton and C. C. Courtney of the Instrumentation and Controls Division and the constructive criticisms of D. L. Manning and Gleb Mamantov, Consultant, Department of Chemistry, University of Tennessee. A third Q-2943 design is being constructed for use with a PDP-8/I (Digital Equipment Corp.) computer by the Reactor Projects Group to monitor the U(IV)/U(III) ratio in on-line studies with MSRE-type salts. The U(IV)/U(III) ratio promises to be a useful criterion of corrosion rate in molten-salt reactors. Earlier work on this project made use of the prototype with an outboard analog differentiator.[10] The latest Q-2943 will incorporate a differentiator/integrator NIM module. Although there will be three NIM-type instruments, each differing from the other in the internal circuitry of its modules, the interconnections have been devised so that functionally corresponding modules may be exchanged between instrument bins. This interchangeability is particularly useful in checking out a new instrument or in later maintenance. We plan to submit a note for publication that will describe the most recent version of the Q-2943 instrument.

Q-5065 Differential Voltmeter. We designed a high-impedance, ultralow-drift, differential voltmeter, ORNL model Q-5065, for Carlos Bamberger of the Reactor Chemistry Division, who needed a voltmeter with which to record electrode potentials in molten-salt media over extended periods of time without having to rezero or recalibrate the measuring equipment. He uses the results of his measurements to construct phase diagrams for various molten-salt systems. In order to obtain valid potential measurements the measuring device must not draw excessive currents through the electrodes. With the Q-5065 voltmeter and strip-chart recorder, combi-

[7] L. B. Anderson and C. N. Reilley, "Thin-Layer Electrochemistry: Steady-State Methods of Studying Rate Processes," *J. Electroanal. Chem.* 10, 295 (1965).

[8] D. T. Napp, D. C. Johnson, and Stanley Bruckenstein, "Simultaneous and Independent Potentiostatic Control of Two Indicator Electrodes," *Anal. Chem.* 39, 481 (1967).

[9] T. R. Mueller and H. C. Jones, "A Controlled-Potential and Controlled-Current Cyclic Voltammeter," *Chem. Instr.* 2, 65 (1969).

[10] M. T. Kelley, R. W. Stelzner, and D. L. Manning, "Computer-Operated Voltammetric Determination of U(IV)/U(III) Ratios," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969*, ORNL-4466, p. 32.

Table 5.1. Examples of Extra-Laboratory Fabrication and Use of Instruments During Past Year

	Polarograph, ORNL Model Q-2792	Pipetter, ORNL Model Q-1348C	Drop-Time Controller, ORNL Model Q-2942	Polarograph, ORNL Model Q-1988-A	Coulometric Titrator, ORNL Model Q-2005–X50
New units in operation		1	1		
Units under construction	4		3		
Anticipated construction	2		4		
Commercially available				x	x

nation recording is continuous and accurate. Four-decade suppression of the input voltage is provided in 1-mV steps up to 10 V. The sensitivity can also be changed from 1 mV to 1 V full scale on the recorder. For the intended application maximum error is ±50 μV. Input impedance approaches that of the input amplifiers; namely, 10^{12} Ω. A maximum of 10 pA (manufacturer's guaranteed maximum amplifier offset current) can flow in the input circuit, preventing direct application to measurements from very high impedance sources. Because the drift in input current, on the other hand, is very small, usually less than 0.01 pA/°C or hr, it is feasible to compensate for the input current if the application requires. However, uncompensated, the error only approaches 50 μV when the input impedance is as high as 5×10^8 Ω. Difficulties in procuring an ultrastable reference diode for the power supply from the manufacturer caused the instrument to be placed into service with a substitute component. We expect that incorporation of the more stable reference diode in the power supply will produce a reference voltage drift of less than ±0.005%/year. The voltmeter is built in a 13- × 17- × 5-in. chassis with a 5¼- × 19-in. front panel for rack mounting. The input voltage is easily read to the nearest millivolt from the front panel. Switching is provided so that the instrument may be used in full differential mode, or the potential of either electrode may be measured with respect to ground. An "offset polarity" switch makes it unnecessary to exchange leads if the input polarity is incorrect or reversed during a measurement. Two voltmeters were ordered. Construction of the second one by the Instrumentation and Controls Division will begin after the present instrument has been in service sufficiently long to establish the validity of the design.

Q-1728A Potentiometric Titrator. We are replacing the remote titrant-delivery units of the two ORNL model Q-1728A potentiometric titrators in the TRU facility in anticipation of the analytical load that will arise from the Laboratory's contract to process slugs containing ^{252}Cf for Savannah River. The old units have been in use for about four years and have been subjected to considerable corrosion. As the new units are being fabricated, we are making design improvements, one of which is to replace the L and N pH indicator with a Philbrick/Nexus PP25AU operational amplifier for impedance transformation in the recorder input. This amplifier is characterized by low drift, high input impedance, and small size. It will be installed as part of the remote unit, so that the impedance transformation takes place before the signal has to traverse some 50 ft of cable back to the control unit. We modified one of the old titrators this way to test the amplifier; it has operated continuously for several months. It is probable that future control units will be built with unmodified Honeywell recorders to take further advantage of this design improvement.

Fabrication Information. Updated information on the Q-2792 polarograph and the Q-2942 drop-time controller and cyclic voltammeter was prepared for DTIE and is contained in CAPE packages 1651, 1652, and 1653. These sets contain drawings, photographs, and construction specifications for the fabrication of each instrument. Further information about the design and performance capabilities of our polarographic instrumentation has been published.[11,12] In addition to the CAPE packages, we have supplied reprints and detailed check-out procedures for our instruments to interested parties. It is gratifying to note that several of our designs are being used routinely throughout the world. Table 5.1 lists the status of some known examples that have been added during the past year. Also, a commercial electromechanical DME drop-time controller has been patterned after our Q-2942 controller.

[11] D. J. Fisher, "A Method for the Design of Instrument Systems for Measurements of Highest Sensitivity," *Chem. Instr.* 2, 1 (1969).

[12] W. L. Belew, D. J. Fisher, M. T. Kelley, and J. A. Dean, "A Cell Design for Minimizing *iR* Error in Controlled-Potential Polarography of High Specific Resistance Solutions," *Chem. Instr.* 2, 297 (1970).

COMPUTER ANALYTICAL SYSTEMS

Programmable Calculator Course. The Division has a Hewlett-Packard model 9100A programmable desk calculator. Peripheral equipment includes a model 9120A printer and a model 9125A *X-Y* plotter. To familiarize the Division staff with this equipment, two courses were offered; the first was given by W. D. Shults of the Methodology Group and the second by T. R. Mueller. About 20 people in the Division have taken part in the courses, and a number of these are making use of the facility for their work.

PDP-8 Computer Programming Course. The Analytical Chemistry Division has started a course in elementary programming for the PDP-8 family of small computers manufactured by Digital Equipment Corp., Maynard, Mass. 01754. Twelve members of the Division were selected for the first class on the basis of imminent need. The instructors are Myron T. Kelley, J. M. Dale, and R. W. Stelzner. The initial stress in the course is on binary, octal and floating point number systems along with simple assembly and machine language coding. We have placed the main emphasis on learning the conversational FOCAL interpretive language. In order to encourage class members to learn by interaction with the computer, we have attempted to maximize available computer time. An advanced course in PDP-8 programming will follow this one.

Voltammetric U(IV)/U(III) Ratio Determination. We have completed the work on computer programming an unattended measurement of the U(IV)/U(III) ratio in molten fluoride salt media.[13] The success of the laboratory-scale project has served as the justification of a PDP-8/I computer system for the Reactor Projects Group to advance their development of in-line methods of chemical analysis for an operating molten-salt reactor. We have discussed phases of this work at three technical meetings and are preparing a paper for journal publication.

GeMSAEC: FOCAL Programs. When we started work with the GeMSAEC Rapid Photometric Analyzer, the computer which was available to use with it was already set up with 4K of core memory plus one 32K disk unit. Although we could have added an additional 4K of core, we felt it was desirable to proceed with programming with the available facility without waiting for delivery of additional core. We also felt it was desirable to demonstrate that the GeMSAEC could be operated with a 4K computer with one 32K disk instead of an 8K machine with two 32K disks, as was set up with the original GeMSAEC unit in the MAN program. The disk monitor supplied by DEC (Digital Equipment Corp.) makes no provision for transferring programs except in units of 200_8 words. This is not only wasteful of disk space but also does not fit very well for storing FOCAL programs, which seldom start or end at page boundaries. Also the DEC Monitor makes no provision for calling FOCAL programs and continuing the operation in the new program. Our first efforts to work out a monitor system for FOCAL programs resulted in a system which would store up to nine FOCAL programs of 700_8 words plus one block of 20_8 data words (single-precision numbers). The system incorporated a provision for calling new programs and continuing operation but required that the initial steps of the two programs be identical in form, namely,

```
1.01  G  1.10
1.02  L  G  7  C
```

and, if these steps were modified in any way, the program had to be punched on paper tape and reloaded to put the steps in the correct order in the memory. Now the system has been further revised to expand its storage capabilities and its flexibility as well. By making use of virtually all the spaces in the FOCAL (1969 version) program which are normally used for 8K operation and for functions not useful for the GeMSAEC for our own modifications, we have been able to provide the following capabilities:

1. Storage of up to 23 FOCAL programs of 1000_8 length, identified by the octal numbers 10 through 36.
2. Programs can be called and started with commands of the form L G 16 C, which can be used anywhere in a program. The new program starts at 0.0 and operates on the same variables as the previous one.
3. Two blocks of 20_8 data points can be stored also.
4. The space for variables and push-down list is 431_8 words, which should permit 40 to 45 defined variables in most cases (56 absolute maximum).
5. A space of 500_8 words for single precision data plus two working registers of 20_8 words is set aside for data from the GeMSAEC or other experiments. This permits collection of 20_{10} sets of data from the GeMSAEC.

[13] M. T. Kelley, R. W. Stelzner, and D. L. Manning, "Determination of U(IV)/U(III) Ratios in Molten Fluoride Salt for the Reactor Projects Group," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969*, ORNL-4466, p. 9.

6. The programs can be freely modified without any restriction on form or necessity of reloading from tape.
7. The top page of the computer memory, normally set aside for the disk monitor, is used also on an interchange basis for our modified monitor. The system is completely compatible with the disk monitor, so that the upper half of the disk is used for programs stored by the disk monitor; for example, an unmodified version of FOCAL is stored. While individual FOCAL programs in the 4K system cannot be as long as with an 8K system, the ability to link programs provides a very similar capability. This capability along with the machine language data-taking patch to FOCAL and the functions for manipulating single-precision data should provide all the computing and data-taking capability required for the GeMSAEC projects now planned as well as that for several other analytical instrument systems.

Using this modified version of FOCAL, a series of five programs was written for studies with the GeMSAEC analyzer. The first of these determines and stores calibration factors for each of the cuvettes vs the No. 1 cuvette, which is always used for a blank solution. The second takes transmittance data at specified time intervals, calculates and prints out absorbances, and then goes to either of two other programs which perform a linear or parabolic regression analysis on the standards in a set of samples. The absorbances from the standards are then plotted on an *X-Y* recorder along with the calculated regression curve. Finally, the parameters of the curve are used to calculate concentrations for those samples which are unknowns. This entire process is repeated until all of the data taken are exhausted. The fifth program prints out absorbances and the logarithm of absorbance differences in a format convenient for the initial phases of studies on the feasibility of using kinetic methods of analysis in the GeMSAEC. These programs are being used in studies of methods of analysis of interest in environmental monitoring, specifically for phosphate and sulfate in water (in cooperation with the Analytical Methodology Group) and for kinetic methods of analysis for various metallic ions as outlined below.

GeMSAEC: Kinetic Methods of Analysis. We are presently investigating a kinetic technique for metallic ions in which the ions are first complexed at high pH with 1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CyDTA) and then the solution is mixed with an acid buffer solution of a "scavenger" ion. The resulting attack of hydrogen ion upon the original complex proceeds at a rate dependent on the type of metal in the complex, the concentration of the complex, and the pH. Each metal complex reacts essentially independently of others, so that mixtures may be resolved by differential rate methods. The scavenging ion produces a complex with CyDTA, whose concentration increase is followed photometrically to observe the reaction rate(s). A large number of metals are amenable to this technique.[14] The range of reaction rates is quite wide and subject to some control by adjustment of the pH. This should enable us to evaluate the present GeMSAEC capabilities for kinetic methods of analysis and to make improvements leading to faster mixing in the rotor. This work is the Ph.D. dissertation research of W. L. Maddox; it is being done in cooperation with Professor Gleb Mamantov, Department of Chemistry, University of Tennessee, Knoxville, and M. T. Kelley.

GeMSAEC: Programs for Clinical Analyses. The Analytical Chemistry Division is participating with the Health Division and the Chemical Technology Division in a program to demonstrate the capabilities of the GeMSAEC analyzer in routine clinical analyses. The GeMSAEC unit being used is one originally used for development of techniques in the MAN program; it has a PDP-8/I computer attached with 8K of core and two 32K disk units. The modified version of FOCAL for the system (quite different from that used in the ACD GeMSAEC unit) was devised by Instrumentation and Controls Division personnel. The programs written in this version of FOCAL for various procedures were written primarily by Instrumentation and Controls Division personnel. As the use of the instrument in the clinical lab has developed, it has become obvious that some of these programs need to be changed to make them better suited for use by clinical laboratory technicians. We have assisted in changing existing programs toward the direction of minimizing the input by the operator, minimizing the number of standards used, and changing the output format to eliminate unnecessary information and to provide optimum legibility. We have also supplied a program to help evaluate procedures by determining the relative standard deviation of a set of results on known samples.

Differential Scanning Calorimeter. In cooperation with members of the Analytical Biochemistry Group, we are using a Perkin-Elmer differential scanning calorimeter for purity determinations. The procedure consists in recording a curve of ΔT vs T over the

[14] D. W. Margerum, J. B. Pausch, G. A. Nyssen, and G. F. Smith, "Differential Kinetic Analysis of the Metallic Elements," *Anal. Chem.* **41,** 233 (1969).

melting range for the sample against a reference sample holder. Essentially this then gives a measure of the fraction melted at each temperature as the sample traverses the melting range. A FORTRAN program for treating the data from these scans is available and has been used, but the data must be transposed by hand from the recorded curves, which is a very laborious process. A simple operational amplifier interface to provide suitable scaling factors to connect the DSC to the PDP-8/I computer has been built, and a five-wire shielded cable approximately 100 ft long has been installed to connect the DSC to the computer. The programs for the DSC use the same versions of modified FOCAL already described for the GeMSAEC. The experiments have demonstrated that the computer can record up to 320 data points from a DSC scan, smooth the data with a nine-point cubic least-squares smoothing function, and replot the smoothed data on an *X-Y* recorder. The computer can then choose the points for the beginning and end of the melting range and the peak of the curve. The PDP-8/I will then type out data which can be used directly as input for the existing FORTRAN program. However, our goal was really to carry out the entire operation on the PDP-8/I, thus avoiding manual transfer of data to cards. The remaining operations for calculating purity from melting point curves consist in calculating the total area and partial areas under the curve and then adding an empirical correction to each of these areas until a "best fit" to a straight line is obtained by regression analysis. Finally, from the intercept of the "best-fit" line for the partial areas (which are proportional to the fraction melted), the true melting point depression is calculated. From the melting point depression a purity figure is calculated. All of these operations have been successfully programmed in modified FOCAL, and the program has been tried on a limited number of pure benzoic acid samples and benzoic acid to which varying amounts of impurity had been added. The results from these samples showed poor correlation with the known impurity levels. One conclusion thus far is that there are some details in the encapsulation of samples that have not been sufficiently well standardized. We are also skeptical of some of the assumptions made in deriving the equations which are implemented in the FORTRAN program and in our FOCAL program. Both points will be examined more thoroughly.

Linear Systems Analysis. The mathematical techniques of Linear Systems Analysis can be used very effectively in the design of passive and active electrical circuits and mechanical devices. A linear system is best defined as one in which the principle of superposition is applicable: If the system response to input X_1 is Y_1, and to input X_2 is Y_2, then if inputs X_1 and X_2 are applied simultaneously, the system response is $Y_1 + Y_2$. The linear equation $Y = mX + b$ does not describe a linear system. In instrumental design we wish to proceed directly from a mathematical equation or model to an electrical circuit; this can be done in the continuous analog domain by solution of the inverse Laplace transform and implementation by passive networks or operational amplifier circuitry. In the nonlinear digital domain, Boolean algebra plus AND, OR, NOT (NAND NOR) modules are employed to realize the design. We have used linear systems analysis in the design of circuits[4] for our Q-2792 controlled-potential dc polarograph. The calculations were made then using a desk calculator. Now we have programmed a small, dedicated computer (PDP-8/I) to make similar calculations and to plot electrical transmission as a function of angular frequency on an *X-Y* recorder. Higher-order high- and low-pass filters and Butterworth and Paynter networks were analyzed. We have succeeded also in programming computerized plotting of network response for a given waveform as input. A numerical method for Fourier analysis of complex waveforms has been programmed for the PDP-8/I. The method involves slicing the waveform into 12 segments (30° intervals) and computing amplitudes of the sine and cosine components up to the sixth harmonic. Fitting of a curve represented by no known analytical expression is exact at each of the 30° data points. A fast Fourier transform (FFT) program based on the Cooley-Tukey algorithm and written in FOCAL (available from Digital Equipment Corp.) has been used also for curve fitting.

