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ORNL-3397
UC-4 – Chemistry

ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
FOR PERIOD ENDING DECEMBER 31, 1962

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

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M. T. Kelley, Director
C. D. Susano, Associate Director

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Summary

PART I. ANALYTICAL RESEARCH

1. Analytical Instrumentation

Evaluation of the direct-readout circuits for the ORNL model Q-2005 controlled-potential coulometric titrator has shown that the precision and accuracy of the direct readout are entirely satisfactory and are as good as those obtained with manual readout. New modifications of the original Q-2005 circuit have been designed for special applications. With low-resistance cells, a new transistor current amplifier, used in place of the original, will deliver up to 3 amp. For high-resistance cells, a second modification eliminates the transistor current amplifier, and the GAP/R USA-3 potential-control amplifier delivers to the cell as much as ±8 ma at ±100 v. In a third modification, a complementary-pair emitter follower stage can supply either anodic or cathodic current without the necessity of switching the titrator from "oxidize" to "reduce."

A high-sensitivity controlled-potential (or constant-current) coulometric titrator was designed, fabricated, evaluated, and put into service. The upper limits of the ranges for full output of the integrating amplifier are 1, 10, 50, and 100 μeq of substance titrated.

Fabrication and maintenance instructions for the indicated models of the following ORNL instruments were brought up to date: coulometric titrators Q-2005 and Q-2005-X50; fluorophotometer Q-1165; flame spectrophotometers Q-1457 and Q-1887; the remotely operated filter photometer Q-1734; and the controlled-potential and derivative polarograph Q-1988A.

Safety devices were assembled and installed on the high-vacuum systems of three vacuum-fusion apparatuses. The devices automatically prevent damage that would otherwise result from unscheduled interruptions or failures of line power.

A sample-cutting jig was designed and built for use in precisely taking successive samples from graphite bars. The samples are used in the measurement of diffusion of uranium into the bars.

Features added to a high-sensitivity, direct-reading, linear, recording conductivity titrator include: a circuit to compensate for changes in solution temperature; and a circuit to compensate for the initial conductance of the solution, so that subsequent conductivity changes can be measured on a scale that is 100 times as sensitive as that which could be used otherwise. With the latter compensator, which is to be used with thermostated cells, full-scale readings can be obtained for small changes (e.g., 0.01 ohm per ohm). Electrical tests indicate an error of ±1% for conductances between 1 μmho and 0.5 mho;

linearity is achieved to within ±0.1%. It is planned to evaluate the performance of this instrument in several applications.

A direct-reading spectrophotometer was designed and built for use in the determination of beryllium. The electronic portion of the instrument perfoms satisfactorily, but the optical section is being improved.

An operational amplifier was used as an impedance-transforming current amplifier between a multiplier phototube and an unmodified recorder. This technique was used to make possible the replacement of a recorder in a scanning flame spectrophotometer by one of faster response.

A new single-beam flame spectrophotometer, designated model VI, was designed and built and is in use. Its circuit has improvements over that of the model Q-1887.

Apparatus and instruments have been provided that make possible the remotely controlled analysis of radioactive samples. A filter photometer was fabricated for use in the MSRE Hot-Cell Mock-Up. An improved absorption-cell attachment for the Welch Densichron reflectance unit was designed and built for the Radioistopes-Radiochemistry Laboratory. A new decapper-pipetter assembly, which includes a decapper having a novel clamping arrangement, was designed; the prototype was fabricated for the Radioisotopes-Radiochemistry Laboratory. A copper capsule was designed for use in the preparation of frozen MSRE salt samples; the sample must be broken free of a ladle, pulverized, mixed, and transferred to a sample bottle. Results of tests of the performance of the capsule have been satisfactory. An apparatus is being designed for remotely opening the sample-transfer tube and removing the ladle that contains the MSRE samples. A prototype will be built and tested.

Several developments in polarography were made. The design of the circuitry of the ac controlled-potential polarograph was improved. In dc polarography, a study was made with the ORNL model Q-1988-ES controlled-potential and derivative polarograph of the relative sensitivity obtained (without resort to preconcentration) with various types of mercury cathodes, including a pool with quiet and with stirred solution and the following variations of a D.M.E.: unmodified and drawn-out "2–5 sec" and unmodified "6–12 sec" Sargent capillaries, Atlas-Werke siliconed capillaries, two varieties of bulb-type capillaries, capillaries having mechanically controlled drop time, and Smoler vertical-orifice capillaries. Because the Q-1988-ES polarograph has high current-measuring sensitivity, no advantage accrued from the use of a mercury pool rather than a D.M.E. Of the D.M.E.'s tested, highest sensitivity was achieved with a small-orifice D.M.E. and with a Smoler 0.5-sec vertical-orifice D.M.E. The use of a 0.5-sec rather than a 5-sec D.M.E. makes it possible to increase the speed of response of the current-averaging and derivative computers, so that the scan rate can be increased about tenfold without adverse effect on the form of the recorded waves. It was learned that polarograms made with a Smoler 0.5-sec vertical-orifice D.M.E. do not have maxima of the second kind, are very reproducible, and are of conventional form. Short drop times and good polarograms were also obtained with a conventional D.M.E. by mechanical control of the drop detachment, but this method requires considerable additional equipment. With the circuit modifications made possible by use of the 0.5-sec drop time, at a scan rate of up to about 300 mv/min, regular and first-derivative polarograms for simple, reversible, diffusion-controlled processes have the theoretical form unaffected by instrument characteristics. Use of scan rates no faster than 300 mv/min is particularly advantageous in obtaining maximum resolution of closely adjacent waves; in determining reversibility, diffusion control, or n values; and in measuring $E_{1/2}$ values. At a scan rate of 3000 mv/min, time lag is appreciable; however, for concentration measurement with resolved waves, this is not deleterious, and the polarogram is recorded in about 6 sec.

The significant gain in resolution and sensitivity of first-derivative polarography over regular polarography indicated that the feasibility and utility of second-derivative polarography should be investigated. An equation was derived that describes the form of a second-derivative polarogram for simple, reversible, diffusion-controlled processes; the height of the two peaks of equal height is directly proportional to i_d, n^2, and the square of the scan rate. Although the resolution of second-derivative polarography is greater than that of first-derivative polarography, the range of concentration ratios over which a peak in each of the second-derivative polarograms of close $E_{1/2}$ values would be resolved and the corresponding first-derivative polarograms would overlap is rather restricted. A second-derivative computer was designed and tested. With a drop time of about 4 sec and a scan rate of 100 mv/min, the sensitivity of second-derivative polarography was not as good as that of first-derivative polarography because of the high level of noise. With a 0.5-sec D.M.E., the new computing circuits, and scan rates of the order of 3000 mv/min, the noise problem is greatly reduced. Work is being continued on second-derivative polarography as a method of obtaining high sensitivity.

An equation was derived for the third derivative of the average dc polarographic current with respect to time for a simple, reversible, diffusion-controlled process. The results of comparisons of plots of the theoretical forms of regular and of first-, second-, and third-derivative polarograms indicated that there is no apparent analytical advantage to be gained from third-derivative polarography.

2. Chemical Analysis of Advanced Reactor Fuels

The development of methods for the analysis of dissolver solutions has continued, the major effort being directed toward the controlled-potential coulometric titration of uranium following its separation from major components of the dissolved fuel.

A method for determining uranium that consists in the extraction of uranium into a cyclohexane solution of tri-*n*-octylphosphine oxide, back-extraction, and coulometric titration at controlled-potential has been developed. This method was evaluated by analyzing synthetic dissolver solutions that were made to represent seven different reactor fuels.

Two controlled-potential coulometric titration methods for the determination of U^{6+} in uranium-niobium alloys were developed.

Sodium tripolyphosphate was studied as an electrolyte for the controlled-potential coulometric titration of uranium. It was found that both U^{4+} and U^{6+} can be determined in this medium.

The polarographic studies with the Teflon dropping-mercury electrode for use in glass-corroding media have continued; two papers and an ORNL topical report that describe this work have been published.

3. Analysis of Molten Salts by Electrochemical Methods

The emf method for the evaluation of association constants for metal complexes in molten nitrate salts was extended to include silver cyanide and lead bromide. The voltammetry of silver in $NaNO_3$-KNO_3 in the range from 246 to 326°C was investigated as the initial step in the general program on molten-fluoride-salt voltammetry. The use of a three-electrode system with a quasi-reference electrode is contemplated.

4. Special Research Problems

Absorption spectrophotometric studies of plutonium were continued to determine the kinetics of the polymerization and depolymerization of Pu^{4+} in nitrate solutions and to determine the properties of the polymer with respect to such parameters as acidity, temperature, and ionic concentration.

Design modification of a high-temperature high-pressure spectrophotometer was continued. The spectrophotometer is to be operable with highly radioactive solutions at temperatures of the order of 330°C and at pressures as high as 5000 psi.

An automatic, digital, data-output system for recording absorbance data was installed on the Cary model 14 CMR spectrophotometer. This instrument is being used in connection with a miniature circulating loop. Spectral studies are to be made with this instrument on systems that will be investigated later on the high-temperature high-pressure spectrophotometer.

A method has been devised for measuring densities of aqueous solutions at high temperatures and high pressures by use of x-ray photographs to show the position of the vapor-liquid interface in a calibrated section of an autoclave.

Spectrophotometric studies were continued on molten-fluoride-salt systems. Causes of solution instability, primarily hydrolysis, were ascertained and corrected. A captive-liquid cell was perfected to contain the corrosive molten fluorides. This cell, which holds the liquid in the plane of the light beam by means of surface tension effects, provides a convex lens shape and thereby promotes improved light transmission. The absorption spectrum of UF_3 in NaF-LiF-KF was recorded for the first time. The absorption peaks occur at 890 (strong), 975, and 1060 $m\mu$. Studies on the absorption spectrum of NdF_3 in NaF-LiF-KF were continued.

Several volumetric titrations were evaluated with respect to accuracy and precision by means of microchemical techniques.

5. Gas-Cooled Reactor Project Analyses

Development of instrumental methods of analysis for the helium (blanket gas) of the Gas-Cooled Reactor, Molten-Salt Reactor, and Pebble-Bed Reactor included the improvement of a process chromatograph for the measurement of parts-per-million concentrations of impurities in helium, the design and installation of a process chromatograph for the determination of impurities in radioactive helium streams, and the evaluation of an electrolytic oxygen analyzer. Modifications to laboratory chromatographs included the installation of dual columns to a Perkin-Elmer chromatograph to provide increased versatility and improved sensitivity in the analysis of samples at low pressures, the adaptation of a Burrell chromatograph for use in studies of the rate of reactions of graphite, and the improvement of the sensitivity of a chromatograph used for the analysis of gases from organic moderators. Techniques were devised for the purification and concentration of fission gases from charcoal traps and for the trapping of carbon tetrafluoride together with krypton and xenon from MSRE capsule tests to effect concentration of these gases for subsequent analysis by chromatographic or mass spectrographic techniques.

Assistance was given in engineering investigations to evaluate techniques of purification of helium and to determine potential contamination of helium from the high-temperature desorption of gases from thermal and electrical insulating materials.

Additional hydrocarbons, principally olefins, in the gases evolved on dissolution of uranium carbides in water were identified and determined by chemical separations and gas chromatographic techniques. A chromatographic column assembly was fabricated for the analysis of radioactive gases evolved during the dissolution of neutron-irradiated samples of uranium carbides. A Teflon-and-glass sampling system was developed for the chromatography of corrosive gases. A combustion method for the determination of traces of residual carbonaceous material that remains in solution after the dissolution of metallic carbides was adapted for the analysis of nitric acid solutions.

The $KBrF_4$ procedure for the determination of oxygen in fluoride salts was modified to reduce the contribution of the blank in the determination of parts-per-million concentrations. The modified procedure was also applied to determine oxygen and nitrogen in metallic lithium. A proposed carbon-reduction method for oxygen is being evaluated by comparison with the $KBrF_4$ procedure.

A modified amalgamation method was found to give precise results in the determination of parts-per-million concentrations of oxygen in potassium. Standard-addition tests to establish the accuracy of the procedure are in progress. A highly sensitive method based on separation by amalgamation and final determination of hydrogen by gas chromatography was developed for the determination of hydrides in alkali metals and NaK. The method has also been applied to the determination of reactive metals in salts.

6. Effects of Radiation on Analytical Methods

The effect of gamma radiation on the colorimetric determination of chromium with 1,5-diphenylcarbohydrazide was studied. Levels of gamma radiation <1000 r were found to cause little error in the method.

The effect of gamma radiation on ethylenediaminetetraacetic acid was also studied. It is destroyed to the extent of $\sim 1 \times 10^{-9}$ mmole per ml of EDTA solution per roentgen.

A study was initiated of the effects of gamma radiation on the thiocyanate–stannous chloride spectrophotometric method for the determination of molybdenum. Effects of gamma radiation on Mo^{6+} and thiocyanate ions in aqueous solutions were measured.

A pyrolytic graphite electrode, which offers considerable promise for applications to radioactive solutions, has been found suitable as an indicator electrode for acid-base and redox titrations and in the voltammetric determination of various metallic ions.

7. X-Ray and Spectrochemical Analyses

Techniques were developed for performing quantitative local microanalysis with the x-ray fluorescence microprobe when known standard alloys are not available. The technique was applied to superconducting zirconium-niobium alloys and other specimens. A computer code (IBM 7090) was written to calculate best-fitting parameters for the determination of a given element by x-ray absorption-edge analysis. A second code was written to use these parameters to calculate the chemical concentration of the element in any sample. An absorption tube was built to be used with a Beckman burner in atomic absorption analysis. This tube gives superior performance in the detection of mercury. The demountable hollow cathode was found to be an inexpensive and versatile light source for determining Pb, Zn, Cd, Ni, and Mg by this method. Fluorine as CF_4 was detected at the 10-ppm level in helium by use of the hollow cathode. A procedure was developed for collecting cesium at the 10^{-10}-g/ml level from water, or at the 10^{-7}-g/g level from solids, and determining the cesium by flame photometry. The cesium content of the U.S. Geological Survey granite G-1 was measured. The accuracy of Quantometric determinations of trace elements in human-tissue ash was checked by independent methods of analysis and was found to be satisfactory. The scope of analysis was extended to bone ash. Losses of trace elements during the ashing process (at 450°C) were found to be less than 20% for elements not known to be volatile. A 21-ft Wadsworth-mount spectrograph was converted for the direct spectrometric determination of oxygen in metals and salts. Oxygen can be determined in steels in ~ 5 min.

The variability of the Baird direct reader—computer system was determined statistically over its entire working range. The relative standard error at the 95% confidence level was less than ±0.5% for the overall system.

Varying the concentrations of several elements was found to have no effect on the ratio of the intensities of several rare-earth metals to the intensity of strontium.

A dc-arc method was developed for determining Ta/Nb ratios in mixtures of tantalum oxides and niobium oxides.

8. Mass Spectrometry

New methods of sampling gaseous samples were developed and used. More laboratory space has become available.

9. Optical and Electron Microscopy

Investigation of methods for the study of radioactive materials by electron microscopy has continued. Cellulose acetate butyrate is promising as a film former for studies of this nature. Use of a modified ion-counter apparatus for direct collection of radioactive particulates of millimicron particle size is being studied. Instrumentation for vaporizing carbon and metals was improved. Research assistance in both microscopy and thin-film work was given to other divisions of the Laboratory.

10. Nuclear and Radiochemical Analyses

Properties of dialkyl phosphorodithioic acids were studied in several extraction systems. The solvent-extraction behavior of metal di-*n*-butyl phosphorodithioates and the use of di-*n*-butyl phosphorothioic acid as a metal-ion extractant were investigated. Tetraphenylarsonium chloride was used as an extractant for fluo-anions. The valence states of five ORNL radioisotope products were determined. A method was developed for separating selenium from tellurium by solvent extraction. The separation and determination of americium in solutions that contained transuranium elements was demonstrated. Radioisotopes have been applied in a radiotracer method for fluoride (Ta^{182}), in methods for the alkaline-earth elements (Ca^{47}, Sr^{85}, and Ba^{133}), in a gamma-neutron method for beryllium (Sb^{124}), and in determination of the surface areas of UO_2 and CaF_2 (U^{237} and Ca^{45}). Work has continued on identification of radioactivities in the ORR pressurized water loop. The decay scheme of Au^{199}, isomer formation and separation in tellurium isotopes, and properties of nuclear levels in odd-A nuclei were studied. Three proposed new radioisotope products, K^{43}, Br^{77}, and I^{123}, were examined. Electronic stripping and computer techniques have been applied to gamma-ray spectrometry. Radioactive gases were determined by conventional gamma-ray spectrometry, and a high-level system was used for hot reactor loop studies. In addition, a number of special irradiated reactor materials (fused salt, graphite, and Zircaloy-2) were studied by gamma-ray spectrometry.

A 150-kv Cockcroft-Walton neutron generator was installed and used for a number of purposes, including the determination of oxygen. Eight Am^{241}(0.6 g)–Be(6 g) sources were fabricated and used for rapid soil and metals analyses. A number of special samples were analyzed for particle-size distribution.

Neutron-activation methods were evaluated for interferences such as high-cross-section contaminants. Methods have been developed for the comprehensive activation analysis of beryllium and aluminum matrices for as many as 67 elements. Backflow-prevention systems and the flow of water through turbines were studied by addition of stable isotopes and later use of activation analysis for determination. Activation methods for sulfur in a number of materials, including a flux-monitoring system using CS_2, were developed. Delayed-neutron counting for U^{235} was applied to samples in which the U^{235} content ranged from 10 to 10^4 μg per gram of uranium. The $Li^6(n,\alpha)t$ and $O^{16}(t,n)F^{18}$ reactions were used to determine oxygen in fused salts. The radioisotope Pa^{231} and a number of stable trace elements were determined in radioactive materials. A method for arsenic was developed using activation and radiochemical techniques. Neutron activation was used for survey and identification purposes with a large variety of materials. Included in the studies have been auto paints, soil, soot, narcotics, drugs, containers and other materials used in the pharmaceutical industry, opium, writing inks, carbon-paper print, typewriter-ribbon inks, barbitals, and meperidine hydrochlorides. Applications to oceanography were also studied. The thermal and resonance neutron fluxes in the ORR were measured by use of cobalt-aluminum and gold-aluminum foils. Neutron fluxes were also measured by use of activation induced into irradiated stainless steel. Development of a glass-loaded liquid scintillator has continued, the solvent being 1-methylnaphthalene.

11. Inorganic Preparations

The preparation of fused salts for the Chemistry Division and, to a lesser extent, for the Metals and Ceramics Division has occupied a major portion of the time. The problems connected with the preparation of iodides were solved.

The work for the Physics Division was concerned almost exclusively with the preparation of alloys of the rare-earth metals and with the behavior of hydrogen toward the palladium-iron system and toward such metals as chromium and nickel.

In the program for the preparation of high-purity K_2O for the Metals and Ceramics Division, moderate success was achieved, and the preparation of the analogous oxides of some of the other alkali metals was undertaken. High-purity MgO was prepared for the Solid State Division, and a preliminary preparation of high-purity TiO_2 was completed.

The study of the chemistry of rhenium was resumed with the aim of producing some of the lower fluorides of this element.

12. Organic Preparations

A number of special organic compounds that are not available commercially were synthesized on request from other research divisions. Among these compounds were arsenazo III (a new reagent for the spectrophotometric determination of thorium), *n*-hexylbenzene, and *n*-heptylbenzene.

The following compounds were purified for use in special applications: diphenyl ether, diphenylcarbohydrazide, tetramethylammonium hydroxide, 1-methylnaphthalene, 1,4-dioxane, and di(2-ethylhexyl)phosphoric acid.

PART II. ANALYTICAL DEVELOPMENT

13. Ionic Analyses

A more rapid method for the determination of thorium in granite was developed. Arsenazo III was synthesized and evaluated as a chromogenic reagent for the determination of thorium.

The amperometric EDTA titration method for the determination of thorium was modified for use in a hot cell.

Several highly radioactive refractory materials were dissolved by use of ammonium bifluoride fusions. For the determination of lithium in beryllium oxide, perchloric acid was found to be the most suitable dissolution reagent.

The use of the gas chromatograph for the determination of < 10 ppm of carbon in high-purity steels was studied. The Leco apparatus was used to determine carbon in NaK. The sodium phenoxide spectrophotometric method was used to determine nitrogen in NaK.

A continuous amperometric titration method for the determination of zirconium was developed for use in a hot cell.

Acetone and pyridine were found to be suitable solvents for the nonaqueous titration of phenols.

The studies on the disposal of radioactive wastes in natural salt have continued in cooperation with the Health Physics Division. It was found that salt samples when heated to 260 to 300°C fracture and release steam. Quantitative measurements are in progress.

14. Infrared Studies

The application of infrared spectrometry to analytical problems increased markedly. Unknown organic compounds were identified by functional groups, and changes in structure due to radiation damage and/or chelation were studied. Some infrared spectral studies were made on potassium pertechnetate, potassium permanganate, and potassium perrhenate. Lithium fluoride crystals were examined for the presence of hydroxyl groups.

PART III. SERVICE ANALYSES

15. Quality Control

The Statistical Quality Control Program was extended. Permissible limits of variation were reduced and the number of blind standards was increased for some methods. Some 3800 control tests were made.

16. Low-Level Radiochemical Laboratory

The Low-Level Radiochemical Laboratory performed some 4300 analyses, primarily for the Health Physics Division; the types of analyses have not changed.

17. Mass Spectrometric Analyses

The Mass Spectrometric Analyses Laboratory reported over 27,000 results from some 3300 samples. About a third of these samples were the separated stable isotopes of 42 elements.

18. Spectrochemical Analyses Laboratory

The Spectrochemical Analyses Laboratory analyzed more than 1800 samples, many of them from the Isotopes Division. The stable isotopes of some 34 elements were determined. Mixed oxides of tantalum and niobium, mollusk shells, and beryllium metal and its compounds were analyzed.

19. Process Analyses

The High-Level Alpha Radiation Laboratory has determined small amounts of Am^{241} in the presence of large amounts of Cm^{242} by chemical separation and by alpha-pulse-height analysis with excellent agreement between the two methods. Controlled-potential coulometry was used to determine the oxidation states of plutonium and the extent of plutonium polymerization in solutions.

The General Analyses Laboratory has put the following new methods into service: chemical determination of Co, free carbon, NO_2^-, Mg, Ge, and Al. Procedures for the determination of carbon and NO_3^- and the apparatuses for the measurement of surface area and yield stress were modified. A Leco Oxygen Determinator and equipment for determining pore-size distribution were installed.

The General Hot Analyses Laboratory adapted several new methods of analysis to remotely controlled operations: determination of thorium and aluminum by EDTA titrations, attrition rates of irradiated ThO_2 pellets, and melting points of salt samples from the Fluoride Volatility Process. Evaluation of methods and equipment for the analysis of MSRE fuel samples was started in a hot cell mock-up. Some techniques of handling the salt remotely and some equipment were tested.

The Materials Testing Laboratory continued to analyze metal oxides, fused fluoride salts, granite, and concrete, as well as samples derived from liquid-extraction processes and waste-disposal tests.

The Vapor Fractometer was altered to give a more complete gas analysis.

The Radioisotopes-Radiochemistry Laboratory has put into use a liquid scintillation counter and a low-background beta proportional counter. A paper on the determination of radioyttrium and radiopromethium was published; one on the chlorostannate method for radiocesium and another on the use of solid-state detectors in radiochemistry were presented at the Fourteenth Southeastern Regional Meeting of the American Chemical Society. Methods were developed for the following special applications: determination of Pr^{231} in U^{232}; determination of Tc^{99} by neutron activation; rapid determinations of specific activities; and measurement of neutron-moderating effects by paraffin in the ORNL Graphite Reactor. The construction of the hot cells in Building 3038 was completed, and the cells are now in operation.

The High-Radiation-Level Analytical Facility has evaluated various manipulator booting materials. Improvements in containment and revision of operating practices for moving radioactive materials in and out of the cells have decreased the possibility of exposures to operating personnel.

Construction of the new High-Level Analytical Laboratory was begun and should be completed by November 1964.

Work is continuing on design of cells and equipment to be used in the Transuranium Program.

20. Reactor Engineering Service Laboratory

The Reactor Engineering Service Laboratory analyzed more than 4300 samples. These were from the Reactor, Reactor Chemistry, and Chemical Technology Divisions. The types of samples and analyses made varied considerably.

21. Gas-Cooled Reactor Project

The Gas-Cooled Reactor Project reported some 3000 results, mostly from gas chromatographic analyses.

PART IV. ORNL MASTER ANALYTICAL MANUAL

22. ORNL Master Analytical Manual

The fourth supplement to the reprinted form of the *ORNL Master Analytical Manual* was made available for public sale. Twenty-eight new methods and one revised method were issued. The Table of Contents of the *Manual* was revised.

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PART I. ANALYTICAL RESEARCH

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PART IV. ORNL MASTER ANALYTICAL MANUAL

Part I. Analytical Research

Research in a variety of fields of analytical chemistry was conducted during the past year for the Reactor, Physical Research, and Isotopes Development Divisions of the Atomic Energy Commission. Research was also conducted for the various research divisions of the Oak Ridge National Laboratory on specific problems related particularly to the programs of the Laboratory.

The progress in these investigations is presented in the following sections.

1. Analytical Instrumentation

M. T. Kelley
D. J. Fisher

EVALUATION OF DIRECT-READOUT CIRCUITS FOR THE ORNL MODEL Q-2005 CONTROLLED-POTENTIAL COULOMETRIC TITRATOR

R. W. Stelzner

The direct-readout circuit modifications[1] of the ORNL model Q-2005 controlled-potential coulometric titrator[2] were evaluated statistically for use in analyzing solutions of Cu^{2+}, Ni^{2+}, and $UO_2{}^{2+}$. The results are given in Table 1.1. The data were obtained with the readout circuits calibrated for 100 mv $\approx$ 1 mg. Most of the analyses were performed by the General Analyses Laboratory of the ORNL Analytical Chemistry Division.

MODIFICATIONS OF THE ORNL MODEL Q-2005 COULOMETRIC TITRATOR FOR SPECIALIZED PURPOSES

H. C. Jones R. W. Stelzner

Modifications of the basic design of the ORNL model Q-2005 controlled-potential coulometric titrator[2] were made to improve the performance for titrations involving low- and high-resistance electrochemical cells and to provide for automatic switching of anodic or cathodic currents.

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[1] R. W. Stelzner, "Direct-Readout Modification of the ORNL Model Q-2005 Coulometric Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, p 4.

[2] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Electronic Controlled-Potential Coulometric Titrator," *Anal. Chem.* 31, 488, 956 (1959).

Table 1.1. Results of Statistical Evaluation of Direct-Readout Circuits for the ORNL Model Q-2005 Controlled-Potential Coulometric Titrator

Ion Determined	N	$\bar{X}$ (mg)	Relative Standard Error (%)[a]
UO_2^{2+}	10	6.193	0.05
	10	11.169	0.06
Cu^{2+}	8	0.566	0.12
	19	1.430	0.22
Ni^{2+}	10	1.946	0.87

[a] At the 95% confidence level.

Low-Resistance Cells ($R_{cell} \approx$ 1 to 10 ohms)

The current capability of the Q-2005 titrator was increased by the addition of a class A driver transistor stage, an auxiliary power supply of ±20 v for the driver, a high-wattage dual-transistor power amplifier to replace the 2N375 transistor, and a heavy-duty power supply. A USA-3 operational amplifier furnishes the signal to the class A driver transistor for electronic control of the cell potential. The amplifier remains connected as indicated in the original Q-2005 drawings. Type 2N458A germanium power transistors are used for the driver and power stages; the transistors of the power stages are mounted in heat sinks with cooling provided by blowers.

Cell currents as large as 3 amp are available at controlled potential. For an electrochemical cell in which the cathodic reaction involved the electrodeposition of copper at a controlled potential of −0.50 v vs the S.C.E., the cell current was initially 1 amp and decreased exponentially to a steady-state value. The USA-3 and the transistorized control circuit maintained the desired controlled potential at the cathode throughout the reaction.

The high currents that flow in the cell require the use of low-ohmic wire for connections in order to minimize the IR drop. (A 1-ft length of No. 20 wire, connected from the 1-ohm integrating resistor to the cell and carrying a current of 3 amp, can produce an error of 30 mv.) The IR error in the controlled-potential loop can be eliminated completely by connecting a fourth wire from the controlled electrode of the three-electrode cell to terminal 9 of the USA-3 amplifier.

A coulometric titrator based on this design is being constructed at Vanderbilt University by L. C. Hall.

High-Resistance Cells ($R_{cell} \approx$ 10 kilohms)

For titrations (or synthesis of organic chemicals) involving electrochemical cells having resistances of the order of 10 kilohms, the performance of the ORNL model Q-2005 titrator can be improved through elimination of the type 2N375 transistor power amplifier and direct use of the output of the USA-3 control amplifier. The USA-3 must be connected in such a way that negative current feedback through the cell is achieved. Approximately ±8 ma at a potential of ±100 v is available from the USA-3 control amplifier.

Automatic Switching of Anodic or Cathodic Currents

When the ORNL model Q-2005 coulometric titrator is used for oxidations, switching circuitry in the control amplifier and in the transistor power amplifier is required. The switching can be performed automatically through the use of switching transistors formed by a complementary-pair (one NPN and one PNP transistor) emitter follower. A class A driver transistor is connected between the output of the USA-3 control amplifier and the emitter follower. The NPN and PNP power transistors are alternatively conducting or cutoff depending on the signal furnished by the dc-coupled class A driver stage. Anodic or cathodic current can flow through the cell without any need for the manual switching required in the original version of the coulometric titrator.

HIGH-SENSITIVITY COULOMETRIC TITRATOR

H. C. Jones D. J. Fisher W. D. Shults

A high-sensitivity controlled-potential (or constant-current) coulometric titrator has been designed and fabricated for use in the titration of small quantities of substances. The maximum electrical sensitivity of this instrument is 500 times that of the ORNL model Q-2005 titrator[2] and is 10 times that of the ORNL model Q-2005-X50 titrator.[3] This titrator uses three GAP/R USA-3 operational amplifiers and one GAP/R R-100B power supply. One amplifier is used to maintain the controlled electrode at ground potential and, by means of various feedback resistors, to furnish a proper input signal for another amplifier that is connected as a time integrator. The remaining amplifier is used to force the counter electrode to such a potential that, by current feedback through the chemical cell, the potential of the controlled electrode with respect to a reference electrode is the desired value. This system of control is essentially the same as that described by Booman[4] and was selected for this application because it is simple and uses unmodified amplifiers. This instrument is similar in many respects to other models described previously[2,3,5] but has higher sensitivity and does not contain circuitry for unneeded current amplification. Also, it has an improved control-potential supply, built-in calibration resistors, and constant-current-output capability. The maximum cell current available is approximately ±8 ma. Four ranges of sensitivity are provided by means of various feedback resistors that can be switched across the amplifier used to maintain the controlled electrode at ground potential. For full output of the integrating amplifier, the upper limits of these ranges are 1, 10, 50, and 100 μeq of the substance being titrated. A recorder output is provided to make possible better interpretation of the output at high sensitivities and easier correction for background.

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[3] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Electronic Controlled-Potential Coulometric Titrator for Plutonium Analysis," *Talanta* **6**, 185 (1960).

[4] G. L. Booman, "Instrument for Controlled Potential Electrolysis and Precision Coulometric Integration," *Anal. Chem.* **29**, 213 (1957).

[5] M. T. Kelley, D. J. Fisher, and H. C. Jones, "Automatic, Electronic, Controlled-Potential Coulometric Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1958*, ORNL-2662, pp 13–14.

Automatic current cutoff is provided, and the meter is protected on all current ranges. This titrator is now being used by the Ionic Analyses Group and is performing very satisfactorily.

The circuit diagram of the instrument has been drawn, and a paper is being prepared that will describe both the instrument and its performance.

REVISIONS OF INSTRUCTIONS FOR FABRICATION AND MAINTENANCE OF INSTRUMENTS

H. C. Jones W. L. Maddox D. J. Fisher

ORNL Models Q-2005 and Q-2005-X50 Automatic, Electronic, Controlled-Potential Coulometric Titrators

Notes that give detailed instructions regarding the construction of the Q-2005 and Q-2005-X50 titrators were added to drawing Q-2005-1-R1, which is now designated Q-2005-1-R2. No changes in the circuitry were made. The check-out and test procedure, ST-172, was revised November 9, 1962, to add a test to prove the ability of the integrator to hold its charge and to add trouble-shooting information. The method that describes the calibration, use, and maintenance of these titrators (*ORNL Master Analytical Manual* Method Nos. 1 003029 and 9 003029) was revised (December 31, 1962) in order to add new information.

ORNL Model Q-1165 Fluorophotometer

Because of the replacement by the manufacturer of a developmental tube with the type 6199 multiplier phototube, pp 1 and 2 of drawing Q-1165-10-R2 were revised to provide for the difference in the physical dimensions of the tubes. The drawing is now designated Q-1165-10-R3.

ORNL Models Q-1457 and Q-1887 Flame Spectrophotometers

The wattage and voltage ratings of certain components in the power supplies of the ORNL models Q-1457 and Q-1887 flame spectrophotometers were increased to improve the reliability of the instruments. Drawing Q-1457-1 was revised from -R3 to -R4, and drawing Q-1887-1 was revised from -R1 to -R2.

ORNL Model Q-1734 Remotely Operated Filter Photometer

The following drawings were revised to clarify the instructions regarding the construction and dimensions of certain component parts of the Q-1734 remotely operated filter photometer and to specify black anodized aluminum instead of black Bakelite as the material of fabrication: ORNL-LR-DWG Nos. 13584A; 13584A-Part 1, -Part 2, and -Part 3. Each of these drawings is now designated -R1.

ORNL Model Q-1988A Controlled-Potential and Derivative Polarograph

The designations of the brand and type of several capacitors to be used in the construction of the ORNL Q-1988A polarograph were changed because those originally specified are no longer manufactured. Drawing Q-1988A-1-R0 was revised to Q-1988A-1-R1, drawing Q-1988a-2-R0 was revised to Q-1988A-2-R1; the parts list, Q-1988A-5, was revised accordingly. No changes were made in the circuit.

SAFETY DEVICE FOR AUTOMATIC PREVENTION OF DAMAGE TO VACUUM-FUSION APPARATUS BY UNSCHEDULED LINE POWER INTERRUPTIONS OR FAILURES

D. J. Fisher

Unscheduled interruptions or failures in line power cause severe damage to an unprotected high-vacuum system of the vacuum-fusion apparatus[6] because air surges through the stalled forepump into the hot oil in the diffusion pump. As a result, carbonized decomposition products are thrown into the glass high-vacuum system. The start-up of the new emergency power-generating system is too slow to prevent this damage. Each of three of these apparatus is now automatically protected from this hazard by means of a safety device that consists of a normally closed, Veeco type SV62, solenoid-operated, high-vacuum valve and a Cramer type 412E (control arrangement C, W.D. 1123) time-delay relay. The valve is a quick-acting, low-leakage, high-conductance valve; it is located between the forepump and the diffusion pump. When the power comes on again, the valve remains closed until the forepump attains running speed and pumps down, after which the valve reopens. This arrangement was tested and proved by H. G. Davis (General Analyses Laboratory). Since this safety arrangement was devised and installed in June 1962, the three vacuum-fusion apparatus have been automatically and successfully protected during several unscheduled power interruptions.

JIG FOR PRECISELY SAMPLING A GRAPHITE BAR

H. C. Jones

A sample-cutting jig was designed and built for use in the study of the diffusion of uranium into graphite bars. A dial indicator that has a full travel of 1 in. is fastened to a small vise in such a way that a graphite bar, clamped in the vise, can be moved a precisely measured distance in order that samples of a specific size can be cut off in succession. A file, used to remove samples from the end of the graphite bar, is clamped in a rectangular holder. The holder is machined to hold the file perpendicular to the longer dimension of the bar. A small machined block is used to support the part of the bar that protrudes from the jaws of the vise and thus to prevent breakage of the bar. The jig is now being used satisfactorily by the General Analyses Laboratory.

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[6] W. R. Laing and H. G. Davis, "Hydrogen, Nitrogen, and Oxygen in Metals, Vacuum-Fusion Method," Method Nos. 1 213793, 1 215693, and 1 215893 (7-2-58), *ORNL Master Analytical Manual*; TID-7015, suppl 1.

HIGH-SENSITIVITY, DIRECT-READING, LINEAR, RECORDING CONDUCTIVITY TITRATOR

T. R. Mueller R. W. Stelzner

A high-sensitivity, direct-reading, linear, recording conductivity titrator is being developed. The basic design criteria were reported earlier.[7]

New Design Features

The design now includes two additional features: a temperature-compensating circuit and a circuit that increases the sensitivity of the instrument by compensating for the initial conductance of the solution.

The temperature-compensating circuit introduces a linear correction for temperature changes during a titration by computing the conductance at 25°C from the measured conductance. A thermistor is used as the temperature-sensing element. The circuit is effective between +15 and +60°C.

Use of a circuit that compensates for the initial conductance of the solution increases the sensitivity of the instrument about a hundred fold compared with the normal sensitivity of 90% of full scale for one decade change in solution resistance. With this addition, it is possible to obtain full-scale readings of less than 10 milliohms on solutions having an initial resistance of 1 ohm. For optimum performance, the compensated initial conductance must be greater than 2×10^{-3} mho. It is necessary to thermostat the cell to within ±0.02°C if the maximum error is to be as small as ±1%.

Accuracy

Electrical check-out indicates that the design goals of a maximum error of ±1% and linearity of readout voltage vs conductance within ±0.1% have been achieved. Accuracy was also checked roughly by comparing measurements made with the titrator and with a Serfass Bridge (Industrial Instruments Model RCM 15B1) on KCl solutions (platinized-platinum electrodes; cell constant, 0.1 cm^{-1}). The range of conductance over which the comparison was made was limited by the inability to obtain a balance on the bridge. The conductances, in micromhos, were as follows:

Bridge	Titrator	Bridge	Titrator
12 to 13	12.50	2.98×10^4	2.99×10^4
203	202.8	4.50×10^4	4.48×10^4
1.59×10^3	$1.59_7 \times 10^3$	$6.3_5 \times 10^4$	6.36×10^4
2.05×10^3	$2.06_7 \times 10^3$	$9.8_2 \times 10^4$	9.89×10^4
3.27×10^3	$3.26_7 \times 10^3$	$1.7_2 \times 10^5$	1.72×10^5
7.38×10^3	7.41×10^3	2.25×10^5	$2.25_5 \times 10^5$
1.15×10^4	1.15×10^4	$4.5–4.7 \times 10^5$	4.63×10^5
1.70×10^4	1.70×10^4		

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[7] T. R. Mueller and R. W. Stelzner, "Automatic, Recording Conductometric Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, p 5.

An error of + 1.3% (with reference to the literature value) was obtained for a measurement of conductance of a solution of 0.01 *N* HCl prepared from Fisher Scientific Company standard 0.1000 *N* HCl by dilution with distilled water from the service tap. A comparison was also made on the basis of the results of actual titrations. The free acid in uranium–nitric acid samples was titrated. The results on 200- and 250-μl aliquots were within 0.5 and 0.8%, respectively, of those obtained by potentiometric titration.

Precision

The precision attainable in a conductometric titration depends on the shape of the titration curve. Good precision is possible with the well-defined curve obtained for the titration of HCl with NaOH. Therefore, this titration was used to evaluate the performance of the titrator. Five samples, each of which contained 1 meq of HCl in 250 ml of water, were titrated with 1 *N* NaOH. Titrant delivery rate was about 0.25 ml/min. The five results, expressed as time required to reach the end point, ranged from 240.0 to 241.3 sec.

These experiments were exploratory only. Following the completion of the construction and electrical check-out of the instrument, its capabilities for practical analyses will be studied more extensively.

DIRECT-READING SPECTROPHOTOMETER FOR DETERMINATION OF BERYLLIUM

H. C. Jones D. J. Fisher

A direct-reading spectrophotometer for measuring the intensity in the first or second order of the beryllium arc line at 3130 A was designed and fabricated to meet the requirements defined by C. Feldman of the ORNL Spectrochemical Analyses Group. An ORNL model Q-1210 high-voltage power supply furnishes power for an RCA 1P28 multiplier phototube. The output of the phototube is amplified by a GAP/R USA-3 operational amplifier used as either an inverting amplifier or a time integrator. Background compensation is furnished by Zener-regulated power obtained from a GAP/R R-100A power supply. The output from the GAP/R USA-3 operational amplifier is fed through a voltage divider to a 5-mv Brown recorder. The electronics of the instrument appear to be performing satisfactorily. The instrument will be checked out more thoroughly by the Spectrochemical Analyses Group when the proper monochromator (or grating for the monochromator) has been selected.

IMPEDANCE TRANSFORMATION BY USE OF AN OPERATIONAL AMPLIFIER

H. C. Jones R. W. Stelzner D. J. Fisher M. T. Kelley

A GAP/R USA-3 operational amplifier, together with a GAP/R R-100A power supply, was used as an impedance-transforming device between a multiplier phototube and an unmodified, 1-mv, 1-sec Brown recorder that has an input impedance of approximately 25 kilohms. It was requested that a 2-sec Brown recorder that had been in use with an ORNL model Q-1457A flame spectrophotometer be replaced by a 1-sec Brown recorder, because it was desired to record more accurately the output of the instrument while scanning more rapidly through the wavelength region of interest. The input circuit of the 2-sec Brown recorder had been modified[8] for high-input impedance in order that a 5-megohm resistor could be used to measure the multiplier-phototube current. It was considered more practical with the 1-sec recorder to use, instead, an operational amplifier for impedance transformation. The latter method is best for recorders with a span much less than 50 mv or a pen speed much faster than 12 sec.

The amplifier was used in a current-amplifier configuration with a 10-megohm input (measuring) resistor, a 100-kilohm output resistor, and a 100-ohm feedback resistor. A 20-v output is produced by an approximately 0.002-μa input. The output is fed to the recorder through a voltage divider in such a way that the recorder input is connected across a 5-ohm resistor. A small variable capacitor (7 to 45 $\mu\mu$f) is connected from input to output of the amplifier in order to prevent oscillation and to provide an adjustment for damping. The system maintained a recorder pen response of about 1 sec per full-scale travel and, at the same time, held the noise level of the amplifier output to less than 0.5% of full scale on the recorder. This system is performing satisfactorily and is being used by the Spectrochemical Analyses Group.