Digital Polarography. We have initiated a project to interface a small, dedicated computer, PDP-8/I (8K-core memory with 12-bit words), to a simple cell transducer to obtain information for the design, control, operation, and interpretation of polarographic systems. The overall objective is the study of techniques and methods for increasing the sensitivity, accuracy, precision, reliability, and usefulness of dc polarography. Computer peripheral equipment includes a DF-32 magnetic disk with 32K bulk-storage words, an analog-to-digital converter (ADC) with 35-μsec acquisition time for 12-bit digitization, a 32-channel multiplexer (MPX), a 3-channel digital-to-analog converter (DAC), a high-speed reader (Digitronics model 2540), an M-series real-time clock, an ASR-33 Teletypewriter for input/output, and a Moseley 2D-2A *X-Y* recorder and a Tektronix 503 oscilloscope for display. The computer-polarographic system operates with a 1969 8K-FOCAL high-level interpretive language that has been modified

to employ several functions written in machine language. The new functions (FADC, FCLK, FDIS) operate the 12-bit ADC, the real-time clock, the 3-channel DAC and the *X-Y* recorder. By means of a multiple-argument FP function, single-precision numbers can be stored for recall from memory field (1). Disk data transfers are handled by an FROW (arg,) function, where arg is a block number from 0 to 19, and the comma indicates a WRITE; if the comma is omitted, the compiler interprets the function as a READ. As many as 20_{10} blocks of 200_{10} octal data words can be stored on the disk on tracks 14 and 15 for later recall into core. Computer control of a system by the FOCAL functions is via the W103 modules, the 6XX1,2,4 instruction set, and transistorized drivers – for grounding the IOS (input/output skip) bus. The computer control is two way: the PDP-8/I can issue commands, and the DME can generate signals to initiate programmed computer operations. In addition the experimenter can communicate with the computer-polarograph system using the keyboard of the ASR-33. A linking monitor has been added to the compiler by enabling the LIBRARY command. Up to eight programs can be stored in blocks of 1000_8 words and called from the disk by L P # and L G # commands, where # is the block number of the program. Sampled data from the experimental current-time (*i-t*) curves are least-squares fitted to a selected polarographic equation. Each sample is the average of 128 measurements of current secured in exactly $1/60$ sec. Discrimination against both random and 60-Hz noise is achieved in using this one ensemble-averaging technique. Mathematical least-squares smoothing and other convolution functions can be applied if desired. Tests on the computer-polarograph system will be conducted using Cd^{2+} in solution as a representative of the class of simple, diffusion-controlled, reversible electrochemical processes.

6. Methods Development and Evaluation Laboratory

L. T. Corbin, Assistant Director
D. A. Costanzo, Group Leader

J. L. Botts G. Goldberg
L. G. Farrar F. L. Moore
P. S. Gouge

The activities of the Methods Development and Evaluation Laboratory were primarily directed to three general areas: LMFBR reactor fuel analysis, the transuranium program, and MSRE fuel analyses. We worked conjointly with the Chemical Technology, Reactor Chemistry, and Metals and Ceramics Divisions on reactor fuel fabrication, characterization, and irradiation studies and on studies of the separation and purification of actinide rare-earth elements. In addition, analytical support and assistance was given to all groups within the Service Laboratories as well as many other divisions. The capabilities of the group are extremely diverse and cover all disciplines of analytical chemistry, as exemplified by this annual summary of activities.

The importance of plutonium-containing ceramics for their potential use as nuclear fuels initiated studies for the preparation of carbides, nitrides, and carbonitrides for LMFBR fuels. The preparation of these compounds by a sol-gel process is being investigated on a laboratory scale. During the initial work, major emphasis was placed on composition of the initial materials and products and the effect of process variables on the products obtained. Thermogravimetry (TGA), chemical, and x-ray analyses have been performed to obtain a complete characterization of the products from the overall process.

Two major difficulties encountered in the analysis of plutonium/uranium carbides and carbonitrides are (1) the ceramic nature of the materials and (2) the chemical reactivity coupled with their radioactivity. The ceramic nature of the materials presents dissolution problems for chemical methods of analysis, since the acid dissolution of a heavy-element carbide is always accompanied by the liberation of carbon and a mixture of organic products. These reaction products are very troublesome when electrometric methods of analysis are used. Some of the problems have been minimized by dissolution of the samples by the sealed-tube technique.

In these investigations one of the factors which is of prime interest is the oxygen content of the solid solutions. Plutonium and uranium carbides are easily oxidized and are pyrophoric in the presence of moisture. This necessitates the handling of these samples in highly inert atmospheres. Although analytical results have indicated the formation of dense (90 to 95%) carbide and carbonitride products with C/M mole ratios of 0.9 to 1.10 for monocarbides and (C + N)/M ratios of 0.97 to 1.2 for carbonitrides, oxygen contents have been high, ranging from 2000 to 6000 ppm. These high values reflect handling problems which should be reduced or eliminated in future operations with improved sample handling techniques and with the use of the new inert-atmosphere glove box systems.

The TGA method that is being applied to the analysis of calcined products is a fast and simple method for the determination of plutonium and carbon content of plutonium carbides; it gives a good approximation of the total metal and carbon or carbon and nitrogen content of the mixed uranium/plutonium products. Advantages of the thermo balance include: precise reaction control, immediate knowledge on completion of a reaction, and minimum manipulation of the material.

The work with the Metals and Ceramics Division on the analytical requirements of the LMFBR program has continued this year.[1] Most significant has been the progress made in the characterization of the final fuel material. Thirteen batches of sintered (U, Pu)N were characterized prior to their being fabricated into pins for placement in a reactor. These pins will remain in the reactor about one year, at which time they will be removed and the material again analyzed. The results of the analysis of this material were quite good, with material balances totaling 100 ± 0.25%. In general the composition of this fuel material was found to be as follows: Pu = 18.25%; U = 76.25%; N = 5.45%; O_2 = 800 ppm; and C = 200 ppm. The nitrogen determination was improved by replacing the old sealed-tube dissolution method with a dissolution of the material using concentrated H_3PO_4. This not only saves time but increases the accuracy of the procedure.

Nine batches of (U, Pu)N were analyzed for the Metals and Ceramics Division in conjunction with a study of the lattice parameters of the nitrides. Each batch of nitride represented a different concentration of uranium and plutonium ranging from 0 to 94.4%. The results obtained here were also encouraging in that they agreed well with the data obtained from x-ray analysis and fell within the limits of the predicted values.

A particle size analyzer system based upon the Coulter technique is being evaluated for the determination of particle size distribution of reactor fuel materials.[2] The system consists of a Nuclear Data series 1100 512-channel pulse-height analyzer, a Nuclear Data model 533 preamplifier and constant current supply, a Tennelec TC-200 amplifier, and a Coulter counter metering assembly. A Teletype model TC-33 ASR is used for data printout and transfer of data to paper tape for computer analyses. This system will be used to determine the distribution of particles of diameters up to 200 μ and densities greater than 10 suspended in conducting aqueous and nonaqueous media.

The high-temperature fluorination method was used to separate ^{233}U for isotopic analysis from irradiated-graphite-encapsulated salt mixtures composed of $NaF \cdot ZrF_4 \cdot {}^{233}UF_6$.[3] Modification of the procedure was necessary in order to handle the more radioactive ^{233}U. The salts were melted and transferred from the graphite capsules to the reaction vessels and fluorinated in much the same manner as described in the original procedure; however, valved nickel traps containing NaF were used in place of glass traps. The NaF was prefluorinated to remove silicon, which interferes in the subsequent desorption of the UF_6 from the traps.

Since the capsules were placed in the MSRE salt for irradiation, the possibility existed of cross contamination of the ^{233}U by the diffusion of the salt through the graphite. To determine whether any contamination had occurred, the residual salts were removed from the reaction vessels and dissolved, and then the resulting solutions were analyzed for lithium. The results, when compared with the original analysis of the charge salt mixture, showed that there was no diffusion of the lithium-containing MSRE fuel through the walls of the capsules. At the same time these solutions were analyzed radiochemically for plutonium.

In the bismuth reductive extraction process, bismuth metal at 600°C containing thorium and lithium is used to separate protactinium from MSBR fuel.[4] Among the

[1] J. L. Botts, "Uranium Nitride and Uranium Carbonitride," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969,* ORNL-4466.

[2] T. Allen, *Particle Size Measurement,* pp. 143–53, Chapman and Hall LTD, London, 1968.

[3] G. Goldberg, "Precise Determination of Uranium in MSRE Fuel," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969,* ORNL-4466.

[4] J. C. Mailen *et al.*, "Extraction of Protactinium from Single-Fluid MSBR Fuels," *MSR Program Semiann. Progr. Rept. Aug. 31, 1968,* ORNL-4344, p. 292.

containment systems considered for the process was graphite. One of the series of compatibility tests devised involves encapsulating lithium in graphite, then heating it to a temperature of 700°C for an extended period of time. Little or no reaction is anticipated; however, the various carbon species soluble in lithium are converted to the carbide at temperatures above 600°. It was necessary to develop a method for the determination of microgram amounts of carbon in lithium, since the methods used in conjunction with the other alkali metals are limited to a sample size not to exceed 200 mg. Due to the inhomogeneity of carbon species in the alkali metals, we preferred to use all of the sample for the analysis.

The procedure involves the preliminary dissolution of the sample in water. (The reaction proceeds slowly due to the formation of a coating of LiOH.) The evolved acetylene is separated from the gas purge stream and is concentrated in a cold trap; the trap is then heated, and the C_2H_2 is passed through a drying tube to remove moisture, then into a collection trap which contains a molecular sieve. The acetylene is determined chromatographically using a flame ionization detector. This method is sensitive to less than microliter amounts of C_2H_2, although the analysis is not influenced by any blank correction due to air contamination.

An absorption spectrophotometric study was carried out to relate differences in the spectral properties of plutonia sols to the presence of amorphous material, degree of crystallinity, and presence of agglomerated material. Sols of polymeric Pu(IV) were prepared by the APEX solvent extraction and standard precipitation flowsheets under process conditions of acidity, temperature, and plutonium and nitrate concentration.[5]

We observed spectrophotometrically that freshly prepared sols of polymeric Pu(IV) exhibit aging effects slowly with time at ambient temperature and at an accelerated rate at reflex temperature. This aging effect was shown by means of electron optical methods to be due to the conversion of amorphous material into crystallites which range in size from 10 to 30 Å. Although the spectrum of a freshly prepared sol containing amorphous material and the spectrum of an "aged" sol containing crystalline material are quite similar in appearance, subtle but significant differences are observed in the absorption peaks occurring at ~610 and ~1100 Å. The presence of agglomerated material is indicated in the spectrum of aged sols by the shape of the absorption peak at ~610 Å. These differences afford a rapid method for characterization of plutonia sols and/or process control. Also, it was observed that the spectra of highly crystalline sols are identical and not dependent upon crystallite size. Therefore we are attempting to relate the half-band width, magnitude, and position of these absorption peaks to the degree of crystallinity of the plutonia sols.

We are evaluating an Orion nitrate specific electrode for possible application to plutonia and urania sol studies. The electrode response has been observed to be Nernstian, with an approximate 59-mV change for a tenfold change in concentration. The electrode is most applicable in the range of 10^{-4} to 10^{-1} M NO_3^- and between pH 2 and 10.

During this period we completed research and development on a new method for the separation of americium from curium and associated elements which will find important application in the TRU program. Recently it was observed that the large AmO_2^+ ion exhibits negligible sorbability on the cation exchanger, zirconium phosphate, from dilute nitric acid. Under such conditions curium, other actinide elements, lanthanide elements, cesium, and many other metal ions sorb strongly, thereby providing an excellent separation from americium. The method is simple, rapid, highly selective, and well adapted to high-level radiochemistry. We have submitted a paper covering the details for publication in *Analytical Chemistry*.

[5] O. K. Tallent and M. H. Lloyd, "Plutonium Sol Preparation by Alcohol Extraction," *LMFBR Fuel Cycle Studies Progr. Rept. No. 5, August 1969,* ORNL-TM-2671, p. 63.

7. Mass Spectrometry

A. E. Cameron, Assistant Director

W. H. Christie
H. S. McKown
W. T. Rainey
D. H. Smith
R. L. Walker
J. R. Walton

The investigation into the mechanism of surface ionization was continued by studying the desorption behavior of the actinides on hot tungsten. We hope that the information gained from this project will lead to improvement of the ionization efficiency of the actinides during routine isotopic analysis. The mean residence times of Th^+, Np^+, and Pu^+ were determined as functions of temperature, and their desorption energies from hot tungsten were measured.[1] The desorption energies were found to be: Th^+, 7.83 ± 0.25 eV; Np^+, 6.32 ± 0.12 eV; and Pu^+, 4.99 ± 0.15 eV. The mean residence time of uranium neutrals was measured as a function of temperature.[2] The desorption energy of uranium neutrals from hot tungsten was found to be 5.85 ± 0.10 eV. The first ionization potential of curium was measured by the surface ionization comparison technique.[3] The value obtained was 6.18 ± 0.09 eV.[4]

This project will be continued by studying the desorption behavior of other neutral species on hot tungsten. The behavior of both the ionic and neutral species of the actinides on rhenium and tantalum surfaces will also be studied.

In an effort to improve our high-resolution mass spectrometer and achieve complete second-order focusing, we have written a computer program[5] that investigates the complex equations involved.[6] Several promising designs have been found, including one that gives an eminently practicable instrument. We hope to build this mass spectrometer, which should result in better resolution than that now available. To analyze our existing high-abundance sensitivity mass spectrometer, which consists of two magnetic and one electrostatic analyzers, we adapted a FORTRAN program originally written by Kaiser[7] to our own needs. Various parameters were scanned in the search for a better configuration, but none was found.

The sample-changing wheel used with the spectrometers in the Referee Analysis Laboratory has been modified to handle ten samples per loading; six samples was the previous maximum. Approximately 200 new filament blocks and 24 mounting wheels have been completed in the shops. These assemblies and the necessary changes for making electrical contact with the filaments are now being operationally tested. This change is desirable because it will increase the number of samples that can be analyzed per day. The amount of machine downtime for sample changing is independent of the number of samples loaded per wheel. It should be noted that sample computational capacity with the 1130 computing system considerably exceeds our current needs. We do not expect computation to be the bottleneck in the forseeable future that it has been in the past.

Final acceptance of the new interface for the 1130 computing system was made in July. It will permit the direct transfer of data from external devices into the computer at rates up to 10,000 words/sec. The data can be in digital or analog form. The interface will permit the processing and calculation of large amounts of data which are now carried out by hand or not done at all. During the acceptance period many assembly language programs were written and many temporary electronic circuits were assembled to test the operation of all of the features of this interface.

---

[1] David H. Smith, A. E. Cameron, and J. A. Dean, "Mass Spectrometric Investigation of Surface Ionization. VI. Desorption of Th^+, Np^+, and Pu^+ from Tungsten Surfaces," *J. Chem. Phys.* (in press).

[2] David H. Smith, "Surface Ionization. V. Desorption of U Neutrals from W Surfaces," *J. Chem. Phys.* **53**, 299 (1970).

[3] G. R. Hertel, "Ionization Potential Measurements by Surface Ionization," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1966,* ORNL-4039, p. 49.

[4] David H. Smith, "Mass Spectrometric Investigation of Surface Ionization. VII. The First Ionization Potential of Curium," submitted for publication to the *Journal of Chemical Physics.*

[5] David H. Smith and W. H. Christie, "FORTRAN Programs to Design Mass Spectrometers with Complete Second-Order Focusing," to be published as an ORNL report.

[6] H. Hintenberger and L. König, "Mass Spectrometers and Mass Spectrographs Corrected for Image Defects," pp. 16–35 in *Advances in Mass Spectrometry,* ed. by J. D. Waldron, Pergamon, New York, 1965.

[7] K. Kaiser, *A FORTRAN Program to Analyze Mass Spectrometer Ion Optics,* ANL-6903 (August 1964).

A magnetic tape reader has been constructed and put into operation using one of the digital inputs of the interface. The reader transfers data from magnetic tape cartridges, which have been previously recorded from the RIDL multichannel analyzers. The new system transfers data three times faster than the old and also frees a multichannel analyzer which will be used for other purposes. An extensive assembly language subroutine was written for use in conjunction with the tape reader and its data reduction.

A number of programs have been written for our IBM 1130 to allow efficient reduction of the large quantities and varieties of data produced in the mass spectrometer lab to meaningful form. All low-resolution organic spectra are now graphically presented on our 1627 plotting attachment. Preliminary programs have been written to process real-time data produced by the low-resolution organic mass spectrometer. These data will be entered into the computer via the recently completed interface.

The task of calculating isotope clusters has been reduced to a computer program that produces an abundance table and a plot of the calculated abundances. This plot can be made on any arbitrarily selected scale to allow direct visual comparison with the plotted spectrum. Occasionally constituents of samples introduced into the mass spectrometer through the gas chromatograph inlet will not be sufficiently resolved to give spectra of the pure components. Under certain conditions these binary spectra can be "purified" with a computer program that subtracts out the undesirable component.

A mass spectral data file of approximately 3200 compounds obtained from ASTM has been placed in disk storage. Unknown spectra can be rapidly compared with entries in this file.

Exponential decay data produced in surface studies[1,2,4] can be accepted directly into the computer via magneitc tape and are processed using a least-squares technique. The experimental data are graphically presented on the plotter along with the least-squares best-fit line.

Further work during the past year on a combined gas-chromatograph–mass-spectrometer (GC-MS) showed the porous stainless steel helium separator to be the most suitable for the samples handled in this laboratory. Since many of the samples submitted are of low volatility, the high temperatures necessary to prevent condensation of sample in the separator preclude the use of silicone membrane separators. Separators using a 2-in. length of porous stainless steel tubing (0.5 in. OD, 0.125 in. wall thickness, 0.1 μ average pore size) have been constructed and are in use. A Varian Aerograph model 1200 chromatograph with flame ionization detector was purchased and is in routine operation. The combined instrument gives adequate mass spectra with submicrogram quantities of materials, although measurements of ultimate sensitivity have not been made.

Most of the samples handled during the year have been received from the Body Fluids Analysis Program. Over fifty additional known compounds have been analyzed and added to the library of known spectra. Results in identification of unknown materials have improved markedly since improvements have been made in sample purification prior to submission to us. The use of gas chromatography as a further check on purity of the samples has aided in interpretation of the spectra.