MODEL VI FLAME SPECTROPHOTOMETER

H. C. Jones

A John Fluke model 412A regulated high-voltage power supply has been incorporated into a single-beam flame spectrophotometer, designated model VI. The power supply has an output of 500 to 2010 v at 0 to 15 ma. This power supply is used to replace the series string of voltage-regulator tubes used in the ORNL model Q-1887 flame spectrophotometer.[8] A 5-megohm current-measuring resistor is used. Variable damping is provided by shunt capacitors and a rotary switch. A 10-mv Brown recorder, modified for high input impedance, is used as a readout device. Flame background compensation is supplied by a Zener-diode-regulated power supply. The instrument is designed for use with an appropriate monochromator and flame source. A holder was designed and built for the International Telephone and Telegraph Company FW-118 multiplier phototube for use with this instrument. Other tubes provided include the RCA type 6217. The instrument is now being used by the Spectrochemical Analyses Group and is performing satisfactorily.

APPARATUS AND INSTRUMENTS FOR REMOTELY CONTROLLED ANALYSIS OF RADIOACTIVE SAMPLES

W. L. Maddox H. C. Jones D. J. Fisher

Remotely Operated Filter Photometers

A sensing unit (ORNL photographs Nos. 59013 and 59014) for the ORNL Model Q-1734 remotely operated filter photometer was fabricated recently according to the ORNL-LR-DWG 13584A-R1 series of drawings. It is to be used in the MSRE Hot-Cell Mock-Up. This unit differs from the previous units[9] in that it is constructed from aluminum that has an electrolytic, nonreflecting, black finish rather than from black Bakelite. The design of the filter photometer is being revised to provide for interchangeable

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[8] M. T. Kelley, D. J. Fisher, and H. C. Jones, "High-Sensitivity, Recording, Scanning Flame Spectrophotometer," *Anal. Chem.* **31**, 178 (1959).

[9] M. T. Kelley *et al.*, "Remotely Operated Filter Photometer," *Anal. Chem.* **30**, 1711 (1958).

Densichron probe units and to simplify the construction of future models intended for use in the High-Radiation-Level Analytical Laboratory.

Absorption-Cell Attachment for a Welch Densichron Reflection Unit

The absorption-cell attachment for a Welch Densichron reflection unit[10,11] was redesigned slightly. The reflection head is now enclosed in a Lucite box that is fastened together with machine screws. The reflection head rests on its side to allow the power cable to protrude at one end of the box. A 0.5-in.-thick Bakelite spacer is inserted between the Lucite box and the absorption-cell attachment. Use of this block makes possible the easy remotely controlled removal of the Beckman absorption cell by means of manipulators. Sketches were made for use in the fabrication of the Lucite box and Bakelite spacer. The instrument was provided for use in the Radioisotopes-Radiochemistry Laboratory.

Remotely Operated Decapper-Pipetter Assembly

A new decapper-pipetter assembly (ORNL photographs Nos. 58916, 58917, and 58918) was designed; the prototype was fabricated and is being used in the 3038 Hot Laboratory. The apparatus is built around the ORNL model E-19550 screw-operated elevator, which has been in use for several years.[12] A station for decapping (or capping) the sample bottle and two stations for delivering test portions from the sample are located on a turntable, which can be rotated about the vertical axis of the elevator by means of the manipulator hands. A mechanical stop is provided to ensure that each vessel occupying a station is properly aligned beneath the pipet.

The decapper has a novel clamp (ORNL photographs Nos. 58234, 58235, and 58236) whose jaws will adjust themselves to produce an increasing amount of tension on the sample bottle as the clamp is rotated. The decapper has been described.[13] A Research Equipment Company "Remote Pipetter" and an attachment for its remotely controlled replacement complete the assembly. This pipetter has an added plunger-travel-limit switch (ORNL photograph No. P-55017).

Copper Capsules for Mixer/Mill

Samples from the MSRE are received as frozen salt mixtures in small copper "ladles." The equipment for the remotely controlled preparation of these samples for analysis was developed cooperatively with M. J. Gaitanis.[14] The sample must be broken free of the ladle, pulverized, mixed, and transferred to a polyethylene sample bottle. These operations are done remotely with the aid of copper capsules that have

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[10] H. C. Jones and D. J. Fisher, "Absorption-Cell Attachment for a Welch Densichron Reflection Unit," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 4.

[11] F. J. Miller and H. C. Jones, "Absorption Cell Attachment for a Welch Densichron Reflection Unit," *Anal. Chem.* **33**, 651 (1961).

[12] L. G. Stang, Jr. (ed), "Screw-Operated Elevator," p 236 in *Hot Laboratory Equipment*, 2d ed., Technical Information Service, Washington, D.C., 1958.

[13] W. L. Maddox, "Remote Decapper," p 335 in *Proceedings of the 10th Conference on Hot Laboratories and Equipment*, Washington, D.C., November 1962.

[14] MSRE Hot-Cell Mock-Up.

been designed for use with the Spex Industries old style model 8000 Mixer/Mill. The copper capsules replace plastic or steel capsules that are ordinarily used with the Mixer/Mill and also provide for the transfer of the pulverized sample to the separate container. The ladle serves the same purpose as do the balls ordinarily used in the Mixer/Mill. Two of the Mixer/Mills have been acquired, and a number of the capsules have been fabricated in ORNL Research Shop A according to preliminary sketches and ORNL-LR-DWG 71678.

Results of the initial "cold" testing program indicate that the capsules are a satisfactory means of accomplishing the necessary operations.[15]

Remotely Operated Apparatus for Opening MSRE Sample-Transfer Tube

MSRE samples are shipped from the reactor site to the analytical laboratory in a sample-transfer tube, which is transported inside a lead-lined cask. The tube is a $1\frac{1}{3}$-in.-diam, 19-in.-long cylinder that weighs about 7 lb and is made in two sections that screw together. A prototype device for remotely removing the sample from the tube is being constructed. Basically, this device is a decapping machine that can bear the weight of the sample-transfer tube. The tube is suspended vertically from a chuck that is rotated by a gearmotor. The sample-containing lower section (plug) is prevented from rotating but is allowed to slide vertically in a second chuck until the threads that join the sections of the tube are released. The chuck that holds the plug section is then slid down a supporting rod until the sample-containing ladle can be lifted out.

AC CONTROLLED-POTENTIAL POLAROGRAPHY

R. W. Stelzner

Continued development in ac polarography has been along the lines of circuit improvement with increased emphasis on transistorized design. The circuit performance of the control amplifier was improved through the introduction of control voltages by means of an analog computer mixer. Transistorized chopper circuits are effective for high-amplitude ac signals but give difficulty for relatively low-amplitude signals; a wide-frequency-range chopper at low levels remains a problem.

Because of uncertainties engendered by instrumentation problems, no further work has been done on ac harmonic polarography.

SENSITIVITY OF DC POLAROGRAPHIC AND VOLTAMMETRIC ANALYSIS OBTAINED WITH VARIOUS MERCURY CATHODES

W. L. Belew D. J. Fisher M. T. Kelley

A study was made of the sensitivity of dc polarographic and voltammetric analysis obtained with various mercury cathodes relative to that obtained with unmodified D.M.E.'s. The cathodes studied were

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[15] M. J. Gaitanis, C. E. Lamb, and L. T. Corbin, "A Pulverizer-Mixer for Solidified Molten Salt Reactor Fuel Samples," p 333 in *Proceedings of the 10th Conference on Hot Laboratories and Equipment*, Washington, D.C., November 1962.

the mercury pool with quiet and stirred solutions and modified D.M.E.'s. The ORNL model Q-1988-ES polarograph[16,17] was used. The sensitivity obtained with each electrode was determined from first-derivative polarograms of 1×10^{-6} *M* solutions of Cd^{2+} in 0.1 *M* KCl.

The sensitivity of polarography and voltammetry with mercury cathodes is limited by the signal-to-noise ratio attained with the cathode, that is, the ratio of the diffusion current plus its variations to the residual current plus its variations. Not only the relative amount of noise associated with a given electrode but also the extent of reproducibility from electrode to electrode is important in practice. When use is made of a sensitive polarograph, such as the Q-1988-ES in which the lowest current range is 0.005 μa for full-scale recorder displacement, the magnitude of the small diffusion currents at low concentrations is not the factor that limits sensitivity. Cooke, Kelley, and Fisher[18] and Hume[19] concluded that the principal limitation with a D.M.E. is the extent of noise present in the cell current. The physical characteristics of the capillary orifice affect the noise level. For example, a capillary with an orifice of small diameter, such as a drawn-out "2–5 sec" Sargent D.M.E. capillary, has less noise than one of larger orifice diameter, and thus its use results in higher sensitivity. This conclusion was verified by comparing the performance of standard Sargent capillaries with different orifice diameters. In general, the noise level of Sargent capillaries of smaller orifice ("6–12 sec") is lower than that of capillaries of larger orifice ("2–5 sec").

Many other modifications of the D.M.E. have been described in the literature. An attempt was made to increase polarographic sensitivity by use of some of these modifications.

Siliconed Capillaries

It was anticipated that a siliconed capillary bore would be water-repellent and thus might prevent aqueous solutions from entering the capillary orifice just after the fall of each drop. This behavior of the solution is a source of D.M.E. noise.[18] Four capillaries whose bores had been siliconed (Atlas-Werke AG, Bremen, Germany; stock No. K-2a; drop time, 2 to 4 sec; length, 175 mm) were tested; only two were satisfactory.

The sensitivity obtained with the two capillaries was approximately the same as that obtained with a "2–5 sec" Sargent capillary. After one of the capillaries was used for several weeks, residual currents became high, and the drop times became erratic. Microscopic examination of the capillary showed that the silicone coating in the capillary bore had failed and was partially plugging the orifice. It was concluded, therefore, that the use of siliconed capillaries of this type does not increase polarographic sensitivity.

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[16] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," *Anal. Chem.* 31, 1475 (1959).

[17] M. T. Kelley, D. J. Fisher, and H. C. Jones, "Controlled-Potential Polarographic Polarizing Unit with Electronic Scan and Linear Residual Current Compensation," *Anal. Chem.* **32**, 1262 (1960).

[18] W. D. Cooke, M. T. Kelley, and D. J. Fisher, "Capillary Behavior in High Sensitivity Polarography," *Anal. Chem.* **33**, 1209 (1961).

[19] D. M. Hume, "Polarographic Theory, Instrumentation, and Methodology," *Anal. Chem.* **34**, 173R (1962).

Bulb-Type Capillaries

Barker[20] has described a capillary with a bulb near the orifice; he states that such a capillary reduces noise and improves the detection limit in square-wave polarography. An attempt was made to modify a Sargent capillary in this manner. Two bulb capillaries were made, but both produced sharp electrical pulses and were useless for polarographic analysis. It was verified that these pulses were not introduced by the performance of the circuitry of the polarograph. No further attempts were made to fabricate a satisfactory electrode of this type.

Several capillaries of the type suggested by Cozzi and Desideri[21] were made. This type capillary has a bulb in the center and drawn-out tips at each end; it is difficult to make. Two of the capillaries made had suitable drop times. The sensitivity achieved with them was approximately the same as that obtained with a Sargent "2–5 sec" capillary. This type capillary therefore offers no sensitivity advantage over a Sargent capillary.

Controlled-Drop-Time Capillaries

It was thought that control of the drop time might lower the noise level. Lockwood[22] has described an apparatus for obtaining constant drop times by dislodging the mercury drop with a sudden, but small, horizontal movement of the capillary at various constant controlled time intervals. Such an apparatus was built and was used with Sargent capillaries and with the siliconed capillaries discussed above. Drop times less than about 0.5 sec gave lower sensitivity because the diffusion currents were smaller. At drop times between 0.5 sec and that of the undisturbed capillary, the sensitivity was not significantly different from that obtainable when drops fall freely from a Sargent D.M.E. capillary.

Vertical-Orifice Capillaries

Smoler[23] and Kalvoda and Smoler[24] have described a "horizontal D.M.E.," the capillary of which has a vertical orifice. The capillary is made by bending a standard polarographic D.M.E. to an angle of 90° and cutting off the end near the bend. Several capillaries of this type were made from Sargent "2–5 sec" D.M.E.'s and were tested for sensitivity. With these capillaries, precise drop times as short as 0.5 sec can be obtained with normal mercury flow rates. The polarograms obtained at 0.5 sec drop time show no evidence of maxima of the second kind and are very reproducible. The useful sensitivity is as good as that obtained

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[20] G. C. Barker, "Square Wave Polarography and Some Related Techniques," *Anal. Chim. Acta* **18**, 118 (1958).

[21] D. Cozzi and P. G. Desideri, "Polarographic Diffusion Currents and the Internal Shape of Capillaries," (Translated), *Contributi teorici e Sperimentali di Polarografia*, Vol IV; suppl. to *Ricerca Sci.* **29**, 162–71 (1959).

[22] W. H. Lockwood, *A Device for the Synchronisation of Two Dropping Mercury Electrodes*, AERE-R-3521 (December 1960).

[23] I. Smoler, "A New Form of Dropping Mercury Electrode," (Translated), *Collection Czechoslov. Chem. Communs.* **19**, 238 (1954).

[24] R. Kalvoda and I. Smoler, "The Possibility of Rapid Recording of Polarographic Curves," *Ind. Lab.* (*USSR*) (*English Trans.*) **27**, 560 (1961).

with Sargent "6–12 sec" D.M.E.'s. The possibility of extending the sensitivity obtained with a vertical-orifice capillary by means of fast scan rates and second-derivative polarography is being investigated.

Mercury-Pool Electrodes

The sensitivity achieved by use of a mercury-pool electrode with a stirred solution was determined. Apparatus and conditions similar to those described by Rosie and Cooke[25] were used. The diffusion current obtained was 1000 times greater than that obtained with a Sargent D.M.E.; this result agrees with results reported by Rosie and Cooke.[25] However, the magnitude and variation of the residual current were also much larger. Similar results were obtained with a quiet solution except that the diffusion current increased by a smaller factor. The sensitivity of the mercury-pool electrode with quiet or stirred solutions does not appear to be higher than that obtained with a Sargent capillary when a high-sensitivity polarograph is used.

Preconcentration of certain ions at a hanging-mercury-drop electrode prior to a voltammetric stripping step might, however, increase the sensitivity relative to that obtainable directly on the original solution.

CONTROLLED-POTENTIAL DC POLAROGRAPHY WITH A RAPIDLY DROPPING MERCURY ELECTRODE

W. L. Belew D. J. Fisher M. T. Kelley

The conditions necessary for obtaining average-current regular and first-derivative dc polarograms of theoretical form by means of the ORNL model Q-1988-ES polarograph and a D.M.E. of ~5 sec drop time have been discussed.[26] When the drop time of the D.M.E. is 4 to 5 sec, it is necessary to use a quadruple, parallel-T, RC filter having a fundamental section that rejects a frequency of 0.2 cps in order to average the current oscillations from the D.M.E. At scan rates faster than approximately 20 mv/min (depending on the value of the electron change, n), the time lag in the filter begins to cause time lag in the recorded polarogram. In quantitative analysis, especially with a resolved wave, the time lag is not deleterious. However, slow scan rates are necessary, although inconvenient, if one wishes to obtain maximum resolution of two closely adjacent waves or to determine reversibility, diffusion control, value of n for the reaction, or an accurate value for $E_{1/2}$. The possibility was studied of using a rapidly dropping mercury electrode (R.A.D.M.E.) to circumvent this problem. By means of such an electrode, circuitry having small time constants could be used – and thus fast scan rates – without causing distortion of wave form due to time lag.

The types of R.A.D.M.E.'s described by Lockwood,[22] by Smoler,[23] and by Kalvoda and Smoler[24] were used; both of these are discussed above. In order to make advantageous the use of R.A.D.M.E.'s with the

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[25] D. J. Rosie and W. D. Cooke, "Polarography with a Mercury Pool Cathode in Stirred Solutions," *Anal. Chem.* **27**, 1360 (1955).

[26] W. L. Belew, D. J. Fisher, and M. T. Kelley, "Quantitative Derivative Polarography," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 8–10.

ORNL model Q-1988-ES polarograph,[27–29] it was modified as follows: a dual parallel-T, RC filter that has two voltage followers and a fundamental section whose rejection frequency is 2 cps was built and added to the polarograph; certain time constants in the derivative circuit were reduced to one-tenth their original value; the gain of the inverter amplifier was made adjustable to reduce the height of a derivative peak by factors of 25 and 250; suitable resistors were installed in the scan-integrator circuit to provide additional scan rates of 300, 1500, and 3000 mv/min; and a fast-response X-Y recorder (1 sec per full-scale displacement) was substituted for the recorder originally used. With the modified Q-1988-ES polarograph, studies were made of the relative sensitivity and reproducibility attainable with the two types of R.A.D.M.E.'s and of the effect of scan rate on the form of the polarographic waves. Polarograms of 10^{-6} and 10^{-5} *M* solutions of Cd^{2+} were made with each electrode. The behaviors of the two types of R.A.D.M.E. electrodes were not significantly different. Of the two electrodes, the Smoler electrode is the simpler and more practical means of obtaining drop times as short as 0.5 sec.

The shift in $E_{1/2}$ value and the form of the first-derivative wave were used as criteria for determining, as a function of scan rate, the time lag in the dual parallel-T, RC filter and modified derivative circuits. The necessary data were obtained at various scan rates from polarograms of Tl^{+}, Cd^{2+}, $UO_2{}^{2+}$, and In^{3+}, each of which undergoes a simple, reversible, diffusion-controlled reaction. At a scan rate of 300 mv/min, the polarograms are of theoretical form and the $E_{1/2}$ values are shifted less than 5 mv in the direction of scan. Because of the time lag in the dual averaging filter at a scan rate of 1500 mv/min, the form of the waves begins to deviate from the theoretical form and the $E_{1/2}$ values are shifted approximately 25 mv. At 3000 mv/min the derivative peaks (especially the second half of the peaks) are slightly unsymmetrical, and the $E_{1/2}$ values are shifted approximately 50 mv; however, the polarograms are very reproducible and should be extremely useful for quantitative analysis, particularly for resolved waves. No maxima of the second kind or other difficulties are associated with use of the Smoler type R.A.D.M.E. The sensitivities of regular and first-derivative polarography were as good as those obtainable with "6–12 sec" Sargent capillaries. Approximately 6 sec is required to record a polarogram at 3000 mv/min; the polarograms are useful for quantitative analysis and obtaining high sensitivity. At 300 mv/min, approximately 60 sec is required to record a polarogram, which shows waves at maximum resolution and of form fixed by the electrochemical reaction.

SECOND-DERIVATIVE, CONTROLLED-POTENTIAL, DC POLAROGRAPHY

W. L. Belew D. J. Fisher M. T. Kelley

The significant gain in resolution and sensitivity of first-derivative polarography over regular polarography indicates that second-derivative polarography may also be useful. The utility of second-derivative, controlled-potential dc polarography is therefore being investigated.

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[27] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," *Anal. Chem.* **31**, 1475 (1959).

[28] M. T. Kelley, D. J. Fisher, and H. C. Jones, "Controlled-Potential Polarographic Polarizing Unit with Electronic Scan and Linear Residual Current Compensation," *Anal. Chem.* **32**, 1262 (1960).

[29] W. D. Cooke, M. T. Kelley, and D. J. Fisher, "Capillary Behavior in High Sensitivity Polarography," *Anal. Chem.* **33**, 1209 (1961).

An equation was derived that expresses the form of the second-derivative wave for a simple, reversible, diffusion-controlled process as a function of diffusion current, n, scan rate, and effective potential of the D.M.E. with respect to the reference electrode. The equation and theoretical form of the polarogram are shown in Fig. 1.1, where percent of maximum value as ordinate is plotted against $(E_{1/2} - E)$ in volts.