The routine use of the GC-MS combination has given us additional information in some cases which were difficult because of impurity problems. Gas chromatography of trimethysilyl derivatives has yielded more reliable molecular weight determinations than were possible by analysis using the direct inlet probe technique.

Since the GC-MS is in constant use, the library of known spectra is being expanded to include the spectra of trimethylsilyl derivatives of the available known constituents of urine. Much of the work in the future is expected to involve GC, and therefore the computer stored library should contain spectra of all expected compounds.

An interesting series of trimethylsilyl derivatives of inorganic anions has been studied with W. C. Butts (Analytical Chemistry Division). Mass spectra of derivatives of ten inorganic anions have been obtained by use of the GC-MS instrument and have proven the structures of the compounds to be as proposed.

Another interesting series of samples was submitted by Snyder and Blank (ORAU) who have been studying the mechanism involved in the biosynthesis of the ether bond in glycerolipids. The lipids are formed by reaction of dihydroxyacetone-phosphate with long-chain alcohols, catalyzed by microsomal enzymes. GC-MS analysis of the isopropylidene derivatives of the glycerolipids formed in vivo and in vitro from ^{18}O-containing hexadecyl alcohol showed that the oxygen of the fatty alcohol was incorporated into the lipid. In addition it was proven that unsaturated glycerolipids (alk-1-enyl glycerols) were formed in vivo from these O-alkyl precursors. These analyses have been expanded with the study of the mass spectra of a series of alkyl glycerol derivatives varying in length of alkyl chain and in

replacement of the ether oxygen by sulfur. This series is being studied because of interest in and lack of knowledge of the mass spectra of such compounds by biochemists in the field.

Laubereau and coworkers (Chemistry Division) have submitted a large number of organometallic complexes for mass spectral analysis. The results of the analyses were of value in determining structural as well as purity information. Complexes of Eu, Ho, Lu, Pr, Sm, Th, Tm, and U with cyclopentadiene, methyl cyclopentadiene, and indene, and in some cases, with one or more halogen ions (Cl, F, I) were studied. Calculated isotopic abundances of the fragment clusters of elements with several isotopes (especially europium and samarium) were almost identical to the experimentally obtained spectra. In the case of a lutecium complex, the mass spectrum proved the unexpected presence of ytterbium impurity.

Various mass spectrometric techniques have been used to assist R. V. Gentry, a visiting scientist in the Chemistry Division, in the investigation of "anomalous" pleochroic halos in biotites of different origin. These halos are presumed to be of radiogenic origin, but some "dwarf" and "giant" halos do not correspond to known alpha energy decays. We have measured uranium and lead isotopic compositions in the search for anomalies. The uranium samples examined were normal in ^{235}U content, but disequilibrium in the 234/238 ratio was observed. Several mineral specimens from Ytterby, Sweden, which occur along with one of the biotites under investigation were outgassed with a "spike" of ^{38}Ar so that a quantitative determination of gas composition and of the ^{40}Ar content could be made. Potassium-argon ages were calculated as a means of estimating whether or not there was excess ^{40}Ar present. There does not seem to be any clear evidence for anomalous amounts of decay products of an element heavier than uranium.

We have also looked by thermal ionization for high-mass ions produced from uranium-thorium extract from the biotite. Molecular ions of various compositions were observed and identified. The spark-source mass spectrometric spectrum up to mass 350 obtained by sparking a sample of Madagascar monozite showed many molecular ions, all of which could be identified.

8. Electron Microscopy

T. E. Willmarth, Group Leader
L. D. Hulett, Assistant Group Leader

H. W. Dunn T. G. Harmon

Transmission and Scanning Electron Microscopy. Whenever the examination of particles, surfaces, or other types of specimens requires the resolution of details as small as 10 to 100 Å, transmission electron microscopy is usually the only technique available. Our section continues to provide this service routinely. Our microscope is a Phillips 200, which is a general-purpose instrument. In addition to providing electron photomicrographs, it has the selected area diffraction capability such that individual particles or areas can be identified by their electron diffraction patterns.

The problems brought to us vary in origin, but specimens are usually of three types: (1) powder samples or other solids which can be ground and dispersed; (2) large specimens which have to be made sufficiently thin for transmission of the electron beam so that internal structure can be revealed; (3) large specimens, not transparent to the electron beam, for which an examination of the surface is required. An example of the first type of specimen was given in the 1969 annual report, in which a photograph of a urania sol prepared by the CUSP process[1] was shown. Type 2 specimens are often biological in origin and can be sliced in thin sections by the microtome to allow transmission of the electron beam. If mechanical deformation is undesirable, as for metallurgical specimens, thinning must be done by electrochemical or

[1] J. P. McBride, K. H. McCorkle, W. L. Pattison, and B. C. Finney, *Symposium on Sol-Gel Processes and Reactor Fuel Cycles, Gatlinburg, Tenn., May 7, 1970,* CONF-700502, pp. 113–36.

etching techniques. In our laboratory a new technique for the electrochemical thinning of graphite in aqueous phosphate solutions is being investigated. For specimens of type 3 it is necessary to make a replica of the surface that is sufficiently thin to transmit the electron beam. In this report we shall feature a problem of this type, as follows:

The Reactor Chemistry Division has a program for testing the ability of microspheres of reactor fuel, coated with pyrolytic graphite and silicon carbide, to contain fission products generated within them. It was found that some of the coatings allowed the release of fission products, and they were suspected of being porous or having microcracks. Replicas of the surface were made by the usual two-step process: (1) Films of cellulose acetate, softened with an organic solvent, were pressed against the spheres and allowed to dry. The conformation of the soft plastic to the surfaces reproduced their contours; where holes or cracks were present, the plastic was extruded as long fingers or extended ribbons. (2) The cellulose acetate was stripped from the microspheres, and thin films of carbon (500 Å) were deposited on the replica surfaces. The plastic was then dissolved in acetone, leaving thin carbon replicas of the surfaces which allowed transmission of the electron beam. Stereopair photographs of these carbon replicas are shown in Fig. 8.1. The dark extended fingers and ribbons, indicated by arrows, show that the microspheres had holes and cracks. If a stereoscope is available, a remarkable three-dimensional effect can be seen.

It is seen that the replication process just discussed is very time consuming. It is necessary, however, whenever one desires to examine surfaces with resolutions of 10 to 100 Å. Another facility under way is a scanning electron microscope, which will greatly reduce the number of cases in which specimens must be replicated. With the scanning microscope surfaces of solids can be examined directly. Images are generated in a point-by-point fashion. A finely focused beam of electrons (50 to 100 Å cross section) is moved across the surface in a rectangular pattern; the secondary electrons ejected are collected, and the magnitude of their current is used to modulate the intensity of a beam in a cathode-ray tube whose sweep is synchronized with that of the microscope. Details as small as 200 Å can be resolved. Depth of field is extremely large, so that photographs have a three-dimensional nature which aids greatly in interpretations. Elemental analysis by x-ray fluorescence can also be done on specimens while they are in place in the microscope.

The scanning electron microscope we are getting is a Phillips 900, just recently marketed. Special accessories will be a nondispersive x-ray detector; a television

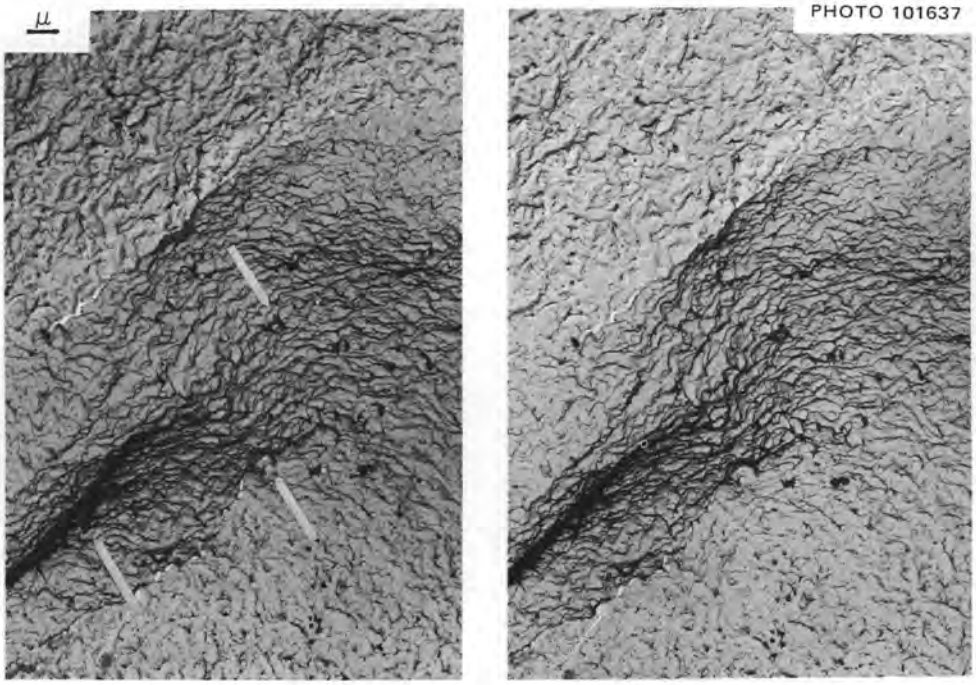

Fig. 8.1. Stereopair Photographs of Carbon Replicas.

monitor, which will allow dynamic experiments to be performed in the microscope; a transmitted electron detector, which will allow thin specimens to be viewed by reflection and transmission simultaneously; and a large-capacity, well-trapped vacuum system, which will accommodate experiments requiring clean-surface conditions.

Electron Spectroscopy. The photoelectron spectroscopy program, first described in the 1969 annual report, has been continued, with the generous cooperation of T. A. Carlson of the Physics Division. The method involves measuring the energy distribution of electrons ejected from matter irradiated with soft x rays or uv light. Spectra consist of peaks at energies corresponding to electron binding energies of elements present. All elements of atomic number 3 or larger can be studied; this method is much more sensitive for light elements than x-ray techniques. If elements are present in more than one oxidation state, peaks corresponding to their binding energies are shifted, broadened, or split. Results of the evaluation program indicate that this technique has many useful applications.

Spectra of tRNA and all its major bases[2] have been measured. In the individual bases, chemical shifts in electron binding energies of all three major elements, carbon, nitrogen, and oxygen, were seen. Shifts for carbon in carbonyl groups were especially large. Spectra of the bases can be interpreted from first principles; that is, agreement between calculated and experimental shifts is good. The spectra of extremely large molecules such as tRNA are not as easily interpreted. Chemical shifts are seen, in that a general broadening of peaks occurs, but elements are present in such a large variety of oxidation states that there is no distinct splitting of peaks.

Other compounds of biological interest that have been studied are the zwitterions, 7-methylguanosine, 7-methylinosine, and 7-methylxanthosine. These compounds have charge separations in their molecules. They have been found in natural biological fluids. 7-Methylguanosine is believed to be involved in chemical mutagenesis processes induced when nucleic acid is treated with methylating agents. We studied these compounds because we thought the photoelectron spectroscopy technique might give direct information about the degree of charge separation in the molecules. We were successful in doing this. The charge separations were reflected strongly in the nitrogen peaks, which were split or broadened greatly. We have made estimates of what the degree of charge separations in the molecules should be by considering different resonance forms and using Pauling's relationship between partial ionic character of bonds and electronegativity differences between atoms. There is good agreement between our estimates and experimental results from the spectra. We are presently adapting an existing computer program for making molecular orbital calculations (CNDO) of charge separations to these molecules. Another motive for studying these zwitterions, especially 7-methylguanosine, is the emphasis on chemical mutagenesis in the Biology Division. We plan to extend this work to other mutagens, fluorinated and brominated bases, in the coming year.

Because of Laboratory emphasis on pollution problems, we are testing the practicality of photoelectron spectroscopy for problems of this nature also. Arsenic in cacodyllic acid, an herbicide, has been studied.[3] In soil samples inoculated with cacodyllic acid, the arsenic could be detected and its chemical shift determined. The results suggested that the arsenic was present as As_2O_3. An air pollution problem was also studied using the helium resonance line (22.5 eV) for excitation of spectra. Spectra obtained in this matter are of electrons from valence orbitals. Air specimens inoculated with NO and NO_2 were examined. Preliminary results show that NO in air is almost totally oxidized to NO_2. The sensitivity of the photoelectron spectroscopy technique for air pollutants is not very high. In practical work it may be necessary to concentrate specimens by gas chromatography or other methods. Preliminary work on mercury pollution has also been started. The chemical shifts seen were small. The study is not complete, however, and more work is necessary.

The binding energies of bromine in KBr, $KBrO_3$, and $KBrO_4$ were measured.[3] Potassium perbromate could not be prepared until recently, and there was theoretical speculation that it was inherently unstable. Considerable work has gone into characterizing this new compound. We were able to provide information about the charge density of the bromine atom by electron spectroscopy. The binding energy of bromine in $KBrO_4$ is 8 V larger than for KBr. Corresponding shifts are 6 V for KI-KIO_4 and 9.5 V for KCl-$KClO_4$. Plots of the binding energy shifts as a function of oxidation number are monotonic for all three halogens. The plots indicate that, in comparison with perchlorate and periodate, the

[2] L. D. Hulett and T. A. Carlson, "Analysis of Compounds of Biological Interest by Electron Spectroscopy," *Clinical Chemistry* 16, 677 (1970).

[3] L. D. Hulett and T. A. Carlson, "Measurements of Chemical Shifts in Photoelectron Spectra of Arsenic and Bromine Compounds," *Appl. Spectry.*, in press (1970).

charge on bromine in perbromate is not odd or unexpected.

The spectrometer used in this work has been the research instrument of the Physics Division which was built by Carlson *et al.*[4] Another spectrometer is warranted to provide a fuller service capability. The Transuranium Research Laboratory iron-free beta spectrometer is being utilized. This is a magnetic instrument that is normally used to measure high-energy beta spectra of nuclear processes, but it can also be used to measure the lower-energy spectra (100 to 1400 eV) of our work.

The adaptation involves building a source chamber to house an x-ray tube, slit system, and specimen mounts. Specimens will be loaded through a vacuum interlock so that rapid specimen change is facilitated without need for breaking vacuum on the source chamber and x-ray tube. A specimen transport chamber has also been built which will allow the mounting of specimens in a dry box or other controlled atmosphere. After mounting, the specimens can be carried to the spectrometer and loaded without intermediate exposure to air. Reaction chambers can also be attached to the spectrometer for specimen preparation. Corrosion studies are an example of the type of problem in which this capability would be useful. Corroding specimens could be studied as a function of time by intermittently halting the reaction and transporting the specimens into the source chamber for measurements.

Shop work for the source and specimen chambers has been completed. They are presently being mounted and tested. The iron-free spectrometer was constructed under the supervision of C. E. Bemis,[5] of the Chemistry Division Transuranium Research Laboratory. His help in adapting it to our work is gratefully acknowledged.

X-Ray Diffraction Studies. X-ray diffraction has been a standard and much-used method of analysis for many years and remains so in our section. It is one of the fastest methods available for identifying compounds. Quantitative analysis of mixtures of compounds can also be done by measuring line intensities of the diffraction pattern. The Debye-Scherrer camera and the diffractometer are the usual tools for such work. Examples of determinations done in the past year are mixtures of BeO and Li_2BeF_4, zeolite (species P), silicon metal in the presence of other silicon compounds, and mixtures of U_3O_8 and UO_2.

Probably the most interesting work done in the past year involving x-ray diffraction was with solid solutions of ThO_2 in UO_2,[6] uranium carbide, and uranium nitride. The uranium-thorium solid solutions were precipitated from mixed-oxide melts. The two oxides are of the same crystal form, and it appears that the metal cations are interchangeable. That is, the thorium ions can substitutionally replace the uranium ions in continuous proportions ranging from pure UO_2 to pure ThO_2. The lattice parameter of the mixed-oxide crystals varies linearly with the degree of substitution. Thus we have an analytical technique by which the degree of substitution in the mixed oxide can be determined. Measurements of lattice parameters with the Debye-Scherrer camera are quite accurate; changes of 0.0006 Å can be detected. Since the difference in parameters between pure UO_2 and pure ThO_2 is about 0.06 Å, the method can detect a 1% change in the degree of substitution in a mixed oxide. Work of the same nature has been done with uranium carbide–uranium nitride mixed salts. A linear relationship between the degree of substitution and lattice parameters was found for the system also, and a 1% change in the degree of substitution could be detected. The Debye-Scherrer camera was used in this work.

The determination of crystallite size is another frequent use for x-ray diffraction. It can be shown that there is an inverse relationship between the width of diffraction peaks and crystallite size; that is, peaks are wider for small crystals than for larger ones. This relationship is useful for determining crystallite sizes in the range of 20 to 200 Å. In the sol-gel programs, for example the CUSP process,[1] it is necessary that crystallite size be determined while the particles (UO_2) are in suspension. The x-ray line-broadening technique is the only method presently developed that can accomplish this. Some of the specimens we have received could be dried and examined by electron microscopy also. Crystallite sizes (40 Å) determined by the two techniques disagreed by less than 10%. Gadolinium and cerium oxide crystal sizes (350 to 400 Å) have also been measured by both electron microscopy and x-ray line broadening; the agreement was quite good for particles of this size range also. Percent crystallinity of sols, that is, the fraction of the material suspended that is in the form of crystals larger than 10

[4] T. A. Carlson, M. O. Krause, W. E. Maddeman, B. P. Pullen, and F. W. Ward, *Phys. Div. Ann. Progr. Rept. Dec. 31, 1968,* ORNL-4395, p. 87.

[5] C. E. Bemis, "The $\pi\sqrt{2}$ Double Focusing Electron Spectrometer," *Chem. Div. Ann. Progr. Rept. May 20, 1968,* ORNL-4306.

[6] C. E. Bamberger and C. F. Baes, Jr., "The Exchange of U^4 and Th^{+4} Between Molten $LiF\text{-}BeF_2\text{-}ThF_4\text{-}UF_4$," *J. Nucl. Mater.* 35, 177 (1970).

to 20 Å, is also desirable information. The ratio of the height of the diffraction peak to the background should be a measure of this. We have attempted to calibrate this method for certain sols, but our work is not complete.

Electron Microprobe Analysis. The electron microprobe performs elemental analysis by impinging a finely focused beam of electrons on the specimen being studied and exciting x-ray emissions. Elements present are identifiable by the wavelengths of their characteristic x rays. Extremely small specimens, ~1 μ cross section, can be examined. Elemental composition as a function of position on larger samples is also routinely done. Differences in composition between points as close as 2 μ on a specimen surface can be resolved. The concentration limit of detectability of most heavy elements is about ½ mole %. The instrument we have is a Phillips AMR/3 with two crystal spectrometers attached. The spectrometer design provides high sensitivity for the determination of elements of low atomic number.

Much of our work with the probe involves homogeneity tests of metal composites and alloys. For example, in the preparation of cobalt alloys containing vanadium, chromium, and nickel for study of diffuse scattering of neutrons by the Solid State Division, it was necessary to determine whether or not the mixtures were free of separate phases and other concentration variations that would have been undesirable. The specimens were examined by traversing them under the electron beam while recording the intensities of x-ray emission as a function of position on a strip chart. The two elements were determined simultaneously. Consistency of results was seen, in that as the concentration of one component increased, the other decreased. We are often requested to determine variations in metal concentrations at welds and brazed joints in research done by the Metals and Ceramics Division.

The diffusion of elements from one phase to another at an interface can be detected by the electron microprobe. Such studies are often done in the molten-salt reactor program, where it is necessary to determine the compatibility of solid materials with molten salts at high temperatures. An example is the corrosion of Hastelloy by molten SrO, where it was believed that silicon was being extracted into the liquid phase. We were given sectioned pipes filled with SrO that had once been molten. We were able to show that silicon was present in the SrO phase, and we could measure its concentration gradient at the interface; the silicon concentration varied by a factor of 10 over a distance of 0.009 in.

A combined examination of specimens by both optical microscopy and the electron microprobe is sometime required, such as in a problem brought to us by the Instrumentation and Controls Division: Rhenium wires in certain of their instruments designed for high-temperature work broke at abnormally low temperatures. Sections of some of these wires showed inclusions under the optical microscope. Microprobe examination showed that the inclusions contained large amounts of tungsten and carbon. The microprobe also provides images of specimen surfaces in terms of elemental compositions for comparison with optical micrographs. This is done by scanning the specimen with the electron beam while using the x-ray output of certain elements to modulate the intensity of a cathode-ray tube whose scan is synchronized with that of the microprobe.

Part B. Service Analyses

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

Summary of Analytical Work

Group Making Analyses	Average Number in Group		Number of Results Reported																						
			For ORNL Divisions																For Others						
	Scientists	Technicians	Analytical Chemistry	Biology	Chemical Technology	Chemistry	Ecology	Health	Health Physics	Instrumentation and Controls	Isotopes	Metals and Ceramics	Neutron Physics	Operations	Physics	Reactor	Reactor Chemistry	Solid State	Knolls Atomic Power Laboratory	Los Alamos Scientific Laboratory	Miscellaneous	Nuclear Fuel Services	Paducah	Y-12	Total
Mass Spectrometry Service Laboratory	1.5	2	5	30	546	34					7,224	865	8	10	30	330	504	17			5756			550	15,909
Process Analyses																									
General Analyses Laboratory	14	16	236	522	79,791	121			403		1,238	5,974	54	848	41	1631	2,479	474	65		439	54		1068	95,438
General Hot-Analyses Laboratory	8	5			3,898						420	1,448		2,897		1161	2,386								12,210
High-Level Alpha Radiation Laboratory	9	6			17,854	2			12		217	703		1,806		32	165			97	2		5		20,895
Radioisotopes-Radiochemistry Laboratory	6	7			7,832	44	40		2096	29	4,345	1,320	24	5,799	1,121	2565	9,563	132			75				34,985
Spark-Source Mass Spectrometry Laboratory	1	2	75		1,644	160			25		1,632	4,798	165	120	449	125	483	840			615				11,131
Spectrochemistry (Y-12)	2	1	107		1,154	360		18,272	65		14,047	4,403	120	49	238	2710	2,403	2637			121			2249	48,935
Transuranium Mass Spectrometry	1.5	1	612		1,287	115					348	621		26		808	309			649	20				4,795
Total	43	40	1035	552	114,006	836	40	18,272	2601	29	29,471	20,132	371	11,555	1879	9362	18,292	4100	65	746	7028	54	5	3867	244,298

9. Spectrometry Services

A. E. Cameron

J. R. Lund
J. A. Carter
R. E. Eby
J. R. Sites
S. A. MacIntyre
M. M. Murray

In order to obtain more quantitative results from the spark-source mass spectrometer used for impurity analyses, relative sensitivity factors, K_r, were established for the rare-earth and certain actinide elements. As reported previously[1] erbium was used as the internal standard, and therefore the relative sensitivity factors are normalized to erbium. For the relative sensitivity determinations these optimum sample excitation parameters and analyzing conditions were used: spark voltage, 30 kV; excitation pulse length, 25 μsec; excitation pulse repetition rate, 100 sec^{-1}; accelerating voltage, 20.2 kV; analyzer vacuum, 2×10^{-9} torr; source vacuum, less than 10^{-6} torr; and electrode systems of gold or graphite.

The relative sensitivity values ($K_r \times$ experimental result = true result) for the rare-earth elements were all near unity, and for the actinide elements, with respect to erbium, the range was from 1.61 to 2.65. The recommended actinide relative sensitivity values are: thorium, 2.65; uranium, 2.28; neptunium, 2.26; plutonium, 2.30; americium, 1.61; curium, 2.30; berkelium, 1.88; and californium, 2.1. The linearity of the erbium-spiked solution and spark-source mass spectrographic technique was demonstrated over a concentration range of 1 to 250. A reproducibility of about 4% over the concentration range indicated that the relative sensitivity constants were independent of concentration.

Since a change with respect to that for erbium in the distribution of singly charged to multiply charged ion ratio and to the complex ion ratio could influence the relative sensitivity value, the distribution observed in the mass spectra for about 2 μg of each actinide element was measured. For this study graphite electrodes were used. Generally the distributions of the metal ions and complex ions for the actinide elements were comparable with that observed for erbium. In all cases, 98% or more of the ions formed were present as the singly (77%), doubly (20%), and triply (1%) charged metal ions. The intensity of the complex ions comprised less than 2% of the total spectrum intensity, and of this small fraction the dominant complexes corresponded to MC_2^+ and MO^+ ions.

The effect of fractional volatilization seemed to be inferred when the relative sensitivity factors of the actinide elements were compared with reported temperatures for thermal ions produced from a hot rhenium filament.[2] These temperatures and the reciprocal of the relative sensitivity factor, $1/K_r$, are plotted in Fig. 9.1. Filament temperatures of 1650 and 1800°C for berkelium and thorium ion emission, respectively, were predicted from the plot of the other data. The predicted value for berkelium was later confirmed, while the predicted value for thorium was found to be about 200°C too low.

By the application of the established relative sensitivity factors, quantitative results for impurities of rare-earth and actinide elements in highly radioactive transuranium samples may be obtained. The average standard deviation was 7.6% for an eleven-element mixture of Pr, Gd, Tb, Ho, Tm, Yb, Th, Np, Am, U, and Cm. The solution and spark-source method did not require any chemical separation prior to the analysis, since interelement effects were found to be negligible for this technique.

The output of the two spark-source mass spectrometers increased 55% over the previous year. Over 11,000 analyses on 660 samples (130 from the hot-source MS-702) were reported. This includes 12 special alloys, 16 separated stable isotopes (for trace impurities), 12 types of intensely radioactive samples (^{14}C, ^{36}Cl, ^{67}Ga, ^{111}In, ^{229}Th, ^{231}Pa, ^{239}Pu, ^{241}Am, ^{244}Cm, ^{248}Cm, ^{249}Bk, ^{249}Cf), and sets of AgCl, T-111, ashes, and fire-assay gold beads. Thorium contents of a series of zirconium-thorium alloys were determined by the isotopic dilution spark-source mass spectrographic technique. The dissolved samples were spiked with a standard solution of 99.96% ^{230}Th.

[1] J. A. Carter and J. R. Sites, "Spark-Source Mass Spectrometry," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969*, ORNL-4466, p. 93.

[2] A. E. Cameron, "Isotopic Mass Spectrometry of the Actinides," *Actinides Rev.* 1, 299 (1969).

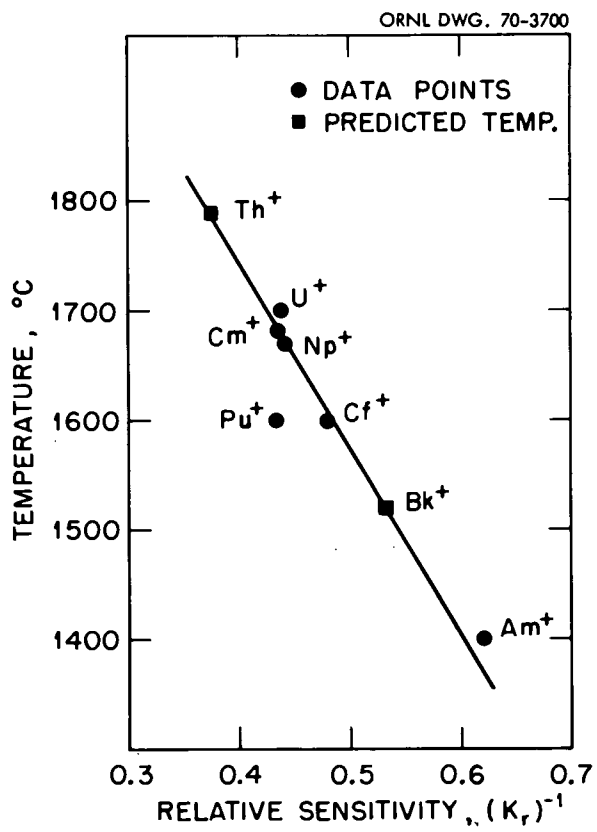

Fig. 9.1. Correlation of the Actinide Relative Sensitivity Values to the Temperature of Metal Ion Formation on a Rhenium Filament.

A 25-ton ring press has been placed in a glove box in order to form silver or bismuth electrodes that support 3 to 6 microspheres of plutonium-uranium oxide fuel samples for spark-source mass spectrographic analysis.

The Mass Spectrometry Service Laboratory continues to analyze the separated stable isotopes for the Isotopes Division and to certify argon, helium, and nitrogen gas cylinders for the ORNL and the Y-12 plant. This constitutes about 80% of the work performed. The relative isotopic abundances of over 1000 stable isotope samples of 40 elements were determined. This includes 370 mercury samples. Over 600 cylinders were certified. There was only a 10% drop in the number of analyses reported for a one-third decrease in personnel.

The Transuranium Mass Spectrometry Laboratory reported 4795 results, essentially the same number as the 4804 reported the previous year. However, this was accomplished with a 16% reduction in manpower expenditure. The Chemical Technology Division continues to be the biggest customer, accounting for about 27% of the analyses. The Reactor Division increased their work load to nearly 17%, but the Isotopes Division dropped from about 20% to less than 8%. About 14% was performed for other plants, primarily for the Los Alamos Scientific Laboratory.

Isotopic determinations were made routinely on all elements for thorium through einsteinium and also on irradiated samples of Ce, Sm, Eu, Gd, Tb, and Tm. Quantitative determinations were made on Sm, U, Pu, and Am using isotope-dilution techniques.

The Laboratory has recently become involved in the "Safeguard" Program. Samples from European reactors are being received and analyzed for uranium and plutonium isotopes.

Samples of irradiated ^{249}Cf and ^{250}Cf were analyzed for J. Halperin of the Chemistry Division. From these results the neutron captive cross section of these two isotopes can be determined. The results of this experiment will be published in the near future. Several samples of the curium decay products of californium were run for R. D. Baybarz of the Chemical Technology Division. These ran as high as 97.7% ^{248}Cm. This material was then used by D. H. Smith of our Division for the determination of the ionization potential of curium.

We continued to supply sample filaments for the Referee Analysis Laboratory and the Mass Spectrometer Service Laboratory. Over 5800 filaments were prepared, a reduction of about 3% from the previous year.

The Spectrochemistry Laboratory reported about 49,000 results (0.6% increase over last year) to more than a dozen ORNL divisions. The Reactor Chemistry Division continued to supply a large number of bismuth and salt samples in connection with the salt cleanup program. Large numbers of metal and alloy samples for specification checks for both major and minor constituents were analyzed for Inspection Engineering, Metals and Ceramics, and the Reactor Division. In connection with these samples, the Paschen direct-reading spectrometer continues to serve well.

Environmental samples from the Industrial Hygiene Department of the Health Division constituted the largest number of reported results. Routinely about 40 metallic elements are surveyed employing semiquantitative techniques on weekly composited air and quarterly composited water samples.

The Isotopes Division submitted about 10% fewer samples than last year; however, trace impurities were determined on more than 40 elements of different separated stable isotopes.

For the second consecutive year the number of results for the Y-12 plant has more than doubled. Sample types include metals and alloys for composition and

specification analyses and environmental air and water samples.

The Y-12 Organic Preparations Group used the services of the Nuclear Magnetic Resonance (NMR) Spectrometry Laboratory to aid in their study of the effects of various curing agents on resins and the effectiveness of separating monomers, dimers, and polymers of resins by molecular distillation. Many of these resins contained units which were made up of the 1-phenoxy-2,3-epoxy-propane ether group

$$(CH_2-\overset{\overset{\displaystyle O}{/\backslash}}{CH}-CH_2-O-C_6H_5-)\,,$$

and much information was available from their NMR spectra, especially about their terminal groups.

Spectra of compounds used or produced in various syntheses were also recorded for various groups throughout the Laboratory. Included in this list are such materials as bisphenol-A, p-$(HOC_6H_4)_2C(CH_3)_2$; ethyl 11-bromoundecanoate; amyl nitrate; diethylenetriamine linoleic acid; 11-bromoundecanoyl chloride; p-chloromercury benzoic acid; and 1-(p-tert-butylphenoxy)-2,3-epoxypropane.

In order to study enol-keto and thiol-thio structure in pyrimidines, B. C. Pal of the Biology Division prepared the mercury derivatives of thymine, 2-thiouracil, 1-methyl-4-thiouracil, and 2-thiocytosine. The NMR spectra of both the parent compound and the mercury derivative were recorded to aid in this study. Also in connection with this study, the spectra of several derivatives of 2-thiouridine were taken.

This year saw the completion of the infrared reference spectra of the biological materials mentioned in last year's report.[3] All spectra were of the materials in the as-received condition and were recorded using the split-mull technique.

Most of the compounds examined were nucleotide salts. It was unfortunate that all the salts did not contain the same cation so that a more significant study could be made of them. However, it was found relatively easy to identify the monophosphates. Differentiating between di- and tri-phosphates was much more difficult by this method of recording the spectra.

A product of this work was a graphical method of determining the number of cations per molecule and the amount of included water per molecule simultaneously. The method, restricted somewhat in scope, required that the original acid be known and of reasonable purity. Knowledge of the percent by weight of cation is also required. This method is not spectrometric.

Another by-product was a modification of the mulling technique from macro (i.e., 25 X 25 mm square plates) to a semi-micro method using 13-mm-diam X 1-mm-thick plates. This improvisation was found necessary because of the cost and dearth of some of these materials. After development the method was used exclusively, since the plates were discarded rather than being reground and repolished as in the case of the macro method.

Other work involving the Infrared Laboratory has been checking the accuracy of the Karl Fischer determination of water in 2-ethyl hexanol. Along with this, current work is being carried out on the possible development of a quantitative infrared method of determining Span-80 (commercial sorbitan monooleate) and Ethomeen (another commercial detergent) in the presence of each other.

Service work over the past year has typified the usual variety of sample types and has included both organic and inorganic materials.

[3] M. M. Murray, "Infrared Spectrometry," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969*, ORNL-4466, p. 104.

10. Process Analyses

L. T. Corbin

HIGH-LEVEL ALPHA RADIATION LABORATORY

J. H. Cooper

Approximately 21,000 determinations were made in the past year. This is a decrease of about 5% from the previous year. Eighty-five percent of these were for the Chemical Technology Division.

Remodeling of Laboratory 4 in Building 3508 was completed. New glove boxes were installed to give more flexibility in the types of analyses performed. A seamless, plastic floor covering was used that affords ease of decontamination.

Two new solid state coulometers were purchased. One is a commercial model, and the other is ORNL designed and fabricated. These coulometers have decreased maintenance problems and increased the precision of analyses.

The precision of the determination of nitrogen in plutonium and uranium nitrides was improved by exchanging sealed Pyrex tubes for the Teflon-lined steel bombs that were used in the past. Advantages of the Pyrex tubes are (1) ease of checking for the degree of dissolution of sample by visual inspection and (2) the ability to form leak-proof closure of the tube, thus avoiding loss of sample during the dissolution step.

An extensive study of the method for the determination of oxygen-to-metal ratios was made for the Metals and Ceramics Division. The method consists basically of measuring the weight change of a sample aliquot when it is converted to the stoichiometric dioxide. At least three sample aliquots are tested on separate days to eliminate any variation that might be due to changes in atmospheric or operating conditions.

All the colorimetric methods for determining corrosion products in the TRU processing solutions have been adapted for the Cary spectrophotometer. Greater accuracy and precision are achieved by the use of this instrument than with the former in-cell filter photometer.

GENERAL ANALYSES LABORATORY

W. R. Laing

Several pieces of equipment were assembled and checked for use in the analysis of samples from the Liquid Metals Fast Breeder Reactor Program. One apparatus was for the measurement of O/U ratios in substoichiometric UO_2. In this method[1] a sample portion was dissolved in partially dehydrated H_3PO_4, and the hydrogen released was determined by gas chromatography. The method was tested for O/U ratios from 1.90 to 1.99. It should also be useful with the coulometric method[2] for O/M ratio measurement in $UO_2 \cdot PuO_2$.