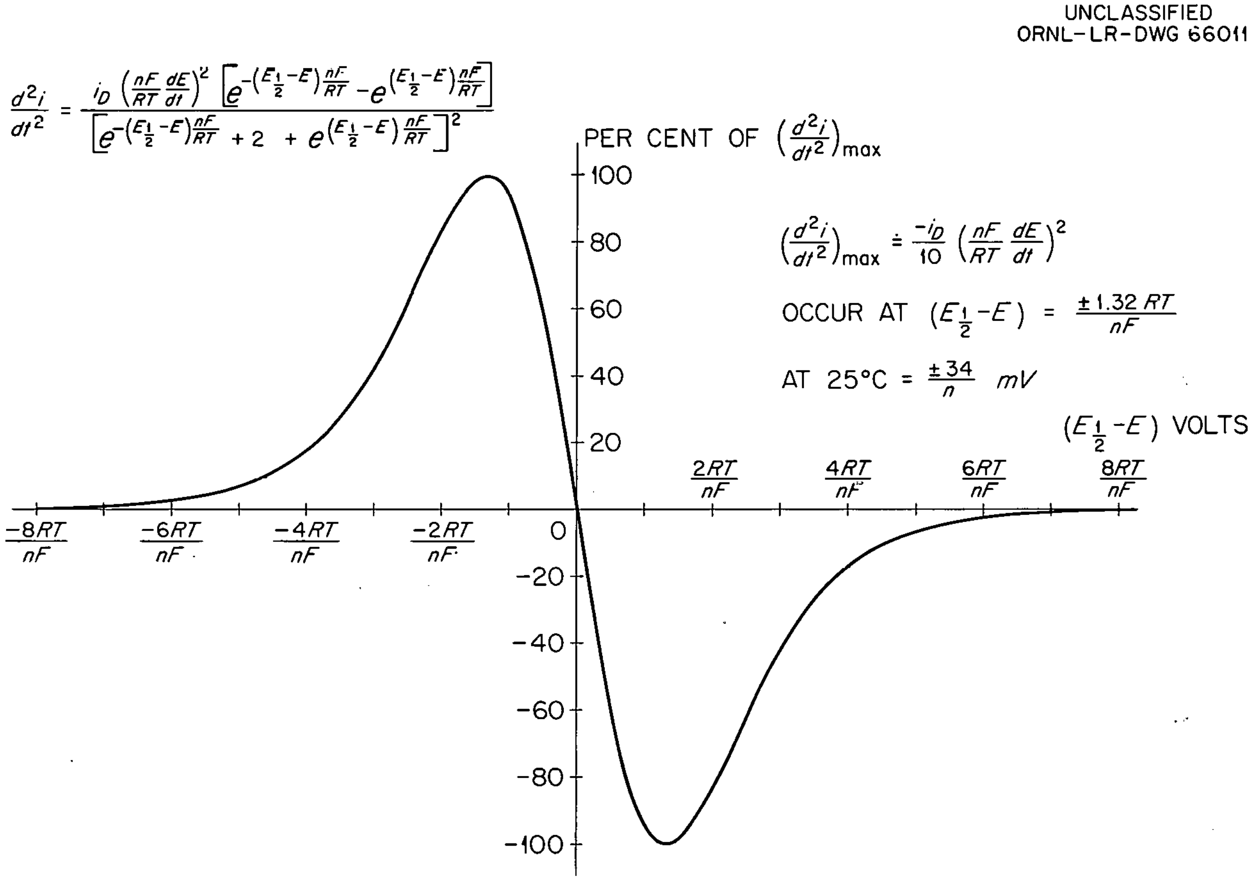

Fig. 1.1. Theoretical Form of a Second-Derivative Polarographic Wave (Simple, Reversible, Diffusion-Controlled Process).

The potential gain in resolution of second-derivative polarography was investigated by plotting regular and first- and second-derivative polarograms. The polarograms were computed for the following conditions by means of the appropriate form of the fundamental equation of the polarographic wave: n of each of the two reactions equals 2, two overlapping waves of equal height, and the second wave overlapping the first wave to the extent that the increase in height of the first wave is 1%. Under the last-mentioned condition, the separations between the $E_{1/2}$ values of the two waves are 118, 77, and 72 mv for regular, first-derivative, and second-derivative polarograms, respectively. The gain in resolution is large from regular to first-derivative polarograms but is small from first- to second-derivative polarograms.

Thus, as a method of obtaining better resolution of polarographic waves – particularly over a reasonable range of concentration ratios – second-derivative polarography does not appear to be greatly superior to first-derivative polarography.

The equation in Fig. 1.1 predicts that the peak height for second-derivative waves will depend on the square of the scan rate. This prediction suggests that at fast scan rates, second-derivative polarography may be a sensitive method of measuring low concentrations.

Second-derivative polarograms have been obtained experimentally with the Q-1988-ES polarograph.[27,28] A derivative computer was built and placed in series with the first-derivative computer in the polarograph in order to obtain second-derivative polarograms. At a drop time of ~4 sec and a scan rate of 100 mv/min, the sensitivity was low for second-derivative polarograms compared with that for first-derivative polarograms because of the high level of noise. When an R.A.D.M.E. ($t \sim 0.5$ sec) and a rapid scan rate (e.g., 3.0 v/min) are used, the sensitivity of second-derivative polarography appears to be at least equal to that of first-derivative polarography. The evaluation of second-derivative polarography as a method of obtaining high sensitivity will be continued.

THIRD-DERIVATIVE, CONTROLLED-POTENTIAL, DC POLAROGRAPHY

W. L. Belew D. J. Fisher M. T. Kelley

An equation was derived for the third derivative of the average dc polarographic current with respect to time for a simple, reversible, diffusion-controlled process. The ordinate at any fixed potential of the D.M.E. with respect to the reference electrode is proportional to the diffusion current and to the third power of the scan rate and of n. Peaks of equal height occur before and after the $E_{1/2}$ value, and an inverted third peak three times larger than the other two occurs at the $E_{1/2}$ value. The results of intercomparisons of plots of the theoretical forms of regular and of first-, second-, and third-derivative polarograms indicate that there is no apparent analytical advantage to be gained from third-derivative polarography. For this reason, no experimental controlled-potential, dc, third-derivative polarograms were made.

2. Chemical Analysis of Advanced Reactor Fuels

J. C. White
P. F. Thomason

DETERMINATION OF URANIUM(VI) BY TRI-*N*-OCTYLPHOSPHINE OXIDE EXTRACTION AND COULOMETRIC TITRATION

W. D. Shults Louise B. Dunlap

A method was developed for determining U^{6+} in nuclear-fuel dissolver solutions. The U^{6+} is extracted into a cyclohexane solution of tri-*n*-octylphosphine oxide (TOPO), back-extracted, and titrated coulometrically at controlled potential. White and Ross[1] have studied the extraction behavior of many elements in the TOPO-cyclohexane system under a variety of conditions. Their data indicate that the TOPO-cyclohexane extraction should be useful for separating U^{6+} prior to its determination by controlled-potential coulometry.

The basic method consists in extracting U^{6+} from 1 *M* HNO_3 into 0.1 *M* TOPO in cyclohexane. The extraction is essentially instantaneous but generally is carried out for 3 to 5 min to ensure quantitative results. The aqueous phase is discarded; the organic phase contains U^{6+} and is essentially free of contaminants. The U^{6+} is back-extracted into 3.5 *M* $(NH_4)_2SO_4$ of pH 2. The aqueous layer is drained directly into the titration vessel, concd H_2SO_4 is added, and the solution is titrated coulometrically.[2]

This method has been used to separate U^{6+} from a variety of solutions. Synthetic solutions representative of the usual dissolver solutions were prepared to contain known amounts of U^{6+}. From each of these solutions, five to ten aliquots that contained 5 to 10 mg of uranium were analyzed for U^{6+}. The precision and accuracy of the complete determinations are indicated in Table 2.1.

The application of this method to the determination of U^{6+} in zirconium fuel solutions is being studied. The use of a solution of sodium tripolyphosphate, $Na_5P_3O_{10}$, to strip U^{6+} from the organic phase will be studied. This reagent should be particularly useful for samples in which the U:Mo weight ratio is less than 10:1 because molybdenum is not a serious interference.

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[1] J. C. White and W. J. Ross, *Separations by Solvent Extraction with Tri-n-Octylphosphine Oxide*, NAS-NS-3102 (Feb.8, 1961).

[2] W. D. Shults, "Uranium, Automatic Controlled-Potential Coulometric Tritration Method," Method Nos. 1 219225 and 9 00719225 (1-29-60), *ORNL Master Analytical Manual*; TID- 7015, suppl 3.

Table 2.1. Precision and Accuracy of Results of Determination of U^{6+} in Synthetic Dissolver Solutions

Related Reactor	Dissolver Solution Components			Results	
	Identity	*M*	~mg/ml	S (%)	U^{6+} Recovered (%)
(Standard solution)	UO_2SO_4	0.03	7	0.1	100.0
Foreign Research	U^{6+}	0.03	7	0.1	100.1
	Al^{+3}	1.5			
	Hg^{2+}	0.01			
	HNO_3	1.3			
Army Package Power	U^{6+}	0.02	5	0.1	100.1
	Cr^{6+}				
	Fe^{3+}	0.0			
	Ni^{2+}				
	HCl	1.3			
	HNO_3	3			
N.S. "Savannah"	U^{6+}	0.55	130	0.1	99.9
	HCl	1.7			
	HNO_3	1.5			
	S. steel	1.4			
Consolidated Edison	U^{6+}	0.06	15	0.2	100.2
	Al^{3+}	0.1			
	Th^{4+}	1.0			
	F^-	0.04			
	HNO_3	8.8			
Consumers Public Power	U^{6+}	0.63	150	0.2	99.8
	Mo^{6+}	0.01			
	HNO_3	4			
Fermi	U^{6+}	1	240	0.2	99.7
	Fe^{3+}	0.5			
	Mo^{6+}	0.07			
	HNO_3	3.7			
Experimental fuel	U^{6+}	0.02	5	0.2	99.7
	Nb^{5+}	0.04			
	HNO_3	5			

CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF URANIUM(IV) AND URANIUM(VI) IN SODIUM TRIPOLYPHOSPHATE MEDIUM

H. E. Zittel   Louise B. Dunlap

A sample can be analyzed for both U^{4+} and U^{6+} by controlled-potential coulometric titration. The oxidation and reduction reactions both take place at a mercury-pool electrode in 6 w/v % $Na_5P_3O_{10}$ solution of pH 7.5 to 9.5. The U^{6+} is reduced coulometrically at a potential of -1.35 v vs the S.C.E. This reduction is a direct measure of the U^{6+} present. The same test solution is then oxidized coulometrically at +0. 10 v vs the S.C.E. This oxidation measures the total uranium present; the U^{4+} content is found by difference.

The precision and accuracy of the method were determined on solutions that contained various amounts of both U^{4+} and U^{6+} (Table 2.2). The method is as accurate as the best chemical methods for determining U^{4+}, U^{6+}, and total uranium; it is accurate to within ±0.5% in the range from 2 to 10 mg of total uranium. The precision of the method decreases for small amounts of both U^{4+} and U^{6+}.

Table 2.2. Accuracy and Precision of Coulometric Titration of U^{4+} and U^{6+} in $Na_5P_3O_{10}$ Medium

Number of Samples Analyzed	U^{4+} Added (mg)	U^{4+} Found (mg)	U^{4+} S (%)	U^{6+} Added (mg)	U^{6+} Found (mg)	U^{6+} S (%)	Total Uranium Added (mg)	Total Uranium Found (mg)	Total Uranium S (%)
8	0.72	0.71	2.0	1.78	1.78	0.8	2.50	2.50	0.4
6	1.09	1.10	1.2	2.78	2.79	0.4	3.87	3.88	0.5
7	1.15	1.16	1.7	2.90	2.90	0.7	4.05	4.06	0.7
9	3.16	3.18	0.7	6.78	6.76	0.3	9.94	9.94	0.1
9	4.46	4.44	0.4	0.04	0.05	2.0	4.50	4.49	0.4

Uranium-containing samples may contain traces of other elements introduced during burnup of uranium reactor fuels. Also, various solvents may be required during the dissolution of such samples. Therefore, the effects of some potential interferences were checked. The cations studied were Cr^{3+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Th^{4+}, and Zr^{4+}. Only Cu^{2+} and Fe^{3+} interfere significantly when present in low concentrations. When present in high concentrations, Th^{4+} and Zr^{4+} interfere, possibly as a result of hydrolysis. A study was also made of the effects of the anions: Cl^-, ClO_4^-, F^-, NO_3^-, and SO_4^{2-}; only NO_3^- introduces much error when present in relatively high concentrations.

Both the procedure and the instrumentation of the method are simple. The optimum total uranium content of the test portion is 2 to 10 mg. The method is both more accurate and faster than many methods now in use for the determination of both U^{4+} and U^{6+} in the same sample. An article that describes this work has been accepted for publication in *Analytical Chemistry.*

CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF URANIUM(VI) IN URANIUM-NIOBIUM ALLOYS

W. D. Shults Louise B. Dunlap

Controlled-potential coulometric titrimetry has been applied to samples that contain uranium and niobium. As a result, two methods have been developed – one in which uranium is titrated in the presence of niobium and another in which uranium is separated from niobium and is then titrated.

According to the one method, the sample test portion is fumed with H_2SO_4 to remove HNO_3 and F^- that are present as a result of the dissolution process; Nb^{5+} remains in solution in concd H_2SO_4. The solution is cooled, and oxalic acid is added to complex Nb^{5+} before the solution is diluted and transferred to the titration vessel. The U^{6+} is then titrated at a mercury cathode.[2] The relative standard deviation of this method is 0.1 to 0.2% when 5 mg of U^{6+} is titrated. The method is not signigicantly biased (Table 2.3). It can be used for the analysis of samples in which the Nb:U weight ratio is 3:1 or less.

Table 2.3. Results of the Determination of U^{6+} in Solutions That Contained Niobium and Uranium

Method	Nb^{5+} (mg)	U^{6+} (mg)		S (%)[a]
	Taken	Taken	Found	
Fuming, titration	None	5.58	5.59	0.1
	10.2	5.58	5.59	0.2
	15.3	5.58	5.59	0.2
	20.4	5.58	5.62	0.1
TOPO extraction, back-extraction, titration	None	5.58	5.57	0.2
	5.1	5.58	5.57	0.2
	30.6	5.58	5.57	0.2
	40.9	5.58	5.57	0.2
	50.1	5.58	5.54	0.5

[a] $N = 4$ to 5.

The other method consists in the separation of U^{6+} from Nb^{5+} by extraction of the U^{6+} into 0.1 *M* TOPO in cyclohexane,[1] back-extraction, and coulometric titration of U^{6+} in the back-extraction medium in the same manner and at the same potentials used for titration in the H_2SO_4 medium.[2] The relative standard deviation of this method is 0.2%, and the recovery is 99.8% when 5 mg of U^{6+} is taken (Table 2.3). This method can be used for the analysis of samples in which the Nb:U weight ratio is as high as 8:1.

A communication that describes this work has been submitted to *Analytical Chemistry*.

INSTRUMENTATION FOR THE AUTOMATIC SIMULTANEOUS MEASUREMENT OF *m, t, w,* AND DROP COUNT OF A DROPPING-MERCURY ELECTRODE

Helen P. Raaen

Instrumentation for the automatic simultaneous measurement of *m*, *t*, *w*, and drop count (*c*) of a dropping-mercury electrode (D.M.E.) was discussed in the last annual report. The instrumentation has continued to function satisfactorily and was used to obtain rapidly the capillary constants and electrocapillary curves needed to evaluate the Teflon D.M.E. being developed for polarography in media that attack glass.

In an open-literature publication,[3] the instrumentation is described in detail and data are presented which show that the accuracy and precision of measurements made with it are entirely satisfactory for polarographic work. It will continue to be used to determine automatically, simultaneously, and rapidly certain of the data needed in fundamental polarographic studies and practical polarographic analyses.

TEFLON DROPPING-MERCURY ELECTRODE FOR POLAROGRAPHY IN HYDROFLUORIC ACID AND OTHER GLASS-CORRODING MEDIA

Helen P. Raaen

A thorough study was made to determine whether the Teflon D.M.E. being developed differs in behavior from the usual glass D.M.E. and, if so, in what ways it differs. This information is needed in order to define the range of usefulness and any limitations of the Teflon D.M.E. To this end, data were taken for a Teflon D.M.E. that consists of a glass-capillary segment (orifice diameter, 70 μ; length, 20 cm) and a Teflon segment of 109-μ-diam orifice.

The capillary constants taken at zero applied potential include m, t, w, and $m^{2/3}t^{1/6}$ at five values of mercury height (h) for both the glass capillary alone (as a reference) and the same glass capillary with the Teflon segment attached (i.e., the Teflon D.M.E.). The data were taken for the following media; air, air-saturated water, nitrogen-saturated water, and nitrogen-saturated 0.1 M KCl. For the Teflon D.M.E., the same kinds of data were also taken for nitrogen-saturated 0.1 M HF. The graphical plots of each of the separate capillary constants vs h indicate that the relationships are generally the same for the Teflon D.M.E. and the glass D.M.E. However, a change in medium has much less effect for the Teflon than for the glass D.M.E. The differences in behavior appear to be caused primarily by the nonwettability of Teflon by both mercury and the test medium. This property of Teflon is very well known, and it is interesting to have obtained in this study experimental data that demonstrate it vividly, that is, $t_{\text{air}}/t_{\text{soln}}$ ratios for the glass D.M.E. that are much larger and of wider range than those for the Teflon D.M.E.

The behavior of the 109-μ-diam Teflon D.M.E. in the presence of negative applied potential was determined by obtaining electrocapillary curves (i.e., plots of t vs applied potential) of mercury in several media. The media used that do not corrode glass were: 0.1 M KCl, 1.0 M KF, 1.0 M $HClO_4$, and 1.0 M HCl. The glass-corroding media were: 0.1, 1.0, 2.0, 5.0, 10, and 28 M HF and 1.0 and 10 M NaOH. The electrocapillary curve for 0.1 M KCl served as a reference by means of which the behavior of the Teflon D.M.E. under negative applied potential was proved to be satisfactory and to be essentially the same as that of a glass D.M.E. The electrocapillary curves for the other media have not been found reported before. Those for KF, $HClO_4$, and HCl solutions were determined in order to obtain supporting information. Those for the HF solutions are of particular interest. They indicate the presence of an electrocapillary-active species in the HF solutions and thus the necessity of measuring m and t values at the same potential at which diffusion-current and diffusion-coefficient data are taken in such solutions. They also indicate the

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[3] Helen P. Raaen and H. C. Jones, "Instrumentation for the Automatic Simultaneous Measurement of m, t, w, and Drop Count of a Dropping Electrode," *Anal. Chem.* 34, 1594 (1962).

limit of negative applied potential for polarography in the HF media, which is determined by the overpotential of hydrogen and may be shifted to more positive potentials if trace amounts of platinum are present. The electrocapillary curves of the NaOH solutions show a maximum at − 0.1 to − 0.2 v vs a mercury-pool anode, as well as a second maximum at about − 0.7 v. The second maximum appeared to be associated with an impurity in the NaOH.

The patterns of drop formation (i.e., the current-voltage relationships) as a function of applied potential were recorded by means of the ORNL model Q-1988A polarograph; the patterns indicate reproducible and satisfactory drop formation. In 10 *M* NaOH, the patterns were much less pronounced than in less viscous media.

The nature of the drop formation at the Teflon D.M.E. was studied by means of high-speed motion-picture photography. Motion pictures were taken of the drop forming in air and in nitrogen-saturated water, 0.1 *M* KCl, 10 *M* NaOH, and 28 *M* HF. For the Teflon D.M.E., it cannot be assumed that during its entire life the mercury drop is spherical and the rate of volume growth uniform, but these ideal conditions seem to be more nearly met with the Teflon than with the glass D.M.E.

No erratic behavior of the 109-μ-diam Teflon D.M.E. (e.g., spraying, variation in size from drop to drop, and cessation of drop formation) has been observed during its continuous operation for almost a year. Just prior to this work, difficulty was experienced from time to time because the glass capillary segments became plugged. By means of microscopic examination, it was learned that the capillaries were becoming plugged with very fine glass particles dislodged from the rims of the capillaries. The condition of the capillaries was called to the attention of the supplier, who determined that an unauthorized deviation had been introduced in the fabrication procedure and assured that the procedure would be corrected. Evaluations of the type made for the 109-μ-diam Teflon D.M.E. will also be made for the Teflon segments of smaller diameter that have already been fabricated.

The design, fabrication, evaluation, and use of the Teflon D.M.E. are discussed in a published paper.[4] The fabrication procedure is described in detail in a topical report.[5] A research proposal has been written in which are suggested areas of both fundamental and applied research in the polarography of glass-corroding media that are opened up as a result of the development of the Teflon D.M.E.

POLAROGRAPHY IN HYDROFLUORIC ACID MEDIA

Helen P. Raaen

Polarography in hydrofluoric acid media is included in the discussion of the Teflon D.M.E. given above and in the published paper.[4]

The Teflon D.M.E. will now be used for polarographic studies of reducible substances in aqueous hydrofluoric acid media. The results of the qualitative studies, which were discussed in the last annual progress report, will be used as a guide in quantitative studies.

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[4] Helen P. Raaen, "Teflon Dropping-Mercury Electrode for Polarography in Hydrofluoric Acid and Other Glass-Corroding Media," *Anal. Chem.* 34, (1962).

[5] Helen P. Raaen, R. J. Fox, and V. E. Walker, *Fabrication and Assembly of a Teflon Dropping-Mercury Electrode,* ORNL-3344 (Nov. 31, 1962).

POLAROGRAPHY IN STRONGLY ALKALINE MEDIA

Helen P. Raaen

The potential usefulness of the Teflon D.M.E. for polarography in strongly alkaline media was demonstrated by using it to determine electrocapillary curves, current-voltage recordings, and polarograms in 1 and 10 *M* NaOH. These are discussed above and in the published paper.[4] Polarograms of Pb^{2+}, as lead acetate, were recorded as a "scouting" experiment. The reduction wave was well formed in 1 *M* NaOH and was just positive to that of the impurity in the solution. In 10 *M* NaOH, the wave had a decided maximum. It is reported that maxima of this type appear when the concentration of alkaline solutions is higher than about 0.5 *M*.[6]

It is planned to use the Teflon D.M.E. for polarographic studies of reducible substances in strongly alkaline solutions.

SPECTROPHOTOMETRIC DETERMINATION OF TECHNETIUM

F. J. Miller

A spectrophotometric method was developed for the determination of technetium. A colored complex is formed with diphenylcarbazide. The optical density of an aqueous solution of the complex may be determined, or the complex may be extracted into carbon tetrachloride and the optical density of the organic phase measured. The extraction into the organic phase can be used to minimize interferences from other ions. The relative standard deviation of the method is less than 3% for the determination of Tc^{7+} at 0.1-μg/ml concentration. The work has been accepted for publication in *Analytical Chemistry*.