A method developed by the Bureau of Mines for the determination of nitrogen in UN was tested. In this extremely simple procedure, a 0.5-g aliquot was dissolved in 7 ml of concentrated H_3PO_4 by gently heating on a hot plate. This solution was transferred to a Kjeldahl flask, and the ammonia was distilled. The relative standard deviation was 0.3%, and material balances on UN samples were from 99.93 to 100.01%.

Three pieces of equipment were assembled for use in the High-Radiation-Level Analytical Laboratory. These were an apparatus for the release and measurement of helium from fast-flux-irradiated metals and alloys, an apparatus for the measurement of hydrogen in irradiated aluminum alloys, and a helium densitometer for use with irradiated graphite specimens.

A Leco impulse heater was used with a gas chromatograph to analyze for oxygen and nitrogen in metals. This approach appears quite promising as a substitute for vacuum fusion on irradiated metals.

Work in support of the Molten-Salt Breeder Reactor continued for both the Chemical Technology Division and for the Reactor Chemistry Division. A recently published method[3] for the analysis of BF_3 in phenolic solutions was adapted to determine BF_3 in $NaF \cdot BF_3$. An aliquot of the salt was refluxed with an excess of $CaCl_2$. The acid formed was titrated to determine the fluoride, then mannitol was added, and the boron was titrated. This method was also used to determine small amounts of $NaBF_4$ in other fluoride salts.

---

[1] A. Tolk, W. A. Lingerak, and D. Börger, "Determination of the Oxygen-to-Uranium Ratio in Hypostoichiometric Uranium Dioxide," *Anal. Chim. Acta* **49**, 437 (1970).

[2] N. E. Bärring and Günther Jönsson, "Controlled-Potential Coulometric Determination of the Oxygen-Metal Ratio in Mixed Uranium-Plutonium Oxides," *Anal. Chim. Acta* **50**, 229 (1970).

[3] D. Rozycka and J. Chmiel, "Determination of Fluorine and Boron in Phenolic Solution of Boron Trifluoride," *Chemia Analityczna* **14**, 509 (1969).

MSRE salt was analyzed for 100 to 200 ppm cerium by extraction of the thorium with TTA and spectrophotometric measurement of the cerium peroxide complexes. Sodium fluoride in mixtures of 8% NaF–92% $NaBF_4$ was measured by titration of a water solution of the salt with a thorium nitrate solution. Gadolinium and dysprosium were extracted from salt and bismuth solutions using TTA. Measurement was by flame emission photometry.

Biological programs continued with work from the Chemical Technology Division and the Biology Division. The major portion of the sample load was the determination of transfer ribonucleic acids, and, in addition, work increased in gel chromatography, end-group analyses, and amino acid analyses.

Atomic absorption was used extensively to determine Ca and Mg in water samples taken by the Ecology Division from sampling stations throughout the ORNL area.

Programs were written for surface-area measurement and mercury porosimetry on the Hewlett Packard model 9100A calculator plotter. Data were both calculated and plotted by this instrument.

Eight chemists and three technicians completed refresher courses taught by J. A. Dean, University of Tennessee. One technician, P. S. Gouge, completed a nine-month chemistry course under the Technical Development Program.

GENERAL HOT-ANALYSES LABORATORY

C. E. Lamb

Although we continued to provide services to programs in several ORNL divisions, there were fewer requests for the analysis of highly radioactive materials. The majority of the radioactive samples were received from the MSRE, which terminated operations in December, and from the Fuel Reprocessing Studies, which were curtailed about the same time. Shift operations in the High-Radiation-Level Analytical Laboratory (HRLAL) were discontinued, the number of personnel was reduced, and the remaining group was reorganized.

During the final operation of the MSRE, samples were received at a rate averaging more than one per day. Some were routinely analyzed for major constituents,[4] and others, that were transported in specially designed ladles to prevent contamination during handling, were prepared for radiochemical analyses.[5] Some samples were received in a heated carrier with the temperature held at 200°C or above to prevent the loss of fluorine. As a precautionary measure, before opening the carrier a vent line was attached to it to remove any volatilized fission product activity. Gaseous vapors were exhausted through a caustic scrubber followed by a water scrubber and a charcoal trap.

New equipment was installed to broaden our capability for the analysis of samples from LMFBR-related programs in the Chemical Technology and the Metals and Ceramics Divisions. A Bell and Howell CEC moisture analyzer was placed in service for measuring the water released by samples of UO_2-PuO_2 at temperatures up to 1000°C. A controlled-potential coulometric titrator from MT Electronics Company, San Leandro, California, and an ORNL model Q-4010[6] were obtained to improve the precision of uranium and plutonium determinations.

An apparatus[7] for evolving gas from metals was used for determining tritium in Zircaloy II.[8] The sample was heated to 1400°C and the evolved gas mixed with a standard of Ne-D_2, after which it was analyzed by mass spectrometry. The apparatus was also used for determining nitrogen in Hastelloy samples and helium in type 304 stainless steel samples.

A modified Kjeldahl distillation unit was assembled in a hot cell, and CsCl samples from the Isotopes Division were analyzed for ammonia. Although none was detected in any of the samples, standard additions of ammonia were recovered. Free carbon in $SrTiO_3$ samples, also from the Isotopes Division, was measured as CO_2 by gas chromatography after igniting the sample in a stream of oxygen.

One of the three filter pits in the HRLAL exhaust system was removed from service for modification and the installation of an iodine adsorber system. The other two pits were scheduled to be modified also.

An inert-atmosphere glove box with a gas purifier was installed in order to prevent the contamination of samples, especially uranium and plutonium nitrides, by

[4] R. E. Thoma, *Chemistry of the MSRE,* ORNL-4548, pp. 93–96.

[5] F. F. Blankenship *et al, Fission Product Behavior,* ORNL-4548, pp. 104–11.

[6] T. R. Mueller, *Coulometer Titrator (ORNL Model Q-4010): Prototype and Instruments for Analytical Services,* ORNL-4466 p. 2.

[7] W. R. Laing, "General Analyses Laboratory," *Anal. Chem. Div. Ann. Progr. Rept. Oct. 31, 1969,* ORNL-4466, p. 106.

[8] J. H. Goode and C. M. Cox, *The Distribution of Fission Product Tritium in a Zircaloy-Clad UO_2 Blanket Rod from PWR-1,* ORNL-TM-2994.

oxygen or moisture during sample preparation and transfer.

RADIOISOTOPES-RADIOCHEMISTRY LABORATORIES

E. I. Wyatt

The various types of analyses performed in the Radioisotopes-Radiochemistry Laboratories have remained about the same as in previous years, with some slight increase in samples from environmental and ecological studies. When the Molten-Salt Reactor was shut down we experienced a big drop in fission product separations work.

Most of our work in neutron activation was in the determination of trace quantities of rare-earth elements in $LiF\text{-}BeF_2$ salts for the Chemical Technology Division. In addition, several samples of silt from the Clinch and Tennessee Rivers were leached with nitric acid and the mercury content determined by neutron activation. Hickory trees have been shown to have a unique affinity for accumulating rare-earth elements in the foliage and nuts; the combination of neutron activation techniques and gamma spectral resolution has drastically reduced the cost of analysis of such samples. Previously digestion, dissolution, and chemical separation were required for these ecological-type materials.

The high neutron flux and almost continuous operation of the High Flux Isotope Reactor has enabled us to determine the half-life of ^{10}Be more accurately than could be obtained previously. We tested samples taken from the beryllium reflector. We find the half-life of ^{10}Be to be $1.6 \pm 0.2 \times 10^6$ years; the previously accepted value was $\sim 2.6 \times 10^6$ years.

A new Ge(Li) detector with an active volume of 54 cm^3 was put into service. This detector coupled with the 4096-channel analyzer has enabled us to determine ^{239}Pu and ^{235}U in microspheres and other encapsulated sources without destroying them. This has proved to be an inexpensive method for determining the homogeneity of batches of fuels prepared by the sol-gel processes.

RADIATION CONTROL AND SAFETY

U. Koskela

A zinc bromide window in the HRLAF, Building 3019, and one in the HRLAL, Building 2026, were drained and washed. The zinc bromide was filtered and reused to fill the windows. The oil from the west storage cell window in the HRLAL was drained; the window was cleaned and refilled. Radiation exposure to personnel was minimal.

During the year there were 16 medical-treatment cases, as compared with 27 last year. The majority of the injuries were from cuts or abrasions.

Some 13 safety and/or housekeeping inspections were made, including the annual divisional safety audit with D. C. Gary of Health Physics and Safety. Of this total, four were requested by the AEC.

Approximately 40 approvals were given various investigators involving safety and/or radioactive operations.

QUALITY CONTROL

G. R. Wilson

Because of budgetary considerations, some of the research programs which generate samples for analysis have been curtailed during the period covered in this report. These changes have resulted in a decrease in the number of control programs from 31 to 20 and a decrease of approximately 700 in the number of control results reported during the year.

The overall quality level, however, increased from 91 to 93% during the year. The General Hot-Analyses Laboratory, with a change from 83% in 1969 to 90% this year, contributed most significantly to this increase in quality level.

In Table 10.1 the quality level for each laboratory is shown, and the results are compared 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 Laboratories of Control Tests for July 1969–June 1970

Laboratory	Number of Control Results		Quality Level[a] (%)	
	Total	Outside Fixed Limits	1969	1970
General Hot-Analyses	749	75	84.1	90.0
General Analyses	1170	44	95.7	96.2
High-Level Alpha Radiation	240	39	82.7	83.8
Total	2159	158	90.7	92.7

[a]Control results within 2S limits.

Table 10.2. Distribution by Methods of Control Results for July 1969–June 1970

Type of Method	Constituent	No. of Control Programs		No. of Control Results	
Amperometric	Chromium	1		27	
	Zirconium	1	2	28	55
Colorimetric	Aluminum	1		11	
	Chromium	1		74	
	Iron	2		120	
	Molybdenum	1		44	
	Nickel	2		97	
	Thorium	2		89	
	Uranium	4	13	94	529
Coulometric	Plutonium	2		48	
	Uranium	3	5	962	1010
Fluorometric	Uranium	2	2	273	273
Gravimetric	Carbon	2	2	97	97
Polarographic	Uranium	1	1	23	23
Photoneutron	Beryllium	1	1	18	18
Volumetric	Aluminum	1		31	
	Nitrate	2		110	
	Thorium	1	4	13	154
Totals			30		2159

INORGANIC PREPARATIONS

D. E. LaValle[9]

Since much of the work in inorganic preparations has been associated with the fused-salt program, the reduction in emphasis on this program has resulted in about a 50% decline in work level. A significant portion of the remaining work is concerned with alloy preparation and heat treatment, the latter mostly for the Neutron Diffraction Group of the Solid State Division. Some compounds prepared for this group were Ti_2O_3, $^{48}Ti_3O_5$, V_2O_3, and $(V_{0.96}Cr_{0.04})_2O_3$.

Most of the alloy preparations were done for the Low-Temperature Nuclear and Solid State Physics Group of the Physics Division. Among these were a series containing Pd, natural Ni, and ^{61}Ni and a series consisting of Au with 4, 2, and 1 at. % each of Ga, In, Zn, and Cd.

The ferrite program for the Neutron Spectrometry Group of the Solid State Division continued with the preparation of substituted magnetites of the type $^{7}Li_{0.5}Fe_{1.5}O_4$.

The preparation of a solid solution of 30 mole % of $^{235}UCl_3$ in $LaCl_3$ was undertaken for Brookhaven National Laboratory. About 20 g of the $^{235}UCl_3$ has been made.

With the increasing use of isotopes as constituents in preparations, a significant amount of time is now spent in salvage operations. Some experimental work has been done, such as ^{18}O exchange reactions, stability tests, and the growth of crystals.

[9]Special assignment.

Part C. Activities Related to Education

The Analytical Chemistry Division has continued activities generally related to education. Discussions with consultants and advisory committee members, who usually also are university faculty members, and thesis-research programs for graduate students are more formal activities related to education. By less formal arrangements, faculty members and students engage in research in the Division. Often alien guests conduct scientific work in the Division which aids in their experience or allows work to be done with equipment that is unavailable in their homeland. In addition, some of our Division staff members contribute time to the exposure of students or employees to facets of topics related to analytical chemistry.

The nature and mutual benefits of many of these educational activities are indicated throughout the report, and publications or theses resulting from these activities are included in Part E.

The varied programs are outlined in the sections below.

Advisory Committee Members

The Division Advisory Committee members presently are:

C. V. Banks
Iowa State University

M. A. Evenson
Harvard Medical School

H. A. Laitinen
University of Illinois

L. B. Rogers
Purdue University

Consultants

The Division consultants who have worked under subcontract in collaboration with our staff during the past year are:

J. A. Dean
University of Tennessee

Gleb Mamantov
University of Tennessee

A. O. C. Nier
University of Minnesota

Great Lakes Colleges Educational Program

The Laboratory and the Great Lakes Colleges Association, a consortium of 12 liberal arts colleges in the midwest, have sponsored an academic program for undergraduate junior and senior science students during the fall semester of 1970. Twenty-two students and three faculty members from the colleges are in residence at Oak Ridge from September 8 through December 18, 1970. During this time they are involved full time in research activities and course work at ORNL and ORAU, Special Training Division. The students, selected from the Biology, Chemistry, and Physics Departments of the Great Lakes schools, are receiving a full semester academic credit for their activities in Oak Ridge.

Two faculty members and three students are involved in research in the Analytical Chemistry Division during the semester.

J. R. Kuempel, Assistant Professor of Chemistry at De Pauw University, Greencastle, Indiana, serves on the faculty of the project. He has also worked with W. D. Shults, Analytical Methodology Group, on electroanalytical air pollutant monitors.

G. R. Norris, Professor of Biology at Denison University, Granville, Ohio, also serves on the faculty of the project. He has also worked with W. S. Lyon and J. F. Emery, Nuclear and Radiochemistry Group, on the neutron activation analysis of human post-mortem tissues.

J. B. Ohlrogge, a chemistry student at Earlham College, worked with M. R. Guerin, Analytical Methodology Group, on the tobacco smoke program.

G. T. Rasmussen, a chemistry student at Wabash College, worked with H. H. Ross, Nuclear and Radiochemistry Group, on Cerenkov spectroscopy of dual isotope systems.

A. J. Thieman, a biology student at Denison University, worked with J. F. Emery, Nuclear and Radiochemistry Group, on the neutron activation analysis of human blood.

ORAU Research Participants

J. R. Kuempel, Assistant Professor of Chemistry at De Pauw University, Greencastle, Indiana, worked with W. D. Shults, Analytical Methodology Group, on electrochemical monitors for air pollutants. He remained at ORNL at the end of the summer as a resident staff member of the Great Lakes Colleges Association, which conducted an undergraduate teaching semester at ORNL.

J. L. Robinson, Assistant Professor of Chemistry at Southeastern State College, Durant, Oklahoma, worked with M. R. Guerin and W. D. Shults, Analytical Methodology Group, and C. D. Scott, Chemical Technology Division, on chromatographic systems for separating and determining polynuclear aromatic hydrocarbons.

Graduate Thesis Research Program

R. W. Morrow, a graduate student in chemistry at the University of Tennessee, completed his predoctoral research work. He worked with M. R. Guerin and W. D. Shults, Analytical Methodology Group, studying the silicon-selective detector for gas chromatography. His major professor was J. A. Dean.

J. E. McCracken, an ORAU predoctoral fellow from the Department of Chemistry, University of Missouri, Columbia, is working in the Analytical Methodology Group with W. D. Shults. He is studying various applications of the controlled-current coulometric titrator that he has developed. His major professor is J. C. Guyon.

R. L. Coleman, an ORAU Predoctoral Fellow from the Department of Chemistry, University of Tennessee, is working with W. D. Shults, Analytical Methodology Group, and M. T. Kelley, Division Director, on environmental applications of the GeMSAEC photometric analyzer. His major professor is J. A. Dean.

F. L. Whiting, an ORAU Predoctoral Fellow from the Department of Chemistry with Professor Gleb Mamantov at the University of Tennessee, Knoxville, finished his thesis research. In the Reactor Projects Group with J. C. White and J. P. Young, he studied the simultaneous electrochemical generation and absorption spectrophotometric identification and characterization of solute ions of unusual oxidation states in molten fluoride melts.

ORNL Loanees

F. R. Clayton, Jr., a graduate student in the Department of Chemistry with Professor Gleb Mamantov at the University of Tennessee, Knoxville, is conducting research toward the Ph. D. degree. In the Reactor Projects Group, with J. C. White and A. S. Meyer, he is studying reference electrodes in fluoride melts to develop a practical reference electrode. Also, he is investigating the behavior of several metallic couples with the objective of extending the electromotive series in fluoride melts and establishing a series in $NaBF_4$ melts.

R. W. Morrow, a graduate student in chemistry at the University of Tennessee, finished predoctoral research in the Analytical Methodology Group. He worked with M. R. Guerin and W. D. Shults to study various applications of the silicon-selective detector that he has developed. His major professor is J. A. Dean.

J. C. Wolford, a graduate student in the Department of Chemistry with Professor J. A. Dean at the University of Tennessee, has been doing his doctoral thesis research in the Analytical Biochemistry Group with Gerald Goldstein. He is studying the separation of compounds of biological interest by ligand-exchange chromatography.

Summer Student Program

W. M. Cottrell, a student at the University of Tennessee, worked with Gerald Goldstein, Analytical Biochemistry Group, on a differential scanning calorimeter.

Project "Available Better Careers" (ABC)

M. R. Guerin functioned as one of the program coordinators for this program. The program is designed to expose local youngsters, particularly those who have implied they may not complete high school, to the opportunities that exist for high school graduates. Pre-high school youngsters are introduced to various personnel and activities at ORNL that demonstrate the value of a high school education. The program was delayed because of a strike. Plans are to execute "Project ABC" in the winter.

ORNL Technical Improvement Program

M. R. Guerin, Analytical Methodology Group, along with J. E. Caton, Analytical Biochemistry Group, were responsible for the General Chemistry course in ORNL's Technical Improvement Program.

Alien Guest in Residency

Hugh D. Livingston, a British subject, presently associated with Bowman-Gray School of Medicine, Winston-Salem, North Carolina, has worked with the Nuclear-Radiochemistry Group under sponsorship of ORAU. His research has been concerned with the development of activation analysis analytical methods for trace metals in tissues from atheromatic patients.

Part D. Extralaboratory Professional Activities

The extralaboratory professional activities of members of the Division are numerous and varied. They reflect participation in a diversity of work, especially at the national and international levels.

A. E. Cameron

Member: International Commission on Atomic Weights (Titular Member), IUPAC

L. T. Corbin

Member: Committee E-10, Radioisotopes and Radiation Effects
Subcommittee I, Burnup
Subcommittee II, Core and Cladding
ASTM

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

Chairman: Subcommittee V, Test Methods, ASTM Committee C-26

J. S. Eldridge

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

Recipient: National Aeronautics and Space Administration Apollo 11 Achievement Award

C. Feldman

Scientific Editor:
Optics and Spectroscopy [English Translation of the Russian journal *Optika i Spektroskopiya,* published by Optical Society of America]

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

D. J. Fisher

Member: Editorial Board, *Chemical Instrumentation*

President-Elect:
Association of Indiana University Chemists

G. Goldberg

Member: Committee G-1, Corrosion of Metals
Subcommittee I, Research
Subcommittee VIII, Corrosion of Nuclear Materials
Task Group B, Liquid Sodium Systems Alkali Metal Corrosion
Task Group C, Liquid Potassium Systems

Committee E-3, Chemical Analysis of Metals
Analytical Methods Committee
Alkali Metals Task Force
Nonferrous Metals Division
ASTM

Gerald Goldstein

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

Chairman: Subcommittee on Nucleotides and Related Compounds

Member: Committee on Specifications for Adenine for Use in Anticoagulant Solutions, NAS-NRC

M. R. Guerin

Member: Panel 3, Chemistry, International Study Group on Tobacco and Health Research

A. D. Horton

Member: Subcommittee III, Research
Committee E-19 on Chromatography
ASTM

C. A. Horton

Treasurer and Committee Chairman:
Tennessee Institute of Chemists, American Institute of Chemists Division

L. D. Hulett

Treasurer: Tennessee Institute of Chemists, American Institute of Chemists Division

W. R. Laing

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

C. E. Lamb

Member: Executive Committee (1967–1970)
Remote Systems Technology Division
ANS

M. T. Kelley

Member: Chemistry Directors' Meeting
Division of Research
United States Atomic Energy Commission

Analytical Specialists Group
Technology Subcommittee
Union Carbide Corporation

Advisory Board, *The Analyst*
Advisory Committee, *Microchemical Journal*
Board of Editoral Advisors, *Analytica Chimica Acta*

W. S. Lyon

Member: Committee E-10
Subcommittee I, Burnup
Subcommittee III, Tracer Applications
Subcommittee V, Neutron Dosimetry
ASTM

Editorial Board, *Chemical Instrumentation*
Scientific Committee 25 on Radiation Protection in the Use of Small Neutron Generators, NCRP
Committee N43-3, Equipment for Non-Medical Radiation Applications, United States of America Standard Institute

Chairman: Referee Committee F, Industrial Wastes
Subcommittee on Radiological Methods for Biological and Environmental Samples American Public Health Association (APHA)

Associate Editor, *Radiochemical and Radioanalytical Letters*

K. J. Northcutt

Recipient: National Aeronautics and Space Administration Apollo 11 Achievement Award

S. A. Reynolds

Member: Committee D-19, Water
Subcommittee 4, Methods of Radiochemical Analysis

Committee E-10, Radioisotopes and Radiation Effects, ASTM
Subcommittee V, Neutron Dosimetry
Task Group on Neutron Cross Sections
Task Group on Nuclear Data and Radiation Safety

Subcommittee on Use of Radioactivity Standards, Ad Hoc Panel, National Uses and Needs for Standard Radioactive Materials, National Research Council
Task Group 1, Committee 18, Standards, NCRP

Subcommittee, Radiological Methods for Biological and Environmental Samples American Public Health Association (APHA)

E. Ricci

Member: Executive Committee, Isotopes and Radiation Division, ANS

Chairman: Subcommittee on Activation Analysis, ANS

W. J. Ross

W. J. Ross is on leave to the Instituto Venezolano de Investigaciones Cientificas (IVIC), Caracas, Venezuela.

Member: Committee D-12, Analysis of Water, ASTM

W. D. Shults

Chairman: Analytical Chemistry Group, East Tennessee Section, ACS

Member: Environmental Pollution Committee, East Tennessee Section, ACS

Committee E-19, Gas Chromatography, ASTM
Committee D-19, Water, ASTM

Co-organizer:
(with J. C. White)
"Modern Chemical Separations", a non-degree course given in Kingsport under the auspices of East Tennessee State University

J. C. White

Chairman: Division of Analytical Chemistry, ACS

Representative from the 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*
Committee on Analytical Chemistry, NAS-NRC

Chairman: Subcommittee on Reference Materials, Committee on Analytical Chemistry, NAS-NRC

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

Part E. Presentation of Research Results

Several of the presentations listed below are made jointly with members of other ORNL divisions, or with consultants, graduate fellows, student guests, visiting scientists, or professors. In these cases such personnel are indicated by a single asterisk. The items included are, with few exceptions, those published or presented from the time of the prior annual report through September 1970.

Publications

CONTRIBUTIONS TO BOOKS

AUTHOR(S)	TITLE	PUBLISHER
1 Kelley, M. T.	"Remote Analysis of Radioactive Materials." pp. 1–9 in *Progress in Nuclear Energy, Ser. IX, Analytical Chemistry,* vol. 10, ed. by D. C. Stewart and H. A. Elion	Pergamon, Oxford, England, 1970
2 Lamb, C. E.	"Sampling, Sample Dissolution, Evaporation, and Combustion." pp. 107–42 in *Progress in Nuclear Energy, Ser. IX, Analytical Chemistry,* vol. 10, ed. by D. C. Stewart and H. A. Elion	Pergamon, Oxford, England, 1970
3 Maddox, W. L.	"Remote Pipetting." pp. 59–82 in *Progress in Nuclear Energy, Ser. IX, Analytical Chemistry,* vol. 10, ed. by D. C. Stewart and H. A. Elion	Pergamon, Oxford, England, 1970
4 Rickard, R. R.	"Equipment and Techniques for Handling Liquid Samples." pp. 143–79 in *Progress in Nuclear Energy, Ser. IX, Analytical Chemistry,* vol. 10, ed. by D. C. Stewart and H. A. Elion	Pergamon, Oxford, England, 1970
5 Ross, H. H.	"Cerenkov Radiation: Photon Yield Application to (^{14}C) Assay," in *The Current Status of Liquid Scintillation Counting,* ed. by E. D. Bransome	Grune and Stratton, New York, 1970
6 Shults, W. D.	"The Application of Electrochemical Techniques to Remote Analysis." pp. 307–57 in *Progress in Nuclear Energy, Ser. IX, Analytical Chemistry,* vol. 10, ed. by D. C. Stewart and H. A. Elion	Pergamon, Oxford, England, 1970
7 Thomason, P. F.[1]	"The Application of Titrimetry to Remote Analysis." pp. 83–105 in *Progress in Nuclear Energy, Ser. IX, Analytical Chemistry,* vol. 10, ed. by D. C. Stewart and H. A. Elion	Pergamon, Oxford, England, 1970
8 Zittel, H. E.	Chapter 14, "Effects of Radiation on Common Analytical Reagents." pp. 393– 412, in *Progress in Nuclear Energy, Ser. IX, Analytical Chemistry,* vol. 10, ed. by D. C. Stewart and H. A. Elion	Pergamon, Oxford, England, 1970

[1] Deceased Apr. 30, 1970.

ARTICLES

	AUTHOR(S)	TITLE	PUBLISHER
9	Anderson, D. H.* J. S. Eldridge many others	"Preliminary Examination of Lunar Samples from Apollo 12"	*Science* **167**, 1325–39 (1970)
10	Attrill, J. E. W. C. Butts J. W. Holleman* W. T. Rainey, Jr.	"Gas Chromatography of Methyl Thiohydantoins of Amino Acids"	*Anal. Lett.* **3**, 59–65 (1970)
11	Bate, L. C. F. F. Dyer	"Investigation of Radioisotope Tagging of Copper Wire"	*Int. J. Appl. Radiat. Isotop.* **21**, 271–75 (1970)
12	Bate, L. C.	"Rapid Radiochemical Strontium Separation"	*Radiochem. Radioanal. Lett.* **4(6)**, 385 (Sept. 24, 1970)
13	Belew, W. L.[2] J. A. Dean* D. J. Fisher M. T. Kelley	"A Cell Design for Minimizing *iR* Error in Controlled-Potential Polarography of High Specific Resistance Solutions"	*Chem. Instrum.* **2**, 297–308 (1970)
14	Blumberg, R.* F. F. Dyer A. Houtzeel*	"Remote Gamma Spectrometry for Fission Product Deposition Studies"	*Trans. Am. Nucl. Soc.* **12**, 842 (1969)
15	Burtis, C. A.* G. Goldstein C. D. Scott*	"Fractionation of Human Urine by Gel Chromatography"	*Clin. Chem.* **16**, 201–6 (1970)
16	Burtis, C. A.* W. C. Butts W. T. Rainey, Jr.	"Separation of the Metabolites of Phenacetin in Urine by High Resolution Anion Exchange Chromatography"	*Amer. J. Clin. Pathol.* **53**, 769–77 (1970)
17	Butts, W. C.	"Gas Chromatographic Separation of Trimethylsilyl (TMS)-Nucleosides: TMS-Methoxime Derivatives of Cytidine and Deoxycytidine"	*J. Chromatogr. Sci.* **8**, 474–76 (1970)
18		"Gas Chromatography of Trimethylsilyl Derivatives of Common Anions"	*Anal. Lett.* **3**, 29–34 (1970)
19	Butts, W. C. R. L. Jolley*	"Gas-Chromatographic Identification of Urinary Carbohydrates Isolated by Anion Exchange Chromatography"	*Clin. Chem.* **16**, 722–25 (1970)
20	Cameron, A. E.	"Isotopic Mass Spectrometry of the Actinides"	*Actinides Rev.* **1**, 299–310 (1969)
21	Cameron, A. E. D. H. Smith J. M. Wampler[3]	"Isotopic Comparison of Lead in Tektites with Lead in Earth Materials"	*Geochim. Cosmochim. Acta* **33**, 1045–55 (1970)
22	Danford, M. D.*/ W. H. Baldwin* J. H. Burns* C. E. Higgins* J. R. Stokely	"Preparation and Properties of Some Rare Earth and Americium Chelates"	*Inorg. Chem.* **9**, 1953–55 (1970)
23	Fisher, D. J.	"A Method for the Design of Instrument Systems for Measurements of Highest Sensitivity"	*Chem. Instrum.* **2**, 1–50 (1969)
24	Fisher, D. J. H. C. Jones* R. W. Stelzner	"The Use of Ensemble Averaging to Increase the Sensitivity of Measurements with Flame Photometers"	*Chem. Instrum.* **2**, 51–64 (1969)

[2] Present address: Technicon Corp., Tarrytown, N.Y.

[3] Permanent address: Georgia Institute of Technology, Atlanta, Ga. 30332.

25 Florence, T. M.* Y. J. Farrar* H. E. Zittel	"Dihydroxyanthraquinone Complexes of Zirconium"	*Aust. J. Chem.* **22,** 2321–32 (1969)
26 Guerin, M. R. W. D. Shults	"Gas Chromatography of Silylated Phenylthiohydantoin Amino Acids. Utility of Sulfur-Specific Detection"	*J. Chromatogr. Sci.* 7, 701–3 (1969)
27 Haire, R. G.* T. E. Willmarth	"Effect of Aging Media on the Morphology of $Pr(OH)_3$"	*Proc. VIIth International Congr. Electron Microscopy Grenoble, France, Sept. 2, 1970,* Soc. Francaise de Microscopie Electronique, Paris, France, 1970
28 Hatcher, D. W.[4] G. Goldstein	"Improved Methods for Determination of RNA and DNA"	*Anal. Biochem.* **31,** 42–50 (1969)
29 Horton, A. D. H. G. Linginfelter*	"Prevention of Backlash of the Recorder Pen on the Aerograph 713 Preparative Gas Chromatograph"	*J. Chromatogr. Sci.* **8,** 539 (1970)
30 Houtzeel, A.* R. Blumberg* F. F. Dyer	"Deposition of Fission Products in a Molten Salt Reactor System"	*Trans. Amer. Nucl. Soc.* **12,** 545 (1969)
31 Hulett, L. D. T. A. Carlson*	"Analysis of Compounds of Biological Interest by Electron Spectroscopy"	*Clin. Chem.* **16,** 677 (1970)
32 Jenkins, H. W.* G. Mamantov* D. L. Manning	"Electrode Potentials of Several Redox Couples in Molten Fluorides"	*J. Electrochem. Soc.* **117,** 183 (1970)
33 Jenkins, H. W.* G. Mamantov* D. L. Manning	"Emf and Voltammetric Measurements of U(IV)/U(III) Couple in Molten $LiF-BeF_2-ZrF_4$"	*J. Electrochem. Soc.* **116,** 1712–14 (1969)
34 Leitnaker, J. M.* W. R. Laing R. A. Potter* K. E. Spear*	"The Lattice Parameter of U(C,N) as a Function of Composition"	*J. High Temp. Sci.* **1,** 389–400 (1969)
35 Lupica, S. B.	"Polyethoxylated Nonionic Surfactants in Toluene for Liquid Scintillation Counting of Tritium in Aqueous Samples"	*Int. J. Appl. Radiat. Isotop.* **21,** 487–90 (1970)
36 Lyon, W. S. E. Ricci H. H. Ross	"Nucleonics"	*Anal. Chem.* **42,** 123R–29R (1970)
37 Moore, F. L.	Book Review: "Ion Exchange and Solvent Extraction of Metal Complexes," by Y. Marcus and A. S. Kertes, Wiley, New York	*Anal. Chem.* **42,** 132A (1970)
38 Mueller, T. R H. C. Jones*	"A Controlled-Potential and Controlled-Current Cyclic Voltammeter"	*Chem. Instrum.* **2,** 65–82 (1969)
39 O'Kelley, G. D.* P. R. Bell* J. S. Eldridge E. Schonfeld*	"Elemental Compositions and Ages of Lunar Samples by Nondestructive Gamma Ray Spectrometry"	*Science* **167,** 580–82 (1970)
40	"Comparative Radionuclide Concentrations of Apollo 11 and Apollo 12 Samples by Nondestructive Gamma-Ray Spectrometry"	*Trans. Amer. Geophys. Union* **51,** 582 (1970)
41 O'Kelley, G. D.* J. S. Eldridge	"Primordial Radionuclide Abundances, Solar Proton and Cosmic-Ray Effects and Ages of Apollo 11 Lunar Samples by Nondestructive Gamma Ray Spectrometry"	*Proc. Apollo 11 Lunar Sci. Conf.* **2,** 1407 (1970); *Geochim. Cosmochim. Acta* **34,** suppl. 1, 1407–23 (1970)

[4]Present address: St. Mary's Hospital, Knoxville, Tenn.

42 Raaen, Helen P.*	"Polytetrafluoroethylene Layers for Thin-Layer Chromatography"	*J. Chromatogr.* **44**, 522 (1969)
43	"Rapid Polarography of Uranium in 1 *M* Hydrofluoric Acid with a Vertical Orifice Polytetrafluoroethylene Dropping-Mercury Electrode"	*Anal. Chim. Acta* **48**, 427 (1969)
44 Reynolds, S. A.	Book Review: "Induced Radioactivity," by M. Barbier, North-Holland, Amsterdam, 1969, 424 pp.	*Nuclear Sci. Eng.* **40**, 359 (1970)
45 Ricci, E.	"Nuclear Microprobe Method (Prompt Nuclear-Reaction Analysis)"	*Trans. Amer. Nucl. Soc.* **12**, 505–6 (1969)
46 Ricci, E. T. H. Handley	"Activation Analysis with Californium-252"	*Anal. Chem.* **42**, 378–82 (1970)
47 Ricci, E. J. H. Gibbons*	"Proton-Reaction Analysis for ^{12}C, ^{13}C, and ^{15}N. Sensitivity and Biomedical Application"	*Trans. Amer. Nucl. Soc.* **12**, 509–10 (1969)
48 Ross, H. H.	"Assay of ^{129}I by Liquid Scintillation Counting: Use of ^{14}C as an Internal Standard"	*Radiochem. Radioanal. Lett.* **3**, 57–61 (1970)
49 Rubin, I. B. G. Goldstein	"An Ultrasensitive Isotope Dilution Method for the Determination of L-Amino Acids"	*Anal. Biochem.* **33**, 244–54 (1970)
50 Smith, D. H. G. R. Hertel[5]	"First Ionization Potentials of Th, Np, and Pu by Surface Ionization"	*J. Chem. Phys.* **51**, 3105–7 (1969)
51 Smith, D. H.	"Surface Ionization. V. Desorption of U Neutrals from W Surfaces"	*J. Chem. Phys.* **53**, 299–301 (1970)
52 Stelzner, R. W.	"The Design of Measuring Circuits for DC Polarograph"	*Chem., Instr.* **2**, 213–47 (1969)
53 Stokely, J. R., Jr. R. D. Baybarz* W. D. Shults	"Direct Potentiometric Determination of the Formal Potential of the Bk(III) -Bk(IV) Couple in Sulfuric Acid"	*Inorg. Nucl. Chem. Lett.* **5**, 877–84 (1969)
54 Toth, K. S.* C. E. Bemis* R. L. Hahn* T. H. Handley M. F. Roche[6]	"Search for ^{172}Hf Alpha Decay"	*J. Inorg. Nucl. Chem.* **32**, 1051–52 (1970)
55 Wampler, J. M.* A. E. Cameron D. H. Smith	"Isotopic Comparison of Lead in Tektites with Lead in Earth Materials"	*Geochim. Cosmochim. Acta* **33**, 1045 (1969)
56 Whiting, F. L.* G. Mamantov* J. P. Young	"Spectral Evidence for the Existence of the Superoxide Ion in Molten LiF-NaF-KF"	*J. Amer. Chem. Soc.* **91**, 6531 (1969)
57 Yoakum, Anna M.[7]	"Recent Advances in Analytical Emission Spectrometry"	*Appl. Spec. Rev.* **3**, 1–44 (1969)
58 Young, J. P.	"Answer to 'Chemical Queries' "	*J. Chem. Educ.* **47**, 73–75 (1970)
59 Zittel, H. E. T. H. Row*	"Radiation and Chemical Stability of Spray Additives"	*Trans. Amer. Nucl. Soc.* **12**, 166–67 (1969)
60	"Radiation and Thermal Stability of Spray Solutions"	*Trans. Amer. Nucl. Soc.* **13**, 205 (1970)

[5]Present address: Associate Professor, Florida Technological University, Orlando, Fla. 32816.