DETERMINATION OF TECHNETIUM BY CONTROLLED-POTENTIAL COULOMETRIC TITRATION IN BUFFERED SODIUM TRIPOLYPHOSPHATE MEDIUM

Anne A. Terry[7] H. E. Zittel

A controlled-potential coulometric method for the determination of technetium was developed. Technetium(VII) is titrated in an acetate-buffered (pH 4.7) solution of $Na_5P_3O_{10}$ at a potential of -0.7 v vs the S.C.E. The relative standard deviation of the method is about 1% in the Tc^{7+} quantity range from 0.5 to 5 mg. Various possible interferences were studied, and procedures were found to eliminate any that occurred. The method is relatively fast and simple. A paper that describes this work was accepted for publication in *Analytical Chemistry*; it will also be presented in March at the 144th National Meeting of the American Chemical Society in Los Angeles.

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[6] G. F. Reynolds, "Polarography in Strongly Alkaline Solutions," pp 257–58 in *Progress in Polarography* (ed. by P. Zuman and I. M. Kolthoff), Interscience, New York, 1962.

[7] Research participant from Texas Woman's University, Denton, Texas.

CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF INDIUM

W. R. Mountcastle, Jr.[8] W. D. Shults P. F. Thomason

A method was developed for the determination of indium by controlled-potential coulometric titration. The method involves the coulometric reduction of In^{3+} to In(Hg) at − 0.66 v vs the S.C.E. in 1 *M* KCl–0.25 *M* HCl. The In(Hg) thus produced can also be oxidized quantitatively to In^{3+} at − 0.50 v vs the S.C.E. in the same medium. At the 5-mg level, the relative standard deviation is about 0.1% and the relative error is 0.1 to 0.2%. Reasonable amounts of Ni^{2+}, Co^{2+}, Fe^{3+}, and U^{6+} do not interfere. The polarographic reduction of In^{3+} in 1 *M* KCl–0.25 *M* HCl can also be used for the determination of submilligram amounts of In^{3+} since the i_d vs C relationship is linear over the 0.005 to 0.10-mg/ml concentration range.

A paper that describes this work was submitted for publication in *Analytical Chemistry*.

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[8] Research participant from Birmingham-Southern College, Birmingham, Alabama.

3. Analysis of Molten Salts by Electrochemical Methods

J. C. White
D. L. Manning

DETERMINATION OF ASSOCIATION CONSTANTS FOR METAL COMPLEXES IN MOLTEN-NITRATE-SALT SYSTEMS

In cooperation with the Reactor Chemistry Division, work has continued on the determination of association constants of metal complexes in molten-nitrate-salt systems. The emf method used is described in detail elsewhere.[1,2] The systems investigated and the results obtained are summarized briefly below.

The association constants K_1, K_2, and $K_{1,2}$ for the formation of AgCN, $Ag(CN)_2^-$, and Ag_2CN^+, respectively, were determined from emf measurements. The very strong association between Ag^+ and CN^- necessitated that measurements be made at extremely low concentrations. Values of K_1, K_2, and $K_{1,2}$ – expressed in mole fraction units – are, respectively, 230,000, 140,000, and 80,000 at 246°C; 220,000, 105,000, and 60,000 at 286°C; and 190,000, (50,000), and (36,000) at 326°C. The entropy of

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[1] J. Braunstein, M. Blander, and R. M. Lindgren, "The Evaluation of Thermodynamic Association Constants in Solutions with an Application to Molten Salt Solutions," *J. Am. Chem. Soc.* 84, 1529 (1962).

[2] J. Braunstein and R. M. Lindgren, "The Association of Cadmium Ion with Bromide and Iodide Ions in Molten Equimolar $NaNO_3$-KNO_3," *J. Am. Chem. Soc.* 84, 1534 (1962).

association of the ion pair involving diatomic CN^- is much more positive than is that of the association of Ag^+ with monatomic Cl^- and Br^-. This work is published in *Inorganic Chemistry.*[3]

The association constants K_1 for the formation of $PbBr^+$ and K_2 for the formation of $PbBr_2$ in equimolar molten $NaNO_3$-KNO_3 were determined and are, respectively (in mole fraction units), 250 and 125 at 240°C, 190 and 85 at 280°C, and 170 and 70 at 300°C. An increase in the KNO_3 content of the solvent causes stronger binding between Pb^+ and Br^- and thus results in an increase in the numerical values of the association constants. The temperature dependence of the association constants, within the experimental error, is predictable from calculations based on theory.[4] A paper that describes this work has been accepted for publication in *Inorganic Chemistry.*

Voltammetry of Silver(I) in Molten Sodium Nitrate–Potassium Nitrate

Voltammetry of Ag^+ in molten equimolar $NaNO_3$-KNO_3 was investigated over the temperature range from 246 to 326°C. Current-voltage curves were recorded by means of a controlled-potential polarograph and a stationary platinum microelectrode coupled with a platinum quasi-reference electrode, which was introduced by Fisher.[5] A third isolated platinum electrode served as the counter electrode. The reduction of Ag^+ to Ag^0 proceeds reversibly, and the limiting current is proportional to the concentration of Ag^+. The half-wave potential is approximately − 0.1 v vs the quasi-reference electrode. The limiting-current constant, *k*, was determined to be 1.37, 1.98, and 3.15 at 246, 286, and 326°C, respectively. The activation energy for the limiting-current process was determined to be approximately 6.4 kcal/mole. A paper that describes this work was accepted for publication in *Talanta.*

This study begins a general program of fused-salt voltammetry the objective of which is to develop apparatus and techniques suitable for work in molten-fluoride systems. The $Ag^+ \rightleftharpoons Ag^0$ reaction was selected for detailed study mainly because it was known to be reversible in molten $NaNO_3$-KNO_3. Knowledge of the behavior of the three-electrode system with respect to a redox reaction known to be reversible in a fused-salt solution is necessary before more complex reactions can be studied.

Voltammetry of Molten Fluoride Salts

An apparatus was designed and fabricated for use in conducting voltammetric studies in molten-fluoride-salt systems. The melt is contained in a graphite cell (2 in. in diameter, 4 in. long). The cell is fitted with a graphite-thimble type inner compartment, which accommodates the isolated counter electrode. A 45-ml volume of melt is convenient to handle. The depths of melt in the cell and in the isolated compartment are kept the same; electrical contact is made through the graphite thimble.

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[3] D. L. Manning and M. Blander, "Association Constants of Silver(I) and Cyanide Ions in Molten Equimolar Sodium Nitrate-Potassium Nitrate Mixtures," *Inorg. Chem.* 1, 594 (1962).

[4] M. Blander, "The Quasi-Lattice Model of Reciprocal Salt Systems. A Generalized Calculation," *J. Chem. Phys.* 34, 432 (1961).

[5] M. T. Kelley *et al.*, "Controlled-Potential and Derivative Polarography," pp 158–82 in *Advances in Polarography*, vol 1 (ed. by I. S. Longmuir), Pergamon, New York, 1960.

To maintain a vacuum or controlled atmosphere within the cell, the cell is enclosed in a quartz jacket (~ $2\frac{1}{2}$ in. in diameter, 10 in. long) which is fitted with a removable cap. In the cap are located five $\frac{3}{16}$-in.-diam Swagelok fittings, which provide access to the melt for the thermocouple, helium-inlet tube, and various electrodes. Connections to vacuum and to an inert gas are provided for by means of a three-way vacuum stopcock.

The LiF-NaF-KF (46.5-11.5-42 mole %) eutectic was chosen as the first solvent electrolyte for study because of the wide range of potential over which the melt itself is not electrolyzed. Current-voltage curves were recorded on the melt at 495°C by means of a controlled-potential polarograph and three platinum electrodes. A cathodic wave at approximately −0.5 v and an anodic wave at approximately +1.1 v vs a platinum quasi-reference electrode were noted. Because the salt was found by chemical analysis to contain 200 ppm iron and 100 ppm chromium, it is believed that these waves are due to metallic impurities.

It is proposed to eliminate these interferences by electrolysis and then to study known reducible metallic ions in the melt under controlled conditions. The reducible species will be added by anodic oxidation of the pure metal directly in the molten-fluoride salt.

4. Special Research Problems

J. C. White
P. F. Thomason

ABSORPTION SPECTROPHOTOMETRIC STUDIES OF PLUTONIUM(IV) IN AQUEOUS NITRATE MEDIA

D. A. Costanzo R. E. Biggers

The absorption spectrophotometric studies of plutonium[1-3] were continued. The purpose of these studies is to determine the kinetics of the polymerization of Pu^{4+}, the kinetics of the depolymerization of polymerized Pu^{4+}, and the properties of Pu^{4+} polymer in solutions whose acidity, temperature, and ion concentrations are representative of those encountered in fuel processing.

The kinetics of the polymerization of Pu^{4+} was studied as a function of Pu^{4+} concentration (1 to 8 mg/ml), nitric acid concentration (0.03 to 0.2 *M*), and temperature (25 to 95°C). Under these conditions,

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[1] R. E. Biggers, *Hazards and Experimental Evaluation for: Studies on the Polymerization and Hydrolysis of Plutonium in Uranyl Nitrate and Nitric Acid Solutions at Elevated Temperatures*, May 9, 1960 (unpublished report).

[2] R. E. Biggers and D. A. Costanzo, "Studies of the Polymerization, Depolymerization, and Hydrolysis of Plutonium in Uranyl Nitrate and Nitric Acid Solutions at Elevated Temperature," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 26–27.

[3] D. A. Costanzo and R. E. Biggers, "Absorption Spectrophotometric Studies of Plutonium in Solutions of $UO_2(NO_3)_2$, $Al(NO_3)_3$, and HNO_3 at Elevated Temperatures," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 20–21.

disproportionation and nitrate oxidation of the Pu^{4+} occur, and the kinetics of these reactions were determined. The effects of $UO_2(NO_3)_2$, $Al(NO_3)_3$, $NaNO_3$, and F^- on the kinetics of polymer formation were also determined at low acidity and elevated temperature. In the presence of high concentrations of any one of these nitrate salts, colloidal Pu^{4+} polymer precipitates. Solutions of Pu^{4+} in 1 to 2 *M* HNO_3 were heated to the boiling temperature and were treated with steam for as long as several hours to determine whether the resulting localized low acidity would cause polymerization of the ionic Pu^{4+}.

Plutonium(IV) polymer was "aged" by refluxing a solution of it for 24 hr to simulate polymer formation at elevated temperature. The precipitation of the "aged" colloidal Pu^{4+} polymer by nitrate-containing electrolytes (e.g., HNO_3, $Al(NO_3)_3$, $NaNO_3$, and $LiNO_3$) was studied at 25°C. The precipitation of polymer reached a maximum at 2 to 3 *M* nitrate concentration and decreased thereafter, none occurring at a nitrate concentration greater than 4 *M*. Thus, it is apparent that if the nitrate concentration of solutions of process importance is maintained above 4 *M*, any polymer that forms will not precipitate.

The kinetics of the depolymerization of freshly prepared Pu^{4+} polymer to ionic plutonium was determined at several concentrations of HNO_3 between 1 and 10 *M* as a function of temperature. The kinetics of the depolymerization reaction was observed to be first order, the order of the reaction depending only on the concentration of polymer at fixed acidity.

The rate of depolymerization of aged Pu^{4+} polymer was determined in 5 *M* HNO_3 as a function of temperature. The separate effects of F^-, of SO_4^{2-}, and of F^- and Al^{3+} in a mole ratio of 1:4 were also studied.

Preliminary results of this work were presented at the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology.[4]

PROGRAM FOR ABSORPTION SPECTROPHOTOMETRIC STUDY OF SOLUTIONS AT HIGH TEMPERATURES AND HIGH PRESSURES

R. E. Biggers

The program for the absorption spectrophotometric study of solutions at high temperatures and high pressures was discussed in a recent report;[5] a more extensive review was given earlier.[6–8] This work is being done jointly with R. G. Wymer.[9]

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[4] D. A. Costanzo and R. E. Biggers, "Studies of the Polymerization of Quadrivalent Plutonium by Spectrophotometric Means," presented at The Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962.

[5] "High-Temperature Chemistry," *Chem. Technol. Div. Ann. Progr. Rept. June 30, 1962*, ORNL-3314, pp 187–90.

[6] R. E. Biggers, "Program for Absorption Spectrophotometric Study of Solutions at High Temperatures and High Pressures," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, p 21.

[7] R. E. Biggers, "Design of a High-Temperature, High-Pressure Spectrophotometric System," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 21–22.

[8] R. E. Biggers and R. Eno, "The Design and Development of a Spectrophotometer System for Optical Measurements on Liquids at High-Temperatures and High-Pressures"; presented at the Symposium on High Temperature Solution Chemistry, 141st meeting of the American Chemical Society, Washington, D.C., Mar. 20–24, 1962; and also at the Symposium on Molecular Structure and Spectroscopy, Department of Physics and Astronomy, Ohio State University, Columbus, June 11–15, 1962. To be published.

[9] Chemical Technology Division.

Design of a High-Temperature High-Pressure Spectrophotometric System

A complete spectrophotometric system that can be operated at temperatures to at least 330°C and at pressures to at least 5000 psi with highly radioactive (alpha) solutions has been designed under subcontract for ORNL by the Applied Physics Corporation, Monrovia, California. It is anticipated that with this system it will be possible to make measurements up to near the critical point (~372°C) in both water and deuterium oxide. The general features and details of this system are discussed more fully elsewhere.[10] A schematic layout of the cell section of the high-temperature high-pressure spectrophotometer system was presented recently.[5] The principal components and special features of the system are shown in Fig. 4.1.

The Applied Physics Corporation has been delayed in completing work on the subcontract. Much of the past year was spent reviewing critically the plans and the anticipated modes of operation of the entire system, the construction bids, and some necessary redesign. Work is being done on problems relative to the construction and redesign.

A number of changes have been made in the control system. It has been necessary to make changes in the sections that control the temperature and operate the two modes of emergency shutdown. A punched-paper-tape, digitally controlled, temperature-plateau programming system has been designed to replace a

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[10] R. E. Biggers and R. G. Wymer, *Design and Development of a High-Temperature High-Pressure Spectrophotometer System: Status Report, Nov. 12, 1960 (unpublished report).*

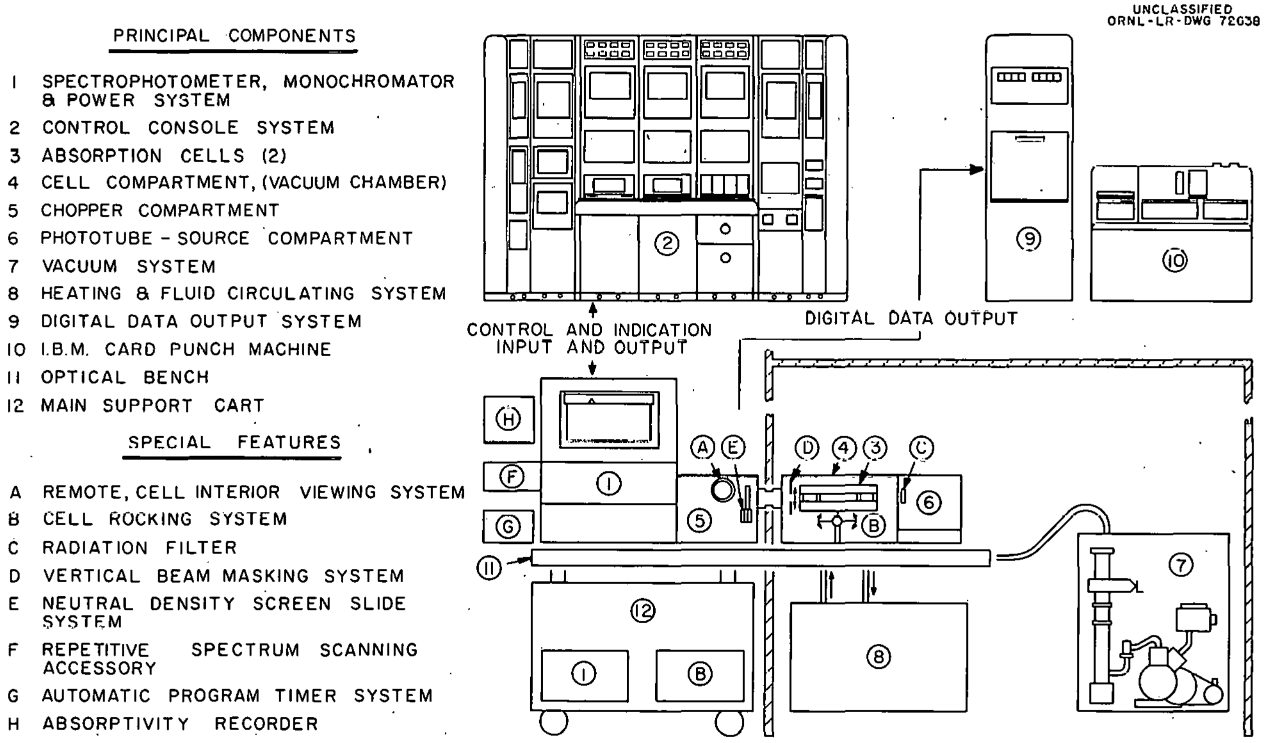

Fig. 4.1. Components of the High-Temperature High-Pressure Spectrophotometer System.

previously proposed electromechanical cam system. The control system is now designed to operate automatically on a temperature program variable with respect to number of operating temperature plateau(s) (any temperature between 25 and 375°C), duration of the plateau, rate of temperature increase or decrease between plateaus, and rate of final cool-down. The desired temperature-vs-time program (any number of hours) is entered into the system continually via a punched-tape temperature program.

The spectrophotometric system can be so synchronized with the control system that absorption spectra can be obtained automatically at any point on a temperature plateau, that is, under such conditions that the sample and the reference cells, as well as the solutions contained therein, are operating under essentially isothermal conditions. Programmed temperature shutdowns (at the rate of 2°C/min) and the modes of emergency shutdown (maximum cooling rate) can be entered automatically, if necessary, at any time during the program.

Thermal stability studies have been carried out[11] on several liquids in order to find one suitable for use as the circulating heating fluid in the thermostating of the sample and reference cell system of the high-temperature high-pressure spectrophotometer. The liquid should be capable of withstanding an elevated temperature (at least 375°C) for a number of weeks, be so cheap that it could be replaced frequently, if necessary, and flow easily at room temperature. Liquids being considered are: Arochlor 1254 (Monsanto), tetracresyl silicate, Dow Corning 550 silicone fluid, and the very recently available Dow Corning XF-1-0184 silicone fluid (450°C announced capability). Studies are being carried out both in the presence and absence of air for prolonged periods (several weeks) of heating. The results are not yet complete but do indicate that at 375°C the Dow Corning fluids are superior. The fluid will not be selected until further tests are made.

Miniature Circulating-Loop and Digital Data-Output Systems for a Cary Spectrophotometer

A new Cary model 14CMR spectrophotometer has been installed to serve as an auxiliary spectrophotometer for the forthcoming high-temperature high-pressure spectrophotometric system. With it, experiments can be carried out from below room temperature up to about 150°C in thermostated sample cells and reference cells. The spectrophotometer is equipped with a thermostated monochromator for very accurate and precise wavelength measurements. With it, spectra of systems that are to be studied in the higher-temperature machine will be surveyed.

The miniature circulating-loop system designed for use with an unmodified Cary spectrophotometer was discussed previously,[6,7] and a schematic layout of it was presented recently.[5] Problems encountered in the operation of some of its valves are being solved. A loop support system for very accurate and precise vertical support (without drift or sag) and an alignment system are being constructed for the present spectrophotometer installation.

The previously discussed[6,7] automatic, digital, data-output system for the Cary spectrophotometer has been transferred to the new spectrophotometer installation. Its performance in the new installation is very satisfactory and conforms with design specifications. A typical example of its output is shown in Fig. 4.2.

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[11] With T. G. Rogers, Chemical Technology Division summer student, 1962.