[6]Present address: Argonne National Laboratory, Argonne, Ill.

[7]Present address: Stewart Laboratories, Knoxville, Tenn.

THESES

AUTHOR	TITLE	PUBLISHER
61 Carter, J. A.	*Quantitative Spark-Source Mass Spectrometric Techniques for the Simultaneous Determination of the Lanthanide and Actinide Elements in Microgram and Sub-Microgram Transuranium Samples*	University of Tennessee, Knoxville, June 1970
62 Morrow, R. W.	*Part A: A Study of the Atomic Emission and Absorption of Organic-Bound Silicon in Oxygen- and Nitrous Oxide–Acetylene Flames; Part B: A Silicon Specific Detector Based on Interfacing a Gas Chromatograph and a Flame Emission or Atomic Absorption Spectrophotometer*	University of Tennessee, Knoxville, March 1970
63 Smith, D. H.	*Mass Spectrometric Investigation of Surface Ionization and Desorption Behavior of Thorium, Uranium, Neptunium, and Plutonium from Hot Tungsten*	University of Tennessee, Knoxville, June 1970
64 Whiting, F. L.	*Studies of the Superoxide Ion and Other Solute Species in Molten Fluorides*	University of Tennessee, Knoxville, August 1970

REPORTS

AUTHOR(S)	TITLE	REPORT NO. AND DATE
65 Eldridge, J. S. V. A. McKay* K. J. Northcutt G. D. O'Kelley*	*Low-Level Gamma-Ray Spectrometer System for Environmental Radioactivity Surveys*	Aug. 3, 1970 (unpublished)
66 Horton, C. A.	*ORNL Decentralized Nuclear Science Abstracts Preparation. First Semiannual Report, Period Ending July 1, 1969*	ORNL-TM-2653 (Oct. 22, 1969)
67 Kelley, M. T.	*Statistical Quality Control Report, Analytical Chemistry Division, July Through September 1969*	Oct. 15, 1969 (unpublished)
68	*Statistical Quality Control Report, Analytical Chemistry Division, October Through December 1969*	Jan. 21, 1970 (unpublished)
69	*Statistical Quality Control Report, Analytical Chemistry Division, January Through March 1970*	April 20, 1970 (unpublished)
70	*Statistical Quality Control Report, Analytical Chemistry Division, April Through June 1970*	July 20, 1970 (unpublished)
71 Lyon, W. S.	*Report of Foreign Travel, May 4–6 and May 9, 1970, to Austria and Scotland*	May 20, 1970 (unpublished)
72 Raaen, Helen P., ed.*	*Analytical Chemistry Division Annual Progress Report for the Period Ending October 31, 1969*	ORNL-4466 (January 1970)
73 Reynolds, S. A.	"Radioisotope Standards, Characterization, and Quality Control," pp. 40–41 in *Division of Isotopes Development Research and Development Programs: 1969*	TID-25372 (February 1970)
74 Stokely, J. R., Jr.	*Installation and Performance of a Perkin-Elmer Model 240 Elemental Analyzer in a Glove Box*	ORNL-TM-2825 (Oct. 13, 1970)
75 White, J. C.	*Analytical Chemistry Division Research and Development Monthly Summary – November 1969*	December 1969 (unpublished)
76	*Analytical Chemistry Division Research and Development Monthly Summary – December 1969*	January 1970 (unpublished)

77	*Analytical Chemistry Division Research and Development Monthly Summary – January 1970*	Jan. 30, 1970 (unpublished)
78	*Analytical Chemistry Division Research and Development Monthly Summary – February 1970*	March 1970 (unpublished)
79	*Analytical Chemistry Division Research and Development Monthly Summary – March 1970*	April 1970 (unpublished)
80	*Analytical Chemistry Division Research and Development Monthly Summary – April 1970*	Apr. 29, 1970 (unpublished)
81	*Analytical Chemistry Division Research and Development Monthly Summary – May 1970*	June 1970 (unpublished)
82	*Analytical Chemistry Division Research and Development Monthly Summary – June 1970*	July 1970 (unpublished)
83	*Analytical Chemistry Division Research and Development Monthly Summary – July 1970*	July 30, 1970 (unpublished)
84	*Analytical Chemistry Division Research and Development Monthly Summary – August 1970*	August 1970 (unpublished)
85	*Analytical Chemistry Division Research and Development Monthly Summary – September 1970*	September 1970 (unpublished)

Oral Presentations

FOURTEENTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

The Fourteenth Conference on Analytical Chemistry in Nuclear Technology, sponsored by the Analytical Chemistry Division of ORNL, was held in Gatlinburg, Tennessee, on October 13–15, 1970. A total of 285 attendees were registered; representatives from Great Britain, Belgium, Australia, and France attended in addition to chemists from throughout the United States.

Members of the Conference Committee were: M. T. Kelley, Division Director; J. C. White, Associate Director; L. J. Brady, Chairman; H. R. Beatty, Exhibits Coordinator and Treasurer; C. Feldman; D. J. Fisher; R. W. Stelzner; W. R. Laing; C. E. Lamb; and W. D. Shults, all of ORNL; and S. S. Yamamura of Idaho Nuclear Corporation. Technical papers were presented in ten sessions during the conference, and a dinner held October 14 featured an address by F. L. Culler, ORNL Deputy Director.

The topics discussed during the technical sessions included:

Application of Digital Computers in Analytical Chemistry. The increasing necessity of automation in analytical methods to reduce labor costs, increase analytical speed, help precision and accuracy, and eliminate some of the steps of procedures gave impetus to the inclusion of a session on this topic in which various laboratory groups could share some of their studies with others.

The application of small computers to control and/or for data acquisition for analytical instruments such as radioactivity counters, neutron activation analyzers, polarographs and coulometers, high resolution liquid chromatographs, spectrographic plate readers, x-ray instruments, mass spectrometers, and the GeMSAEC centrifugal photometric analyzer comprised most of the presentations, a number of which were from ORNL.

Sample Preparation and Dissolution Technology. As instrumental analytical methods increase and the complexity and often the refractory character of actual samples increase, methods for taking various types of sample into solution become one of the more troublesome aspects of the analytical methods. At this session types of materials whose preparation and dissolution were considered included: plutonium and its alloys and compounds; uranium and its compounds; metals; irradiated molten-salt reactor samples; and both unirradiated and irradiated reactor fuels.

Environmental Analysis. The recent summer environmental project and proposed greater involvement of ORNL in scientific studies related to environmental conditions and pollution led to the inclusion of this and the next topic in the program for the conference.

New Sensors and Detectors for Environmental Analysis. A number of new devices and facilities for environmental work were described in this session. ORNL contributions included a gas monitor for alpha radioactivity contamination and neutron and photon analysis capabilities using the HFIR or ORELA facilities.

Purity of Analytical Reagents. Increasing interest in the detection or determination of submicrogram quantities of elements and compounds or concentrations down to parts per billion, and the interest in faster, more sensitive precise automated methods have made the purity of analytical standards and reagents increasingly more important. In addition, differential and many isotopic ratio determinations require precise pure standards. These were among the topics discussed.

Analysis of Nuclear Fuel Materials. The increased number of reactors coming into service and the intensification of reprocessing of fuel materials are two reasons why this and the next topic in the program are of importance. Included besides papers on uranium and plutonium determination were ones on surface areas of fuels and on water and gas contents of such materials.

Determination of Trace Impurities in Nuclear Fuel Materials. Traces of various elements in nuclear fuel materials are important either as a criterion of corrosion, contamination, or possible effects on the behavior of the material during processing or later service. Papers were concerned with impurities in thorium, uranium, plutonium-thorium fuels, uranium hexafluoride, and uranium recovery process wastes.

General Radiochemistry. The Laboratory continues its long time interest in radioactivity, actinide compounds, and uses of radiotracers, and these were discussed here. The solution absorption spectra of Bk(IV) and Bk(III), studied at several laboratories, show promise in analytical applications. A talk on information centers as a reference source for chemists was especially well received.

Address of Floyd Culler. One highlight of the conference was the address of Floyd Culler, ORNL Deputy Director, at the Conference dinner. He discussed the importance of providing disposal methods for radioactive wastes as the use of nuclear reactors for power generation increases. Work at ORNL indicates that disposal of wastes is best in exhausted salt mines, and this has proved satisfactory in a Kansas mine. Other possible sites of salt mine waste storage in the United States and foreign countries were mentioned briefly.

AT MEETINGS OF PROFESSIONAL SOCIETIES, CONFERENCES, AND THE LIKE

	AUTHOR(S)	TITLE	PRESENTED AT
86	Butts, W. C.	"Gas Chromatographic Identification of Urinary Carbohydrates Isolated by Anion Exchange Chromatography"	Second Annual Symposium on Automated, High-Resolution Analyses in the Clinical Laboratory, Oak Ridge, Tenn., Mar. 12–13, 1970
87		"Current Applications of Gas Chromatography"	Modern Separations Course, Kingsport, Tenn., Apr. 9, 1970
88	Butts, W. C. W. T. Rainey, Jr.	"Gas Chromatography and Mass Spectrometry of Trimethylsilyl Derivatives of Common Anions"	160th American Chemical Society National Meeting, Chicago, Ill., Sept. 13–18, 1970
89	Carter, J. A.	"Analytical Spectrochemistry – Research and Industrial Applications"	University of Tennessee, Knoxville, Tenn., Feb. 12, 1970
90		"Spark-Source Mass Spectrometric Techniques for Solution Sample Types"	18th Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry Committee VII. San Francisco, Calif., June 15–19, 1970

91 Caton, J. E., Jr.	"Analytical Gel Electrophoresis"	Modern Separations Course, Kingsport, Tenn., Apr. 9, 1970
92 Caton, J. E. N. G. Anderson*	"Comparison and Evaluation of Separations in Polyacrylamide Gel Electrophoresis"	160th American Chemical Society National Meeting, Chicago, Ill., Sept. 13–18, 1970
93 Eldridge, J. S.	"Popular Discussion of Apollo 11 and 12 Lunar Missions"	Athens Kiwanis Club, Athens, Tenn., Feb. 13, 1970
94	"Popular Discussion of Apollo 11 and 12 Lunar Missions"	Karns Elementary School (6th through 8th grades), Karns, Tenn., Feb. 19, 1970
95 Goldstein, G.	"Analytical Centrifugal Methods and Membrane Filtration Separation"	Modern Separations Course, Kingsport, Tenn., Apr. 9, 1970
96 Guerin, M. R.	"Practical Applications of Gas Chromatography"	Modern Separations Course, Kingsport, Tenn., Apr. 9, 1970
97	"Biomedical Applications of Gas Chromatography"	University of Tennessee, A.E.C. Agricultural Research Laboratory, Oak Ridge, Tenn., May 22, 1970
98	"ORNL Tobacco Smoke Program – What We Have Learned"	ORNL Analytical Chemistry Seminar, Oak Ridge, Tenn., Sept. 22, 1970
99 Haire, R. G.* T. E. Willmarth	"Effect of Aging on the Morphology of $Pr(OH)_3$"	VIIth International Congress of Electron Microscopy, Grenoble, France, Sept. 2, 1970
100 Hatcher, D. W.[1]	"Clinical Analyses in Parallel: What Impact Will It Have on Automation?"	Association for the Advancement of Medical Technology, Boston, Mass., Mar. 23, 1970
101 Horton, C. A.	"The ORNL Decentralized Indexing Project, A Review"	Atomic Energy Commission Information Panel, Bethesda, Md., Nov. 5, 1969
102 Hulett, L. D. T. A. Carlson*	"The Analysis of Compounds of Biological Interest by Electron Spectroscopy"	Second Annual Symposium on Automated High-Resolution Analysis in the Clinical Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tenn. Mar. 12–13, 1970
103	"Application of Electron Spectroscopy in Analytical Chemistry"	Mid-American Symposium on Spectroscopy, Chicago, Ill., June 2–5, 1970

[1] Present address: St. Mary's Hospital, Knoxville, Tenn.

104		"Studies of Chemical Shifts in Inner Shell Binding Energies by Photoelectron Spectroscopy"	Symposium on Electron Spectroscopy, 160th American Chemical Society National Meeting, Chicago, Ill., Sept. 14–18, 1970
105	Kelley, M. T. D. L. Manning R. W. Stelzner	"A Computer Operated System for Stationary Electrode Voltammetry in High Temperature Molten Salt Media"	Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov. 5–8, 1969
106		"Research in Analytical Chemistry at ORNL"	Institute Venezolano de Investigaciones Cientificas, Caracas, Venezuela, Apr. 22, 1970
107		"Some Projects of Analytical Chemistry Research in ORNL"	Department of Chemistry, University of Athens, Athens, Greece, Aug. 22, 1970
108		"Modern Trends in Radiochemical Analytical Methods"	Symposium on Radiochemical Working Methods, Graz, Austria, Sept. 9–11, 1970
109		"Some Projects of Analytical Chemistry Research in ORNL"	Nuclear Research Center "Democritus," Athens, Greece, Sept. 30, 1970
110		"Some Projects of Analytical Chemistry in ORNL"	Seminar, Department of Chemistry, University of Athens, Greece, Sept. 22, 1970
111			Seminar, Nuclear Research Center "Democritus," Athens, Greece, Oct. 1, 1970
112	Kelley, M. T. R. L. Coleman* J. A. Dean* W. D. Shults	"Application of the GeMSAEC Rapid Photometric Analyzer to Inorganic Microanalysis"	VIth International Symposium on Microtechniques, Graz, Austria, Sept. 7–11, 1970
113	Lyon, W. S.	"Recent Developments and Uses of Forensic Activation Analysis"	Chairman, Panel Discussion, Winter Meeting, American Nuclear Society, San Francisco, Calif., Nov. 30–Dec. 4, 1969
114		"Activation Analysis"	University of Tennessee, Knoxville, Tenn., Feb. 9, 1970
115		"The Role of Activation Analysis in the Study of Environmental Problems"	Mid-American Symposium, Society of Applied Spectroscopy, Chicago, Ill., June 3, 1970
116		"Nuclear Techniques for the Determination of Hg"	International Conference on Environmental Mercury Contamination, Ann Arbor, Mich., Sept. 30, 1970

117 Moss, M. L.	"Techniques for Biochemical Analysis of the Single Cell"	Analytical Chemistry Seminar, University of Tennessee, Knoxville, Tenn., Feb. 28, 1970
118 Mueller, T. R.	"Report on the 23rd Annual Summer Symposium on Analytical Chemistry, sponsored by the American Chemical Society Division of Analytical Chemistry, Las Cruces, N. M., June 17–19, 1970"	Department of Chemistry, University of Tennessee, Knoxville, Tenn., July 8, 1970
119 O'Kelley, G. Davis* P. R. Bell* J. S. Eldridge E. Schonfeld	"Elemental Compositions and Ages of Lunar Samples by Nondestructive Gamma-Ray Spectrometry"	Apollo 11 Lunar Science Conference, Houston, Tex., Jan. 5–8, 1970
120 O'Kelley, G. Davis* P. R Bell* J. S. Eldridge E. Schonfeld*	"Comparative Radionuclide Concentrations of Apollo 11 and Apollo 12 Samples by Nondestructive Gamma-Ray Spectrometry"	Fifty-First Annual Meeting, American Geophysical Union, Washington, D.C., Apr. 20–24, 1970
121 Ricci, Enzo	"Nuclear Microprobe Method (Prompt Nuclear-Reaction) Analysis"	1969 Winter Meeting of the American Nuclear Society, San Francisco, Calif., Nov. 30–Dec. 4, 1969
122	"Recent Advances in Activation Analysis"	Department of Nuclear Engineering, Georgia Institute of Technology, Atlanta, Ga., Apr. 9, 1970
123 Ricci, Enzo J. H. Gibbons*	"Proton-Reaction Analysis for ^{12}C, ^{13}C, and ^{15}N. Sensitivity and Biomedical Application"	1969 Winter Meeting of the American Nuclear Society, San Francisco, Calif., Nov. 30–Dec. 4, 1969
124 Ross, H. H.	"Physical Models of the Liquid Scintillation Process"	ORAU course on Radioisotope Technology, Oak Ridge, Tenn., June 16, 1970
125	"Liquid Scintillation and Cerenkov Spectroscopy: The Chemical System"	ORAU course on Radioisotope Technology, Oak Ridge, Tenn., June 18, 1970
126	"The Resolution in Nuclear Detector Instrumentation"	Special Seminar, ORAU, Oak Ridge, Tenn., Aug. 10, 1970
127	"Performance Parameters of Selected Waveshifting Compounds for Cerenkov Counting"	International Conference on Organic Scintillators and Liquid Scintillation Counting, San Francisco, Calif., July 7–10, 1970
128 Shults, W. D.	"Introduction: The Literature Language and General Principles of Chemical Separation Methods"	First lecture in a course in Modern Chemical Separations given by ORNL personnel at Kingsport, Tenn., May 5, 1970
129 Smith, D. H.	"Mass Spectrometry at ORNL"	Seminar, University of Tennessee, Knoxville, Tenn., Apr. 9, 1970
130 Strain, J. E.	"Neutron Activation Analysis"	Naval Research Reserve Seminar, Unit 6-12, Oak Ridge, Tenn., Dec. 6, 1969