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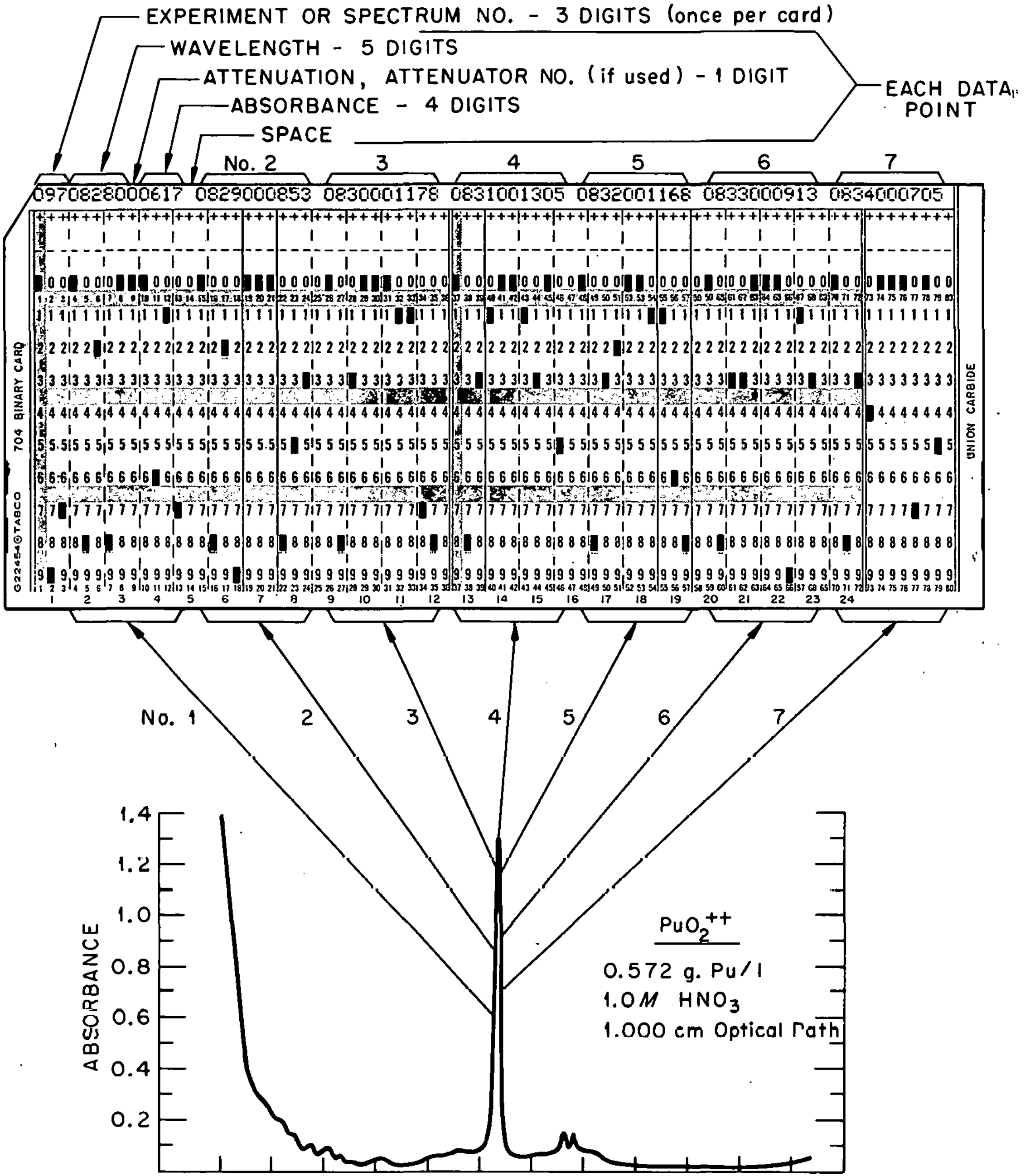

The No. of data cards obtained per spectrum is proportional to the wavelength span & sampling frequency.	Sampling Frequency ——— 1 pt/sec Wavelength Sweep Rate —— 10Å/sec Wavelength Span per Point- 10Å

Fig. 4.2. Automatic, Digital, Data-Output System: Typical Spectrum and Decimal Digitized Output – IBM Data Card Format.

Measurement of Liquid Densities at High Temperatures and High Pressures

As an important adjunct to the program of spectrophotometry of solutions at high temperatures and high pressures, a method has been devised[12] for measuring the densities of aqueous solutions at accurately measured temperatures and pressures up to the solution critical points.[11] A knowledge of solution densities is needed in order to calculate the ionic concentrations of solutions at temperatures in the range from 25°C up to the critical point (~372°C).

The liquid volume of a weighed solution of known composition is determined in an autoclave of suitable material, and an x-ray photograph is made to show the position of the vapor-liquid interface in a calibrated section of the autoclave. The density is determined from the weight of solution and the location of the interface. Recently, a prototype high-temperature autoclave for this use was designed and constructed entirely from pure titanium. A view of the disassembled autoclave is shown in Fig. 4.3. The autoclave consists of a bulb section that contains an internal thermowell, a uniform-bore expansion chamber (12 in. long), and a high-pressure closure head with a fitting that contains a 0.015-in.-ID titanium capillary, which leads to a Baldwin pressure transducer. The bulb section of the autoclave holds about 4 ml of liquid at room temperature.

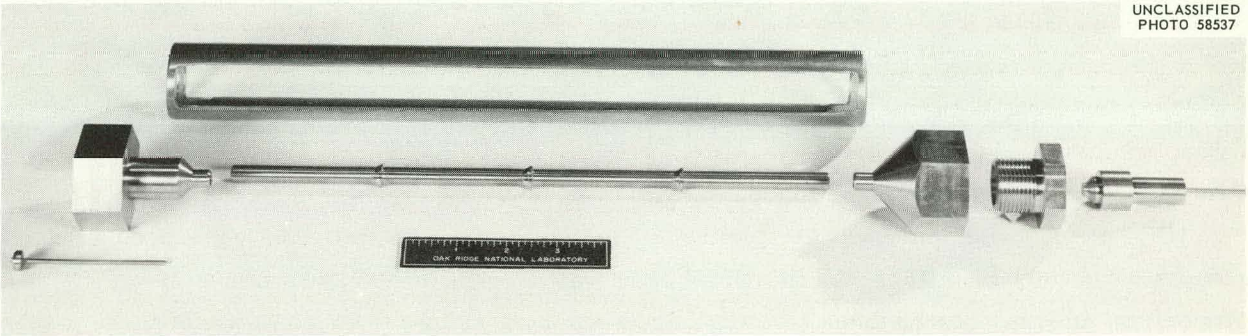

Fig. 4.3. Exploded View of the High-Temperature High-Pressure Liquid Density Autoclave.

The autoclave is designed for the operating temperatures and pressures in the region of the critical point of water and beyond. The expansion section is supported and protected by the slotted support section and has markers of a configuration to permit the x-ray measurement of the solution interface.

A special furnace and the necessary control instrumentation were designed and constructed to maintain the autoclave in an essentially isothermal state over its entire 18-in. length. The furnace is also slotted so that x-ray photographs of the unobstructed expansion chamber can be obtained easily. A motor-driven x-ray film cassette and support were also designed and constructed. The x-ray film can be driven past the slit behind the autoclave at a rate of from about 0.05 in./min up to several inches per minute. Two modes of operation are being investigated: operation at a series of isothermal temperature plateaus and operation

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[12] N. A. Krohn and R. G. Wymer, "X-Ray Method for Determining Liquid Densities at High Temperatures and Pressures," *Anal. Chem.* **34**, 121 (1962).

by a continuous and simultaneous change of film position and autoclave temperature to yield, in effect, a plot on the film of interface height vs temperature. A 300-kv Norelco x-ray system is being used with this device to obtain the necessary x-ray photographs.

SPECTROPHOTOMETRIC STUDIES OF MOLTEN-SALT SYSTEMS

J. P. Young

Spectrophotometric studies of various molten-salt systems were continued. The identification and correction of various causes of solution instability have been of major interest.

Hydrolytic Reactions

As the problems of physically maintaining a drop of corrosive molten fluoride salts in a windowless container for spectrophotometric study were solved, it became evident that the colors of many molten-fluoride salt solutions are not stable with respect to time. The instability is caused by hydrolytic reactions of the colored solutes to form the respective insoluble oxides. Uranium tetrafluoride is particularly sensitive to hydrolysis. Solutions of UF_4, each in LiF-NaF-KF (46-12-42 mole %), and of CoF_2 were used to establish the conditions necessary to maintain stable solutions of molten-fluoride salts. A vacuum-tight nickel bomb was used. It is so designed that a sample can be melted in a suitable container located in the bomb and then, when cool, be transferred to the high-temperature spectrophotometric cell assembly without being exposed to the atmosphere. Although the salts in the bomb cannot be observed, the atmosphere surrounding the sample can be controlled, even to the inclusion of a hydrofluorinating environment (e.g., $NH_4F \cdot HF$). Argon, which was used as the flush gas to maintain an inert atmosphere in the bomb, caused some hydrolysis of UF_4, even though the argon was of high purity and was dried over $Mg(ClO_4)_2$. When helium, dried by passage through a trap of liquid nitrogen, was used instead, it was possible to prepare stable solutions of UF_4 in LiF-NaF-KF in the nickel bomb. That these solutions were stable was indicated by the facts that the cooled melt was green and that there was no insoluble UO_2 in it. However, these solutions of UF_4 decomposed when they were re-melted in the cell assembly. It is believed that water vapor is adsorbed on the large surface of the insulation located inside the cell assembly and is then slowly desorbed as the cell is heated. Hydrolytic contamination was decreased significantly by making the cell assembly vacuum-tight and by evacuating the apparatus to a pressure of 20 μ at 600°C prior to the insertion of a sample, which is accomplished without exposure of the cell assembly or sample to the atmosphere. Under these conditions, solutions of CoF_2 and of UF_4 in LiF-NaF-KF maintained at 550°C for 16 hr showed only a 10% decrease in absorbance. At temperatures above 600°C, however, these solutions decolorized. This instability is believed to be the result of further desorption of water from the insulation at the higher temperatures.

The experimental conditions required for spectral study of molten-fluoride salts contribute to the ease of their hydrolysis. For such studies, a small amount of solution ($\sim$200 mg) is held in a container that is open at both ends; therefore, a relatively large area of the sample is exposed to the atmosphere of the cell assembly. Furthermore, only a small amount (usually <2 wt %) of solute is present in the molten-fluoride solvent. For these two reasons, the molten-salt solution is very sensitive to its environment.

A newly designed all-metal high-temperature cell assembly is being fabricated; it should eliminate the problem of adsorbed hydrolytic contaminants. The sample compartment will be vacuum-tight; except for the corundum windows, it will be made from nickel. Thus, the gaseous environment of the molten salt can be controlled strictly; the cell assembly will even be compatible with gaseous HF. Heat loss from the all-metal system could be a major problem. The assembly was designed to operate at temperatures up to 1100°C with the outside water-cooled walls being maintained at about 50°C. Heat loss is minimized by several means, such as vacuum insulation, judicious use of thermally reflective and absorptive surfaces, and minimization of metallic contacts between hot and cold areas. It is estimated that only about 500 w of power will be required to heat this cell assembly to its maximum temperature. This power will be supplied by tungsten heating elements of special design, which are located outside the sample compartment of the cell assembly. As was the case with the previous cell assembly, this new assembly is designed to be used with an unmodified Cary model 14M recording spectrophotometer.

Captive-Liquid Cell

A particularly significant advance has been made in the method of confining a corrosive liquid for spectrophotometric study. Liquid can be retained in a $\frac{1}{4}$-in.-OD metal cylinder, held vertically, that has a hole ($\leqq \frac{3}{16}$ in. in diameter) drilled through each side. The holes are opposite each other and are centered on a line normal to the long axis of the cylinder. Light from the spectrophotometer passes through the cell by way of these apertures (light ports). Liquid is prevented from flowing out through these ports by the presence of four to six smaller holes ($\sim \frac{1}{16}$ in. in diameter) evenly spaced about the circumference of the container and in a plane immediately above the light ports. Surface-tension effects keep the liquid level at the plane of the small holes.

The chief optical difference between the captive-liquid cell and the pendent-drop container is that the shape of the liquid in the former is that of a double convex lens, whereas in the latter the liquid forms a double concave lens. The convex-lens shape provides better transmission of light through the liquid. The spectrophotometric path length of a liquid in the captive-liquid cell is much more constant than is that of the liquid in a pendent drop. The maximum volume of liquid that can be held in the area of the light ports, as well as the total volume held in the cell, would seem to be a function of the surface tension and density of the liquid. Thus, the liquid capacity of the cell is relatively independent of the amount of liquid initially placed in the cell provided the initial liquid level is above the plane of the small orifices.

Although the absorbance of a transparent liquid in the cell has not yet been measured completely reproducibly, a series of absorbance curves obtained under seemingly identical conditions appear to be of similar shape and to represent a family of curves that are essentially independent of wavelength and of slit widths less than approximately 0.8 mm. As the slit width increases above 0.8 mm, the absorbance increases because a smaller percentage of incident light can pass through the light ports. From the evaluation of spectra of aqueous solutions of the dye sulphonated copper phthalocyanine in a captive-liquid cell, a relative standard deviation of 3% was found for the absorbance of peaks at wavelengths of 626 and 666 mμ. These data were obtained from duplicate measurements of the spectra of seven samples of the aqueous solution. The spectra of the solution were measured vs air as the reference medium, and the net absorbance of the absorption peaks was determined by subtracting the absorbance of the solvent, obtained from earlier data with water in the cell, from the absorbance of the sample at the respective wavelengths.

Based on the average absorbance obtained with this dye solution, as compared with the absorbance of the same solution in a quartz cell of 1-cm light path, the path length of an aqueous solution was calculated to be 0.68 ± 0.02 cm in a $\frac{1}{4}$-in. (0.635-cm)-OD captive-liquid cell. It is expected that path-length determinations of molten-salt solutions will be as precise; however, the measured path length will be different as a result of differences in density and surface tension.

With water in the captive-liquid cell, the ultraviolet portion of the spectrum can be scanned essentially to the wavelength limit of the instrument. The ultraviolet transmittance of molten alkali-metal fluoride salts is now being studied. Preliminary data indicate that the eutectic of LiF-NaF-KF is transparent to most of the ultraviolet region. If the ultraviolet cutoff is defined as the wavelength at which the absorbance of a liquid is 1.0, then the cutoff for the molten alkali-metal fluoride eutectic at 500°C is 210 mμ. The path length of this sample is approximately 0.65 cm. In one of the several different batches of LiF-NaF-KF studied, an absorption peak was noted at 246 mμ. It is probable that this peak is due to some metallic ion impurity in the solvent, but this contaminant has not been identified.

Both the captive-liquid-cell and the pendent-drop techniques will be useful for spectral studies of corrosive liquids. The captive-liquid cell offers the advantages outlined above, but it does require a relatively large amount of sample (~ 2 g) and does not lend itself to the variety of sample-loading techniques that can be used with the pendent drop. The captive-liquid cell could be useful in in-line instrumentation since it can be filled by flowing liquid into the cell. The captive-liquid cell might also find application in the field of Raman spectroscopy.

Spectrum of Uranium Trifluoride

One of the goals of the study of the absorption spectra of molten salts has been to obtain the spectra of U^{3+} in molten-fluoride media so that a direct spectrophotometric determination of U^{3+} in molten-fluoride salts of interest can be made. It has been most difficult to form and retain U^{3+} in molten-fluoride salts, particularly LiF-NaF-KF. In early experiments hydrolytic reactions ruled out any possibility of preparing a solution of U^{3+}. As these problems were solved, it became evident that excess HF, which seems to be present in alkali fluorides, is an excellent oxidant for U^{3+}:

$$UF_3 + HF \longrightarrow UF_4 + \tfrac{1}{2}H_2 .$$

In fact, once the adsorbed H_2O in the insulation of the cell assembly was minimized, U^{3+} could be maintained for short periods of time (before precipitating as UO_2) in molten alkali fluorides known to contain oxide contamination, whereas the U^{3+} could not be seen even during the melting of alkali fluorides known to contain contaminant HF. In the latter case, U^{4+} was formed either before or just at the time of melting; its presence was indicated by the green color of the solution.

When the concentrations of oxide and HF were decreased to reasonable levels (200 ppm oxide and an estimated 140 ppm HF) in a specially prepared melt of LiF-NaF-KF, it was possible to prepare solutions of U^{3+}. The chemistry of the reaction is not yet understood completely, but to date, the best method of preparation is to react clean uranium metal with the molten solvent, LiF-NaF-KF. A red solution is formed slowly, and the resonance absorption lines of both potassium and sodium metal can be observed in the gas phase surrounding the sample. The appearance of these lines proves that sometime during the reaction KF and NaF are being reduced to the metal. These studies have been carried out in copper rather than platinum containers. Work on this problem is continuing. The dissolution of UF_3 and the reaction of uranium metal will be studied in other molten-fluoride salts of interest.

A spectrum of UF_3 in LiF-NaF-KF is shown in Fig. 4.4; the spectrum should be considered to be tentative. Because of the problems involved in preparing the melt, the concentration of U^{3+} in the melt is not known. The spectrum is similar to the spectrum of UCl_3 in LiCl-KCl that is described by Gruen and McBeth.[13] In the fluoride melt, absorption peaks are seen at 890 (strong), 975, and 1060 mμ. At a much lower concentration of U^{3+}, the absorbance in the visible region increases as the wavelength decreases, a plateau appearing in the region from 475 to 550 mμ.

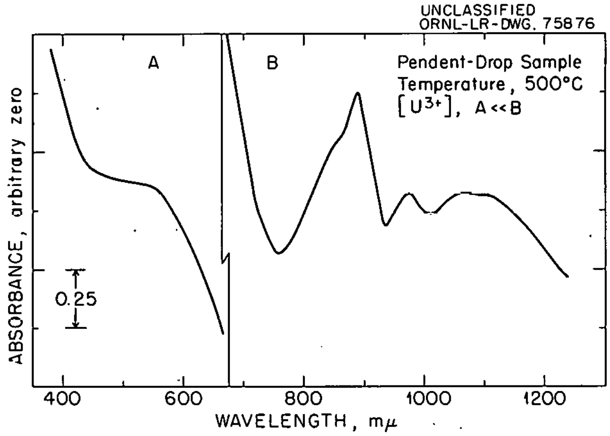

Fig. 4.4. Tentative Absorption Spectrum of U^{3+} in Molten LiF-NaF-KF (46.5-11.5-42 Mole %).

The published spectra for U^{3+} in molten LiCl-KCl exhibit more detail. Peaks occur at 885 and 995 mμ, and a broad absorption peak occurs in the region from 1040 to 1070 mμ. Strong absorption occurs in the visible region, there being peaks in the region from 460 to 550 mμ.

Studies of the Spectra of Neodymium(III)

Ever since molar absorptivities were calculated for the 582-mμ absorption peak of Nd^{3+} in various molten-fluoride media,[14] it has been of interest that these molar absorptivities were of the order of 2 compared with the value obtained by Banks and co-workers, who reported that the same peak of Nd^{3+} in molten

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[13] D. M. Gruen and R. L. McBeth, "Oxidation States and Complex Ions of Uranium in Fused Chlorides and Nitrates," *J. Inorg. and Nuclear Chem.* **9**, 290 (1959).

[14] J. P. Young, "Absorption Spectrophotometric Studies of Molten-Salt Systems," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 30–33.

LiCl-KCl at ~400° exhibited a molar absorptivity of 11.90.[15] The fluoride spectra were obtained with pendent-drop samples, whereas the chloride spectra were obtained from samples held in a 1-cm quartz cuvette. In order to demonstrate that quantitative data obtained by the pendent-drop technique, within its limit of precision of ±10%, are comparable with data obtained by the more acceptable spectrophotometric techniques, the spectrum of a pendent-drop sample of Nd^{3+} in molten LiCl-KCl at 400°C was determined. The molar absorptivity for the 582-mμ peak was calculated to be 11 for the pendent-drop sample as compared with 11.90, the value reported by Banks and co-workers. Thus, the spectrum of Nd^{3+} is shown to be very sensitive to its solution environment. Praeseodymium(III) is not sensitive to the composition of its molten-halide environment.[14,15]

The effect of slit width on the absorbance of the 582-mμ peak of Nd^{3+} in LiF-NaF-KF was also studied. The sample was held as a pendent drop, and the spectra were recorded by means of a Cary model 14M recording spectrophotometer. At slit widths less than 0.6 mm, the absorbance of the 582-mμ peak of Nd^{3+} was independent of slit width. Over the range of slit widths from 0.6 to 2.0 mm, the observed absorbance decreased by 40% because of the relatively broad wavelength band that is passed by the larger slit widths. Normally with the pendent-drop technique, slit widths of 0.3 to 0.5 mm are necessary in order to transmit sufficient light through the sample for proper operation of the spectrophotometer.

MICROCHEMICAL ANALYSIS

Lucy E. Scroggie

Because of the increasing number of very small samples submitted for analysis, sometimes less than a few milligrams or 1 ml, micro methods for volumetric analysis were studied.

Apparatus

Preparatory to micro volumetric analysis, micro volumetric apparatus, such as micropipets and Micro-Metric syringe burets, were calibrated by weighing mercury or water delivered from them and by titrating accurately standardized solutions.

Relatively simple and easily obtained equipment was used. A small, white, porcelain dish is the most useful titration vessel because it provides a good background for observing indicator color changes, its shape allows insertion of several accessories, and it has a convenient volume (1 to 2 ml). The fairly large concentrations of indicator required because of the thin layer of liquid and the large surface-to-volume ratio are disadvantages. The absorption of CO_2 causes some difficulty during the titration of a weak acid when phenolphthalein is the indicator. Placing a transparent shield over the titration dish and admitting a stream of CO_2-free gas during the titration provides an atmosphere that reduces this problem. Other special atmospheres can be provided similarly.

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[15] C. V. Banks, M. R. Heusinkveld, and J. W. O'Laughlin, "Absorption Spectra of the Lanthanides in Fused Lithium Chloride—Potassium Chloride Eutectic," *Anal. Chem.* **33**, 1235 (1961).

The glass beaker that comes with a Beckman model G pH meter was also used. It holds about 5 ml and is useful when solutions are heated prior to or during titrations.

Magnetic stirring was the most acceptable method of mixing. Special stirring bars were made by carefully sealing 0.5- to 1-cm-long pieces of steel wire in glass capillaries. Other stirrers considered were a vibrating glass thread, which was not efficient when a dish was used, and an air-driven rotating platform with a small beaker cemented to it.