131 White, J. C.	"Capabilities of a National Laboratory in Bioengineering"	Oak Ridge Associated Universities Fifth Annual Conference on Engineering at ORNL, Oak Ridge, Tenn., Apr. 7, 1970
132 White, J. C. M. L. Moss	"The GeMSAEC in the Clinical Laboratory"	Symposium on Instrumentation, American Society of Medical Technologists, 38th Annual Convention, Detroit, Mich., June 14–19, 1970
133 Willmarth, T. E.	"Effect of Aging Media on the Morphology of $Pr(OH)_3$"	VIIth International Congress of Electron Microscopy, Grenoble, France, Sept. 2, 1970
134	"Applications of Transmission Electron Microscopy to Sol-Gel Technology"	The Swiss Institute for Reactor Research, Würenlingen, Switzerland, Sept. 8, 1970
135 Young, J. P.	"Spectral Studies of Actinides in Molten Fluoride Solution; Application of a New Hot-Cell Spectrophotometric Facility"	Los Alamos Scientific Laboratory, Los Alamos, N. M., June 18, 1970
136 Zittel, H. E.	"Radiolytic Decomposition of Spray Solutions"	Nuclear Safety Program Annual Information Meeting, ORNL, Oak Ridge, Tenn., Feb. 10, 1970
137	"Radiation and Thermal Stability of Spray Solutions"	16th Annual Meeting, American Nuclear Society, Los Angeles, Calif., June 28–July 2, 1970

Patents

AUTHOR	TITLE	PATENT NO.	DATE ISSUED
138 Hatcher, D. W.	"Photometric Thermometer and Method of Operation"	3,513,704	May 26, 1970

Articles Reviewed or Refereed for Periodicals

Reviewer or Referee	Number of Articles Reviewed or Refereed for Indicated Periodicals																
	Anal. Biochem.	*Anal. Chem.*	*Anal. Chim. Acta*	*Appl. Spec.*	*ASTM Method for Emission Spec. Analysis*	*Chem. Instrum.*	*Environ. Sci. Technol.*	*Health Phys.*	*Isotopes Radiat. Technol.*	*J. Chromatogr. Sci.*	*J. Electrochem.*	*Nucl. Appl. Tech.*	*Nucl. Safety*	*Nucl. Sci. Eng.*	*Radiochem. Radioanal. Lett.*	*Talanta*	Total
Butts, W. C.		2															2
Cameron, A. E.		2															2
Costanzo, D. A.		1															1
Emery, J. F.													1				1
Feldman, C.		4		2	7												13
Goldstein, G.	1	1				1											3
Handley, T. H.		4														2	6
Horton, A. D.										1							1
Lyon, W. S.		3												1	1		5
Manning, D. L.		3									1						4
Moore, F. L.		2	2														4
Mueller, T. R.		3															3
Reynolds, S. A.								1	1			1	1				4
Ricci, E.		2					1										3
Ross, H. H.		2															2
Shults, W. D.		2	1													2	5
Stelzner, R. W.		3				1											4
White, J. C.		1															1
Young, J. P.		1															1
Zittel, H. E.												1					1
Total	1	36	3	2	7	2	1	1	1	1	1	2	2	1	1	4	66

ANALYTICAL CHEMISTRY DIVISION

OCTOBER 1, 1970

M. T. KELLEY, DIRECTOR
B. ELIZABETH YOUNG, SECRETARY
J. C. WHITE, ASSOCIATE DIRECTOR
EDITH M. ZARZECKI, SECRETARY

CONSULTANTS
J. A. DEAN, UNIVERSITY OF TENNESSEE
GLEB MAMANTOV, UNIVERSITY OF TENNESSEE
A. O. C. NIER, UNIVERSITY OF MINNESOTA

ADVISORY COMMITTEE
H. A. LAITINEN, EXP. 12-31-70, UNIVERSITY OF ILLINOIS
L. B. ROGERS, EXP. 12-31-70, PURDUE UNIVERSITY
C. V. BANKS, EXP. 12-31-73, IOWA STATE UNIVERSITY
M. A. EVENSON, EXP. 12-31-73, HARVARD MEDICAL SCHOOL

STAFF
M. L. MOSS, BIOANALYTICAL PROGRAMS
C. FELDMAN, ENVIRONMENTAL POLLUTION PROGRAM
D. E. LAVALLE, INORGANIC PREPARATIONS
F. S. JONES[5]
H. R. BEATTY,[8] BUDGETS AND COSTS
U. KOSKELA,[1] RADIATION AND SAFETY OFFICER
J. S. ELDRIDGE,[1] COORDINATOR FOR RADIOCHEMICAL ANALYSES IN AN EMERGENCY
A. L. HARROD, ADMIN. ASST.
A. H. MATTHEWS
LINDA F. AMBURN,[7] SECRETARY

ANALYTICAL SERVICES
L. T. CORBIN, ASSISTANT DIRECTOR
SUZANNE Q. THOMPSON, SECRETARY

HIGH-LEVEL RADIATION FACILITY
U. KOSKELA[1]

METHODS DEVELOPMENT AND EVALUATION LABORATORY
D. A. COSTANZO, GROUP LEADER
J. L. BOTTS
D. C. CANADA[7]
L. G. FARRAR
G. GOLDBERG
J. R. LUND
F. L. MOORE

ANALYST
P. S. GOUGE

GENERAL HOT-ANALYSES LABORATORY
C. E. LAMB, SUPERVISOR
C. K. TALBOTT, ASST. SUPERVISOR
S. R. DINSMORE[4]
R. E. JONES
F. L. LAYTON
E. C. LYNN
J. C. PRICE

ANALYSTS
R. BURNS
B. E. GILL
WANDA C. MASSEY
W. F. ROGERS

HIGH-LEVEL ALPHA RADIATION LABORATORY
J. H. COOPER, SUPERVISOR
W. F. VAUGHAN

BUILDING 3508
ANALYSTS
R. W. HARVEY
K. C. LANNOM
D. D. PAIR

BUILDING 7920
H. C. MEYER, ASST. SUPERVISOR
E. C. FEARNOW
J. M. PEELE

A SHIFT	B SHIFT	C SHIFT	D SHIFT
T. G. SCOTT*	P. W. PAIR*	C. P. BAKER*	J. D. PENDLETON*
	C. C. FOUST**[1]		
ANALYST	ANALYST	ANALYST	ANALYST
J. H. OXENDINE	W. H. AKERS	R. A. JONES	G. R. ARCHER

*SHIFT SUPERVISOR
**RELIEF SHIFT SUPERVISOR

GENERAL ANALYSES LABORATORY
W. R. LAING, SUPERVISOR
L. J. BRADY, ASST. SUPERVISOR
M. V. CONNELLY
H. G. DAVIS
J. A. EALY[7]
N. MARION FERGUSON
K. W. GENTRY
C. F. HARRISON[3]
F. K. HEACKER
D. R. MATTHEWS
J. H. MONEYHUN
M. M. MURRAY
W. R. MUSICK
R. L. SHERMAN
C. D. STRINGER
G. R. WILSON

ANALYSTS
C. SUE ALLEY
W. E. BAYLESS
EDNA E. BONIFACIUS
GERTRUDE S. BROWN
MARTHA R. CHILDS
C. A. CLARK
C. J. COLEY
J. H. HACKNEY
J. D. HILL
A. H. MARSHALL
B. PHILPOT
ROBERTA M. RAMSEY
G. W. ROBINSON
PATRICIA M. ROWAN
KATHLEEN I. WEBB
J. V. WINCHESTER

RADIOISOTOPES-RADIOCHEMISTRY LABORATORY
E. I. WYATT, SUPERVISOR
R. R. RICKARD, ASST. SUPERVISOR
W. T. MULLINS
H. A. PARKER
M. E. PRUITT
J. S. WIKE

ANALYSTS
J. H. DAVIDSON
C. L. GHANN
L. R. HALL
E. C. HENDREN[4]
RUTH H. HOLLAND
K. J. NORTHCUTT[6]
SUE H. PRESTWOOD
J. SLESSINGER, JR.
W. R. WARREN

RESEARCH AND DEVELOPMENT

ANALYTICAL INSTRUMENTATION
D. J. FISHER, GROUP LEADER
R. W. STELZNER, ASSISTANT GROUP LEADER
W. L. MADDOX
T. R. MUELLER

REACTOR PROJECTS
A. S. MEYER, GROUP LEADER
J. M. DALE, ASSISTANT GROUP LEADER
R. F. APPLE
C. M. BOYD
A. D. HORTON
D. L. MANNING
A. L. TRAVAGLINI
J. P. YOUNG
F. R. CLAYTON[9]

ELECTRON MICROSCOPY
T. E. WILLMARTH, GROUP LEADER
L. D. HULETT, ASSISTANT GROUP LEADER
H. W. DUNN
T. G. HARMON

NUCLEAR AND RADIOCHEMISTRY
W. S. LYON, JR., GROUP LEADER
H. H. ROSS, ASSISTANT GROUP LEADER
L. C. BATE
F. F. DYER
J. S. ELDRIDGE[1]
J. F. EMERY
T. H. HANDLEY
S. B. LUPICA
S. A. REYNOLDS[5]
E. RICCI
J. E. STRAIN
H. E. ZITTEL
H. D. LIVINGSTON[13]
G. R. NORRIS[11]
G. T. RASMUSSEN[12]
A. J. THIEMANN[12]

ANALYTICAL BIOCHEMISTRY
G. GOLDSTEIN, GROUP LEADER
J. E. ATTRILL
W. C. BUTTS
J. E. CATON, JR.
H. KUBOTA
I. B. RUBIN
J. C. WOLFORD[9]

METHODOLOGY
W. D. SHULTS, GROUP LEADER
M. R. GUERIN
C. A. HORTON
C. A. PRITCHARD
R. B. QUINCY
W. J. ROSS[7]
J. R. STOKELY
H. W. WRIGHT
R. L. COLEMAN[10]
J. R. KUEMPEL[11]
J. E. MCCRACKEN[10]
J. B. OHLROGGE[12]

ANALYST
GERALDINE OLERICH

MASS AND EMISSION SPECTROMETRY (Y-12)
A. E. CAMERON,[1] ASSISTANT DIRECTOR
DORIS C. SMITH, SECRETARY

SERVICE ANALYSES
J. A. CARTER[1]

MASS SPECTROMETRY SERVICE
R. E. EBY, SUPERVISOR

ANALYSTS
TINA P. BACON
L. GUINN
MABEL M. HONAKER

DEVELOPMENT
J. R. SITES, SUPERVISOR

SPECTROCHEMISTRY
J. A. CARTER,[1] SUPERVISOR
S. A. MACINTYRE

ANALYSTS
R. C. BRYANT
G. I. GAULT
E. H. WATERS

MASS SPECTROMETRY RESEARCH
D. H. SMITH

REFEREE ANALYSIS SERVICE
R. L. WALKER, SUPERVISOR

ANALYSTS
E. G. MILLER
J. L. SHARP
H. C. SMITH
DORA I. WHALEY
N. WILSON

DEVELOPMENT
A. E. CAMERON,[1] GROUP LEADER
W. H. CHRISTIE
H. S. MCKOWN
W. T. RAINEY, JR.
J. R. WALTON

PERMANENT STAFF	MONTHLY	WEEKLY	TOTAL
ADMINISTRATIVE AND CLERICAL	4	6	10
SCIENTISTS	103		103
ANALYSTS		50	50
SUBTOTAL	107	56	163
OTHERS			
ALIEN GUEST	1		1
STUDENT GUESTS (UT)	2		2
FACULTY GUESTS (GLCA)	2		2
ORAU FELLOWS	2		2
STUDENT GUESTS (GLCA)	3		3
LOANEE FROM OTHER DIVISION	1		1
SUBTOTAL	11		11
GRAND TOTAL	118	56	174

[1]DUAL CAPACITY
[2]ON LOAN TO K-25
[3]ON LOAN TO SOLID STATE DIVISION
[4]ON LOAN TO CHEMICAL TECHNOLOGY DIVISION
[5]ON LOAN TO ISOTOPES DIVISION
[6]ON LOAN TO CHEMISTRY DIVISION
[7]ON LEAVE OF ABSENCE
[8]ON LOAN FROM THE BUDGET DEPARTMENT
[9]STUDENT GUEST (UT)
[10]ORAU FELLOW
[11]FACULTY GUEST (GLCA)
[12]STUDENT GUEST (GLCA)
[13]ALIEN GUEST

INTERNAL DISTRIBUTION

1. R. F. Hibbs (Y-12)
2. A. M. Weinberg
3. F. L. Culler
4. H. I. Adler
5. N. G. Anderson
6. S. I. Auerbach
7. J. C. Barton (K-25)
8. S. E. Beall
9. M. Bender
10. D. S. Billington
11. R. E. Blanco
12. E. G. Bohlmann
13. C. J. Borkowski
14. G. E. Boyd
15. R. B. Briggs
16. O. W. Briscoe (Y-12)
17. R. E. Brooksbank
18. K. B. Brown
19. F. R. Bruce
20. W. D. Burch
21. S. F. Carson
22. H. P. Carter
23. J. A. Cox
24. J. E. Cunningham
25. D. E. Ferguson
26. J. L. Fowler
27. J. H. Frye, Jr.
28. J. H. Gillette
29. W. R. Grimes
30. W. O. Harms
31. Frances Hurley
32. W. H. Jordan
33. O. L. Keller
34. M. T. Kelley
35. Ann S. Klein
36. T. A. Lincoln
37. J. L. Liverman
38. R. S. Livingston
39. R. N. Lyon
40. F. C. Maienschein
41. K. Z. Morgan
42. Lewis Nelson
43. G. D. Novelli

44–45. R. B. Parker

46. H. Postma
47. M. E. Ramsey
48. J. H. Rowan (Y-12)
49. D. E. Rose
50. M. W. Rosenthal
51. A. F. Rupp
52. H. E. Seagren
53. M. J. Skinner
54. A. H. Snell
55. E. G. Struxness
56. D. A. Sundberg
57. E. H. Taylor
58. P. R. Vanstrum
59. G. M. Watson
60. C. W. Weber (K-25)
61. M. E. Whatley
62. R. G. Wymer
63. U. Koskela
64. A. E. Cameron
65. W. H. Christie
66. H. S. McKown
67. W. T. Rainey, Jr.
68. D. H. Smith
69. J. H. Cooper
70. H. C. Meyer
71. L. T. Corbin
72. C. Feldman
73. D. J. Fisher
74. R. W. Stelzner
75. G. Goldstein
76. W. C. Butts
77. J. E. Caton
78. W. R. Laing
79. L. J. Brady
80. C. E. Lamb
81. C. K. Talbott
82. D. E. LaValle
83. W. S. Lyon
84. H. H. Ross
85. F. F. Dyer
86. E. Ricci
87. H. Kubota
88. H. E. Zittel
89. S. A. Reynolds

90. M. L. Moss
91. A. S. Meyer
92. W. Fulkerson
93. J. H. Gibbons
94. J. M. Dale
95. J. P. Young
96. Helen P. Raaen
97. W. D. Shults
98. M. R. Guerin
99. C. A. Horton
100. W. J. Ross
101. J. R. Stokely
102. J. R. Sites
103. R. E. Eby
104. J. A. Carter
105. R. L. Walker
106. D. A. Costanzo
107–110. J. C. White
111. T. R. Willmarth
112. L. D. Hulett
113. E. I. Wyatt
114. R. R. Rickard
115. H. A. Laitinen (advisory committee)
116. C. V. Banks (advisory committee)
117. M. A. Evenson (advisory committee)
118. L. B. Rogers (advisory committee)
119. S. Siggia (advisory committee)
120. J. A. Dean (consultant)
121. G. Mamantov (consultant)
122. A. O. C. Nier (consultant)
123. Biology Library
124–126. Central Research Library
127. Laboratory Shift Supervisor
128. ORNL – Y-12 Technical Library Document Reference Section
129–165. Laboratory Records Department
166. Laboratory Records, ORNL R.C.

EXTERNAL DISTRIBUTION

167. Sterling Forest Laboratory, Union Carbide Corporation, New York
168. J. A. Swartout, 270 Park Avenue, New York 17, New York
169. R. C. Shank, Idaho Falls
170. T. W. McIntosh, Division of Reactor Development and Technology, U.S. Atomic Energy Commission, Washington, D.C. 20545
171. duPont Company, Wilmington
172. Bettis Plant, Westinghouse Atomic Power Laboratory
173. William Mott, Division of Isotope Development, AEC, Washington, D.C.
174. Lt. J. C. Courtney, MCL-NI, 1155 Technical Operations Squadron, McClellan Air Force Base, Calif. 95652
175. Library, Nuclear Fuel Services, Inc., Erwin, Tenn. 37650
176. J. Frazer, Lawrence Radiation Laboratory, Livermore, Calif.
177. W. W. Grigorieff, Assistant to the Executive Director, Oak Ridge Associated Universities
178. Robert Lewin, Paducah
179. Research Center Library, Union Carbide Corporation, P.O. Box 324, Tuxedo, New York
180. W. W. Meinke, Analytical Chemistry Division, National Bureau of Standards, Washington, D.C. 20234
181. Gio B. Gori, National Cancer Institute, National Institutes of Health, Bethesda, Md. 20014
182. R. K. Stevens, National Air Pollution Control Adm., 3820 Merton Dr., Raleigh, N.C.
183. R. L. Belcher, Reactor Center, Nuclear Eng. Dept., University of Maryland, College Park, Md.
184. Laboratory and University Division, AEC, ORO
185. Patent Office, AEC, ORO
186–379. Given distribution as shown in TID-4500 under Chemistry category (25 copies – CFSTI)