A Beckman model G pH meter served as a satisfactory instrument for potentiometric titrations.

Acid-Base Titrations

Solutions of acids and base were prepared in 0.02 *N* concentrations. Sodium hydroxide was standardized against potassium acid phthalate; sulfuric and hydrochloric acids were standardized against the sodium hydroxide. Two indicators were used for the visual detection of end points: phenolphthalein and screened methyl red (2:1 methyl red–methylene blue). The screened methyl red was far superior to methyl red with respect to distinctness of end point. Its transition point (at pH about 6) prevents any noticeable effect of CO_2 absorption, the color change is very sharp, and the titration error is very small because the color transition takes place very close to neutrality. The phenolphthalein end point must be approached with care and is made indistinct by the absorption of CO_2. The drop error (i.e., the last small portion of added reagent that changes the indicator only), which is usually relatively large in microgram titrations, is measured readily by use of proper blank and control titrations. The titration error (which results when the indicator change does not occur exactly at the end point and which is a function of the sensitivity of the indicator), the initial and final volumes of the solution, and the normality of the solution titrated are reduced if small volumes of solutions of concentrations in the range from 0.02 to 0.05 *N* are used.

The precision attained in the titration of standard solutions is indicated in Tables 4.1 and 4.2.

Table 4.1. Precision of Microgram Titrimetric Standardization of Acids and Base[a]

Standard Solution		Indicator[b]	N, Number of Titrations	Test Solution		S (%)
Identity	*N*			Identity	*N* found	
KHP[c]	0.0200	Ph	8	NaOH[d]	0.02002	0.10
NaOH[d]	0.02002	Ph	6	HCl	0.01984	0.20
NaOH[d]	0.02002	Ph	6	H_2SO_4	0.01993	0.13
NaOH[d]	0.02002	SMR	5	H_2SO_4	0.01980	0.26

[a] Titration of 499.7-µl volumes of approximately 0.02 *N* solutions diluted with two pipet volumes (~1 ml) of rinse water; titrated using 0.20 or 1.00 µl-per-division calibrated syringe buret.

[b] Ph = phenolphthalein; SMR = screened methyl red.

[c] KHP = potassium acid phthalate.

[d] Titrant.

Table 4.2. Precision of Titration of Microequivalent Quantities of 0.01993 N H_2SO_4

N, Number of Titrations	Indicator[a]	H_2SO_4 Taken		H_2SO_4 Found	S (%)
		μl	μeq	μeq	
5	Ph	99.86	1.990	2.001	0.27
6	Ph	49.94	0.9953	0.9943	0.17
3	SMR	99.86	1.990	1.990	0.24
5	SMR	24.91	0.4965	0.4967	0.37

[a] Ph = phenolphthalein; SMR = screened methyl red.

Oxidation-Reduction Titrations

Several micro oxidation-reduction titrations were carried out. The ferron end point of the titration of ceric sulfate with ferrous ammonium sulfate was found visually to be less distinct than the screened methyl red end point for acid-base titrations. Since the reagents used for oxidation-reduction titrations are usually more dilute than those for acid-base titrations and since larger amounts of indicator are used, the drop error is larger. Also, special precautions must be taken in the preparation of solutions for micro oxidation-reduction titrations. A method known as derivative polarographic titration[16] was investigated and found to give sharp end points for relatively large volumes of about 0.01 N solutions but has not been applied to smaller volumes.

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[16] C. N. Reilley, W. D. Cooke, and N. H. Furman, "Derivative Polarographic Titrations," *Anal. Chem.* 23, 1223 (1951).

5. Gas-Cooled Reactor Project Analyses

J. C. White
A. S. Meyer

A portion of the research and development work of this group is reported in the progress reports of the Gas-Cooled Reactor Project.[1–4]

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[1] A. S. Meyer, Jr., C. M. Boyd, and J. E. Attrill, "Gas Chromatographic Analysis of Helium," *Gas-Cooled Reactor Program Quart. Progr. Rept. Dec. 31, 1961*, ORNL-3254, pp 252–56.

[2] A. S. Meyer, Jr., and C. M. Boyd, "Equipment for Helium Analysis," *Gas-Cooled Reactor Program Quart. Progr. Rept. Mar. 31, 1962*, ORNL-3302, pp 321–24.

[3] A. S. Meyer, Jr., and J. E. Attrill, "Analytical Procedures for the Determination of Low-Level Impurities in Helium," *Gas-Cooled Reactor Program Semiann. Progr. Rept. Sept. 30, 1962*, ORNL-3372 (to be published).

[4] A. S. Meyer, Jr., and J. E. Attrill, "Tests of a Proposed Insulating Material," *Gas-Cooled Reactor Program Quart. Progr. Rept. Sept. 30, 1962*, ORNL-3372 (to be published).

STUDY OF GAS FORMATION IN ORGANIC MODERATORS

J. E. Attrill

A gas chromatograph designed and built at ORNL by L. B. Yeatts and T. M. Gayle was adapted for the analysis of low-boiling reaction products of the pyrolysis of biphenyl, which is being studied as a reactor moderator. Initial studies made with this chromatograph were unsatisfactory because it lacked sensitivity toward certain components and because air leaked into the system causing interferences.

After the sources of leakage were checked, the instrument was equipped with a 10-ft column of silica gel coated with 3 wt % squalane, followed by a Veco thermistor-type detector. This assembly was put in series with another 10-ft column of 5A molecular sieve and a Gow-Mac detector. The flow rate of carrier gas, bridge-current settings, temperature of columns, and test-portion size were optimized. As a result, the sensitivity of detection was increased by several orders of magnitude. Low-boiling gases identified in the products from the pyrolysis of biphenyl were hydrogen, methane, carbon dioxide, carbon monoxide, ethane, propane, ethylene, and acetylene. Several other gases present in trace amounts have not yet been identified. Oxygen and nitrogen were also present as a result of leakage into the sample when it was collected.

PURIFICATION OF KRYPTON AND XENON

I. B. Rubin A. S. Meyer

An apparatus was designed and assembled for separating krypton and xenon from whatever contaminants accompany them in a sample and to collect these gases in pure form. They are adsorbed on activated charcoal in the course of tests concerning the in-pile melting of UO_2. After the noncondensable and nonadsorbable gases are evacuated from the charcoal, the remaining gases are drawn off through a purification train that consists of a tube filled with copper oxide (at 425°C), a cold trap (at −80°C), and a titanium scrubber (at 780°C). The krypton and xenon are caught in a trap (immersed in liquid nitrogen) that contains 13X molecular sieve and are then transferred to a stainless steel container of volume 40 times that of the molecular-sieve trap. The transfer is accomplished by immersing the container in liquid nitrogen and then heating the molecular-sieve trap. The last traces of krypton and xenon are desorbed and flushed from both the charcoal and molecular-sieve traps with helium. A small portion of the sample is submitted for radiochemical analysis; the remainder may be analyzed by mass spectrometry. The concentrations of krypton and xenon present have been of the order of 10^{-8} g/cc at STP each.

MODIFICATION OF PERKIN-ELMER VAPOR FRACTOMETER

I. B. Rubin

The Perkin-Elmer Vapor Fractometer has been used for the analysis of graphite off-gases.[5] However, when only a molecular-sieve column is used, one of the major constituents of the gas mixture (i.e., carbon

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[5] I. B. Rubin, "Off-Gas from Graphite, Gas Chromatographic Method," Method No. 10901 (2-12-62), *ORNL Master Analytical Manual*; TID-7015, suppl 5.

dioxide) cannot be determined. In order that the carbon dioxide may be determined along with hydrogen, oxygen, nitrogen, methane, and carbon monoxide, a parallel-column adapter (Perkin-Elmer No. 154-0359) was installed in the Vapor Fractometer. With the use of this accessory, the stream of sample gas is split into two portions, the relative sizes of which depend on the flow through a metering valve situated between the two columns. By selection of silica-gel and molecular-sieve columns of the proper length and by adjustment of the metering valve, the retention times of the various gases can be controlled well enough to effect separation and allow subsequent determination of the gases in the mixture.

A number of combinations of silica-gel and molecular-sieve columns were tested; the best combination was a 3-ft silica-gel column placed in the left ports of the adapter and a 2-m 5A molecular-sieve column (Perkin-Elmer column I) in the right ports. It was found best to leave the metering valve wide open. The operating temperature was decreased from 100 to 50°C, and the carrier flow was increased from 50 to 60 cc/min. Under these conditions the retention time of the last gas to be eluted is about 18 min; this is approximately the same time required before the parallel adapter was installed. As calculated from measurements of peak height, the sensitivity of the instrument for the various gases increased; the increase is in inverse proportion to the retention time. The sensitivities for hydrogen and oxygen increased by a factor of 1.9; for nitrogen, by 1.5; for methane, by 1.3; and for carbon monoxide, by only 1.1. The sensitivity for carbon dioxide is of the same order of magnitude as that for carbon monoxide. The relative standard deviation was about 5% for each gas. The sample sizes ranged from less than 10 to about 600 μl, except in the case of hydrogen, for which the sample sizes were between 40 and 400 μl. A representative chromatogram is shown in Fig. 5.1.

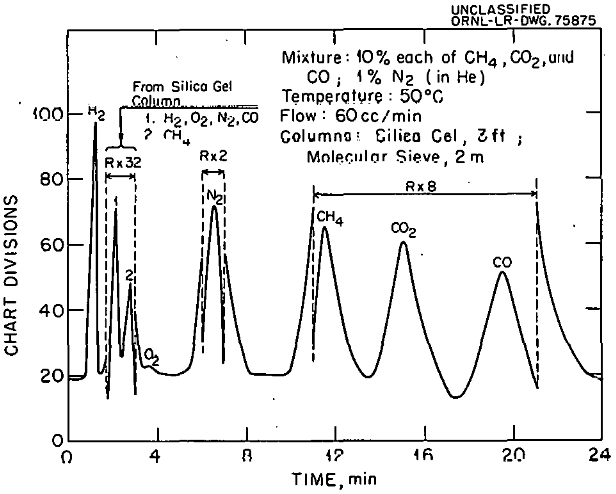

Fig. 5.1. Gas Chromatogram of Synthetic Mixture of Gases Analyzed by Means of the Parallel-Column System.

The gases that are separated on the molecular-sieve column, except hydrogen, are delayed until all the gases, except carbon dioxide, have passed through the silica-gel column. A distinct separation of methane is effected by the silica gel, but the accuracy of the measurement of this peak depends on the relative concentrations of the various gases. If this peak can be used, the sensitivity for methane can be increased almost threefold. When the Vapor Fractometer is operating with the parallel-column system, the base line is extremely sensitive to changes in flow of the carrier gas; therefore, a flow controller has been installed in the instrument.

COMPARISON OF METHODS FOR THE DETERMINATION OF OXYGEN IN HELIUM

I. B. Rubin

Previous work[6] had indicated the efficacy of hot titanium to remove oxygen from streams of helium. The effluent gas had been analyzed by means of a Greenbrier Chromolab 950 gas chromatograph with a molecular-sieve column. Since the determination of oxygen in helium is to be applied to the gas blanket of the MSRE, a continuous method of analysis and one not subject to interference by argon was desired. Therefore, the coulometric Lockwood and McLorie model 0-1000 Oxygen Analyzer, which operates continuously, was obtained. The Oxygen Analyzer and the gas chromatograph were connected in parallel to the effluent gas stream from the titanium scrubber. Various tests were carried out in essentially the same manner as described previously[6] in order to compare the capabilities of the two instruments for determining various concentrations of oxygen in helium. The test gases contained about 100 and 1000 ppm of oxygen and were passed through a 2-in.-OD combustion tube that contained a 5-in. layer of sponge titanium. The gas flows ranged from 2 to 12 liters/min, and the tests were conducted at temperatures between 360 and 540°C.

The results obtained by the Oxygen Analyzer and by the gas chromatograph were as well correlated as the differences between the two systems would allow. When the test gas that contained 100 ppm of oxygen was passed through the titanium scrubber under conditions such that the oxygen should have been virtually completely removed, values of 0.2 to 0.4 ppm were measured by the Oxygen Analyzer and values of 0.1 to 0.2 ppm by the gas chromatograph. The former figures were found to average out to the instrument blank, whereas the latter results could have been caused by traces of argon.

The Oxygen Analyzer is suitable for the continuous monitoring of helium streams for oxygen. This instrument is capable of determining quantitatively less than 1 ppm of oxygen and is sensitive to rapid changes in the oxygen content of the sample gas; the change can be detected in about 30 sec when the gas flow through the instrument is 200 cc/min.

DETERMINATION OF CARBON IN AQUEOUS AND NITRIC ACID SOLUTIONS

I. B. Rubin A. S. Meyer

In connection with a reactor fuel-dissolution program being carried out by the Chemical Technology Division, a study was initiated to establish a means of determining milligram quantities, or less, of carbon in water and nitric acid solutions of reactor fuels. An apparatus similar to that described by Naughton and Frodyma,[7] but with important modifications, was designed and assembled. The system is capable of measuring quantities of carbon dioxide equivalent to 0.01 to 4 mg of carbon.

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[6] "Analysis MSRE Cover Gas," *Molten-Salt Reactor Program Progr. Rept. Mar. 1–Aug. 31, 1961*, ORNL-3215, p 129.

[7] J. J. Naughton and M. M. Frodyma, "Microdetermination of Carbon and Hydrogen in Organic Compounds," *Anal. Chem.* 22, 711 (1950).

Aqueous solutions of several carbon compounds (sucrose, methanol, oxalic acid, and mellitic acid) were prepared and analyzed. The average recovery of carbon was 90%; the average relative standard deviation was 5%; and the average test-portion size was 1 mg. The carbon content of a number of aqueous solutions of uranium carbide was found to range from 0.010 to 0.075 mg/ml.

Blanks were tentatively established for various quantities of nitric acid. The results were somewhat anomalous, as the smallest blank was obtained for the largest quantity of nitric acid. However, the maximum of the differences among the averages of the blank determinations for the various levels of nitric acid was equivalent to only 0.01 mg of carbon, which amount would not be significant at the 1-mg level of carbon. The recovery of carbon from nitric acid solutions of sucrose was somewhat smaller than from aqueous solutions; it ranged from 83% in the presence of 0.1 ml of 8 *M* HNO_3 to 88% in the presence of 0.2 ml of 16 *M* HNO_3. For mellitic acid, the recovery of carbon increased when nitric acid was present, being 94% when the solution contained 0.2 ml of 16 *M* HNO_3. Work is being continued to increase the accuracy of the determination.

GAS CHROMATOGRAPHIC DETERMINATION OF PRODUCTS OF DISSOLUTION OF URANIUM CARBIDES IN WATER

A. D. Horton

Further investigation of the qualitative analysis of the gaseous products of the dissolution of uranium carbide (UC) in water[8] has shown that two peaks in the C_6 molecular-weight range were incorrectly identified. Also, peaks that were previously unidentified were identified.

Standard gases and liquids were used to identify the various effluent gases; they were obtained from the Matheson Company, Phillips Petroleum Company, and the Farchan Laboratory. In order to identify the compounds in a sample, a series of standards was injected into two or more columns used in the analysis. If, for both the columns, the retention time for the standard peak corresponded to the retention time for a peak from the sample, the latter was considered to have been identified. The identification of the components associated with the remaining peaks is limited by the lack of suitable standards.

An olefin absorber,[9] which is an 8-in.-long, $\frac{1}{4}$-in.-ID Pyrex tube packed with mercuric perchlorate on Chromosorb, was used to classify the organic compounds in the off-gas samples. Table 5.1 gives a revised identification of the gaseous products of the dissolution of uranium carbides in water.

For use in identifying some of the olefins, two 2.5-m-long, $\frac{1}{4}$-in.-ID columns were prepared that would separate olefins from paraffins. One column contained 3 wt % squalane on Burrell medium-activity silica gel and was used for separations in the C_2 through C_5 molecular-weight range. The other column was packed with 25 wt % tricresyl phosphate on C-22 firebrick and was used for separation of compounds in the C_6 through C_7 molecular-weight range and of *n*-octane (Table 5.1).

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[8] A. D. Horton, "Gas Chromatographic Determination of Products of Dissolution of UC," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961,* ORNL-3243, pp 38–39.

[9] R. L. Martin, "The Determination of Hydrocarbon Types in Gasoline by Gas Chromatography," *Anal. Chem.* 34, 896 (1962).

Table 5.1. Classification of Gaseous Products from Dissolution of Uranium Carbides in Water

Absorber, $Hg(ClO_4)_2$ on Chromosorb
Reference, bottom chromatograms of Fig. 5.2

Peak Number	Olefins (Absorbed)	Saturates (Not Absorbed)	New or Corrected Identifications
1	Partly		
2		X	
3		X	
4	X		Propyne-1
5	Partly		*n*-Butane, butene-1
6	X		
7	X		
8	X		Butyne-1
9	X		Unidentified
10	Partly		*n*-Pentane, pentene-1
11	X		
12	X		*cis*-Pentene-2
13	X		*trans*-Pentene-2
14	X		Unidentified
15	X		Unidentified
16	X		Unidentified
17	Partly		3-Methylpentane, hexyne-1
18	Partly		*n*-Hexane, hexene-1
19	X		Hexene-1
20	X		Hexene-2
21	X		Heptene-2
22	X		
23	X		
24		X	*n*-Heptane

In Fig. 5.2 are given the chromatograms of the gaseous products of the dissolution of UC_2 and U_2C_3 in water. Chromatograms of similar samples obtained on the modified silica-gel column are given in Fig. 5.3. Chromatograms of the same samples on the tricresyl phosphate column are shown in Fig. 5.4.

The gaseous dissolution products of UC_2 and U_2C_3 contain the same compounds that are found in the dissolution products of the UC samples; in addition, they may contain acetylene, *cis-* and *trans*-hexyne-2, *n*-hexane, and *n*-octane plus several unidentified compounds in the C_7 molecular-weight range.

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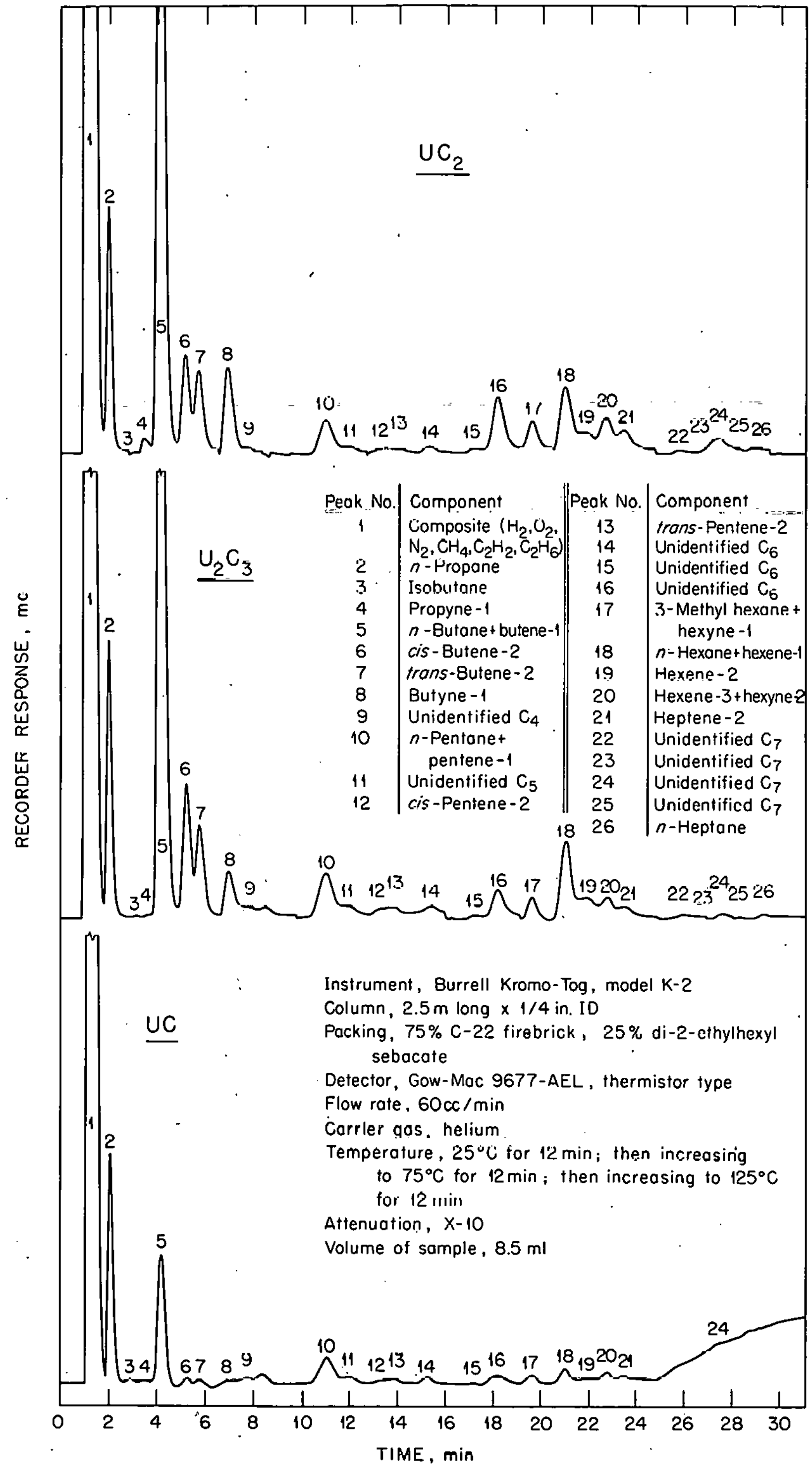
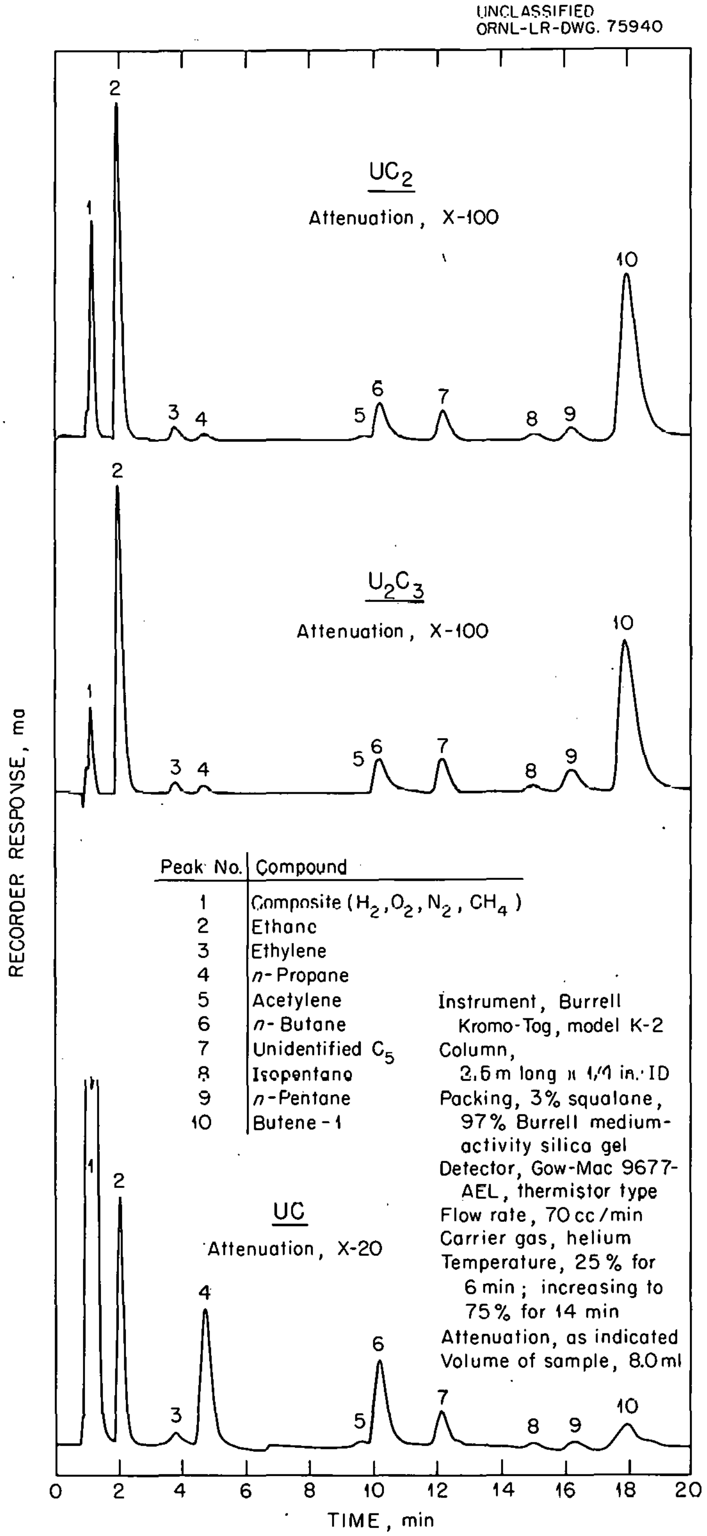


Peak No.	Component	Peak No.	Component
1	Composite (H_2, O_2, N_2, CH_4, C_2H_2, C_2H_6)	13	*trans*-Pentene-2
2	*n*-Propane	14	Unidentified C_6
3	Isobutane	15	Unidentified C_6
4	Propyne-1	16	Unidentified C_6
5	*n*-Butane+butene-1	17	3-Methyl hexane+ hexyne-1
6	*cis*-Butene-2	18	*n*-Hexane+hexene-1
7	*trans*-Butene-2	19	Hexene-2
8	Butyne-1	20	Hexene-3+hexyne-2
9	Unidentified C_4	21	Heptene-2
10	*n*-Pentane+ pentene-1	22	Unidentified C_7
		23	Unidentified C_7
11	Unidentified C_5	24	Unidentified C_7
12	*cis*-Pentene-2	25	Unidentified C_7
		26	*n*-Heptane

Instrument, Burrell Kromo-Tog, model K-2
Column, 2.5 m long x 1/4 in. ID
Packing, 75% C-22 firebrick, 25% di-2-ethylhexyl sebacate
Detector, Gow-Mac 9677-AEL, thermistor type
Flow rate, 60cc/min
Carrier gas, helium
Temperature, 25°C for 12 min; then increasing to 75°C for 12 min; then increasing to 125°C for 12 min
Attenuation, X-10
Volume of sample, 8.5 ml

Fig. 5.2. Chromatograms of the Products of Dissolution of UC$_2$, U_2C_3, and UC in Water; Di-α-ethylhexyl Sebacate Column.



Peak No.	Compound
1	Composite (H_2, O_2, N_2, CH_4)
2	Ethane
3	Ethylene
4	*n*-Propane
5	Acetylene
6	*n*-Butane
7	Unidentified C_5
8	Isopentane
9	*n*-Pentane
10	Butene-1

Instrument, Burrell Kromo-Tog, model K-2
Column, 2.6 m long x 1/4 in. ID
Packing, 3% squalane, 97% Burrell medium-activity silica gel
Detector, Gow-Mac 9677-AEL, thermistor type
Flow rate, 70 cc/min
Carrier gas, helium
Temperature, 25% for 6 min; increasing to 75% for 14 min
Attenuation, as indicated
Volume of sample, 8.0 ml

Fig. 5.3. Chromatograms of the Products of Dissolution of UC_2, U_2C_3, and UC in Water; Modified Silica-Gel Column.

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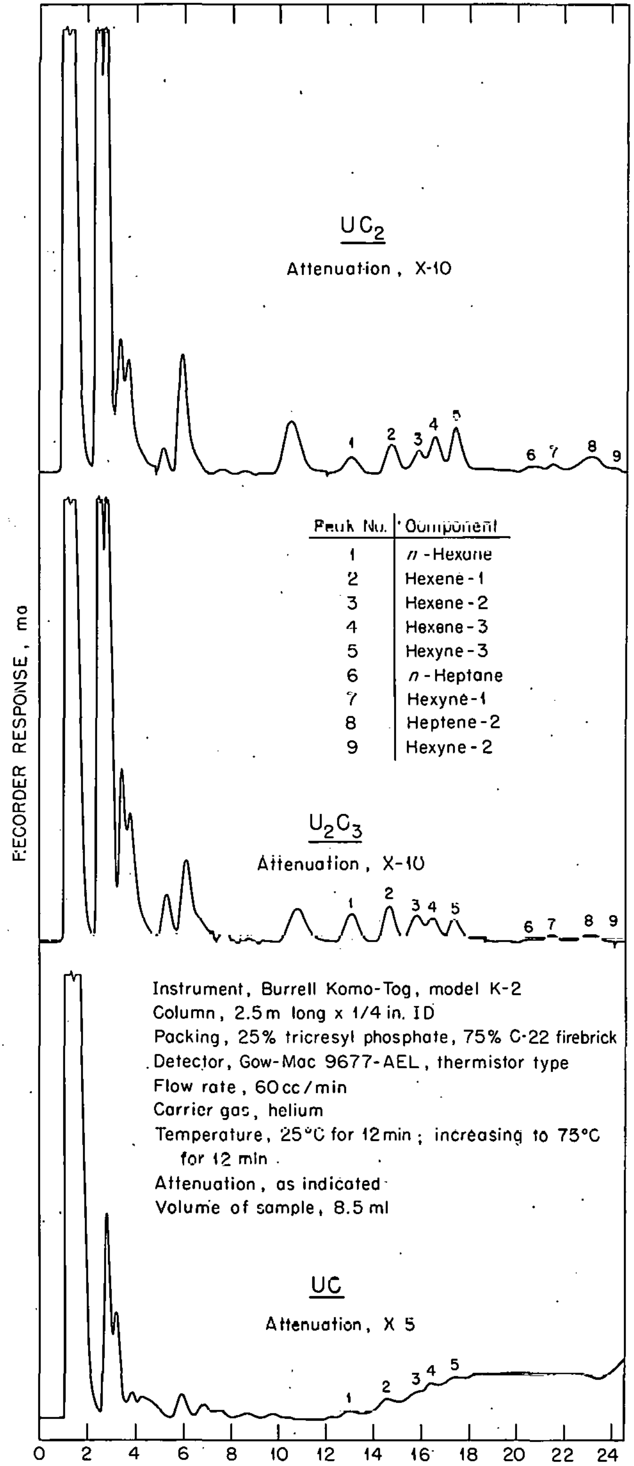

Peak No.	Component
1	*n*-Hexane
2	Hexene-1
3	Hexene-2
4	Hexene-3
5	Hexyne-3
6	*n*-Heptane
7	Hexyne-1
8	Heptene-2
9	Hexyne-2

Instrument, Burrell Komo-Tog, model K-2
Column, 2.5 m long x 1/4 in. ID
Packing, 25% tricresyl phosphate, 75% C-22 firebrick
Detector, Gow-Mac 9677-AEL, thermistor type
Flow rate, 60 cc/min
Carrier gas, helium
Temperature, 25°C for 12 min; increasing to 75°C for 12 min
Attenuation, as indicated
Volume of sample, 8.5 ml

Fig. 5.4. Chromatograms of the Products of Dissolution of UC$_2$, U$_2$C$_3$, and UC in Water; Tricresyl Phosphate Column. Compounds associated with unnumbered peaks were identified by means of other columns.

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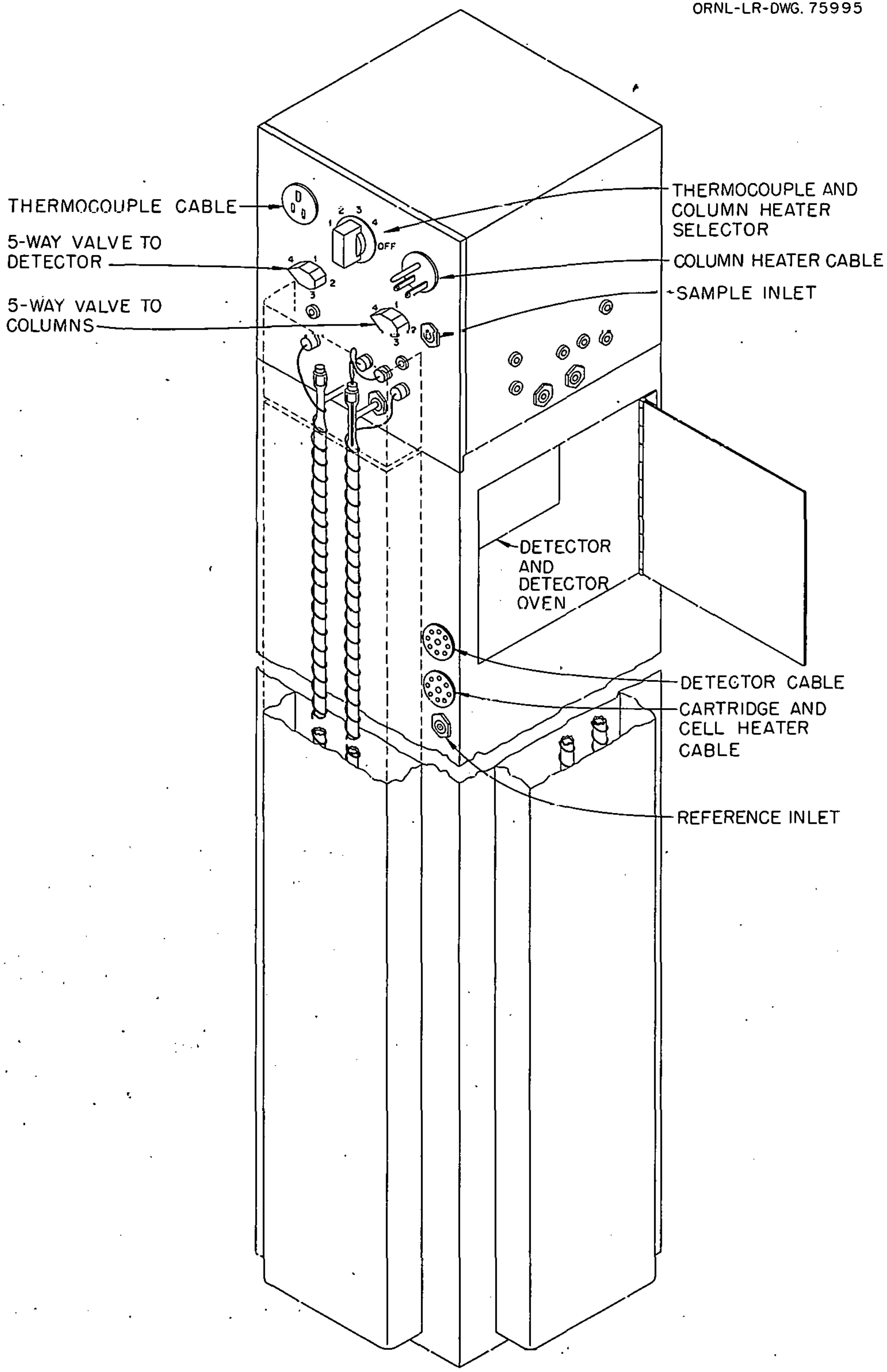

Fig. 5.5. Apparatus for Remotely Controlled Gas Chromatographic Determination of Gases in Radioactive Samples.

GAS CHROMATOGRAPHIC ANALYSIS OF RADIOACTIVE SAMPLES

A. D. Horton A. S. Meyer

An apparatus that contains the sampling and analytical parts of a multicolumn gas chromatograph was designed and built for remotely controlled operation (Fig. 5.5). It is operated by means of cables from the electronic controlling circuit of the Burrell Kromo-Tog (K-2). It will accommodate four columns and has a four-position selector switch that connects the cables to the column heaters and thermocouples. A five-way Conant valve directs the sample to the column; a second such valve directs the effluent from the column to the detector. Only one column can be operated at a time. The standard Burrell gas sampler is used to collect the sample at reduced pressure; Burrell gas connectors are used throughout the system. The entire electrical and gas-flow systems are enclosed in or attached to an 8-in. cast-aluminum cubicle. A removable Micarta face plate contains the controls and connections to the gas and electrical lines. The casting is heated to the desired temperature by four Variac-controlled cartridge heaters, one being inserted in each corner of the casting base. The casting is mounted on a sheet-metal support that is long enough to accommodate a 2.5-m-long U-tube column.

This apparatus has been tested with samples of off-gases from the dissolution of uranium carbides in water; it is satisfactory for remotely controlled manual operation.

GAS CHROMATOGRAPHIC DETERMINATION OF THE OXIDES AND CHLORIDES OF NITROGEN

A. D. Horton

A grease-free test manifold for sampling nonfluoride corrosive gases was described previously.[10] It was found to be leak-tight and resistant to corrosion by and adsorption of the oxides and chlorides of nitrogen. A complete sampling manifold (Fig. 5.6) was built; it includes the grease-free Delmar-Urry needle-valve stopcocks and a Dynisco 0- to 760-mm pressure transducer.

TRAPPING AND GAS CHROMATOGRAPHIC DETERMINATION OF KRYPTON, XENON, AND CARBON TETRAFLUORIDE

A. D. Horton A. S. Meyer

A method was desired for trapping krypton, xenon, and carbon tetrafluoride from a reactor test capsule at a helium purge rate of 200 cc/hr. A stainless steel U-tube cold trap (8 in. long × $\frac{1}{4}$ in. OD) that contained 2 g of Fisher 13X, 30- to 60-mesh molecular sieve, which had been dried under vacuum at 300°C, was immersed in liquid nitrogen. Helium flowed through the trap at 50 cc/min, which is the optimum rate for the 13X molecular-sieve column. The outlet of the trap was connected to the column inlet of the Burrell Kromo-Tog (K-2). A mixture of 0.3 ml each of krypton, xenon, and carbon tetrafluoride was injected into the trap and was allowed to remain for 1 hr; other mixtures were allowed to remain for different periods of time. The liquid nitrogen was then replaced by a beaker that contained warm water (50 to 60°C). The

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[10] A. D. Horton, "Gas Chromatographic Determination of the Oxides and Chlorides of Nitrogen," *Anal. Chem. Div. Quart. Progr. Rept. June 15, 1962* (unpublished report).

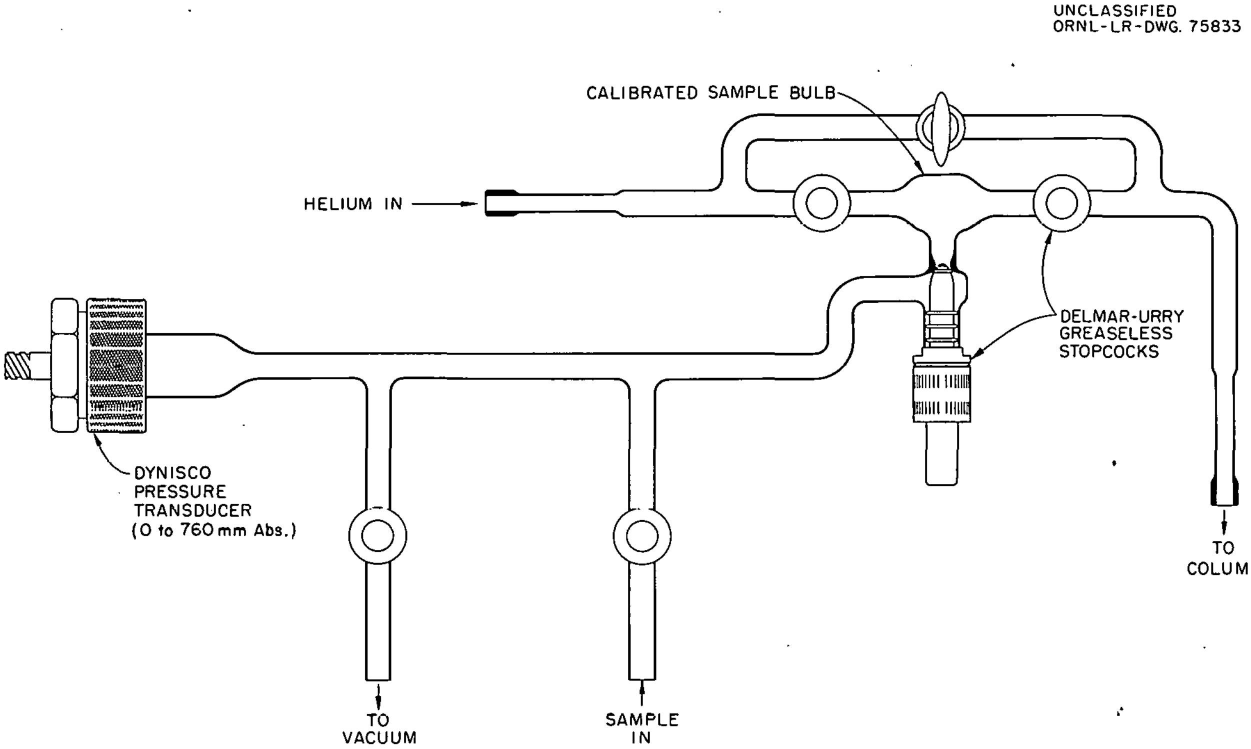

Fig. 5.6. Grease-Free Vacuum Sampling Manifold for Nonfluoride Corrosive Gases.

gases passed from the trap into a 13X molecular-sieve column (2.5 m long × $\frac{1}{4}$ in. ID) at a temperature of 50°C and at a helium flow rate of 50 cc/min. The gases were separated as shown in Fig. 5.7. The retention volume and peak area obtained for 0.3 ml of each gas after the specified time in the trap are shown in Table 5.2. The air that corresponds to the peak which appears on the chromatogram was present in the helium carrier and was trapped by the 13X molecular sieve at liquid-nitrogen temperature.

Table 5.2. Retention of Krypton, Xenon, and Carbon Tetrafluoride on 13X Molecular Sieve at Liquid-Nitrogen Temperature

Contents of trap, 2 g of 13X, 30- to 60-mesh molecular sieve
Volume of each gas, 0.3 ml

Volume of Helium Carrier (liters)	Equivalent Trapping Time at 200 cc/hr (hr)	Peak Area (integration counts)			Gas Retained (%)		
		Kr	Xe	CF_4	Kr	Xe	CF_4
0	0	206	152	220	100	100	100
3.6	18	204	152	219	99	100	100
14	72	203	150	221	99	99	100
29	144	186	148	208	90	97	95

Krypton, xenon, and carbon tetrafluoride were retained quantitatively on a 13X molecular-sieve trap at liquid-nitrogen temperature for as long as 8 hr at a continuous carrier flow of 50 cc/min.

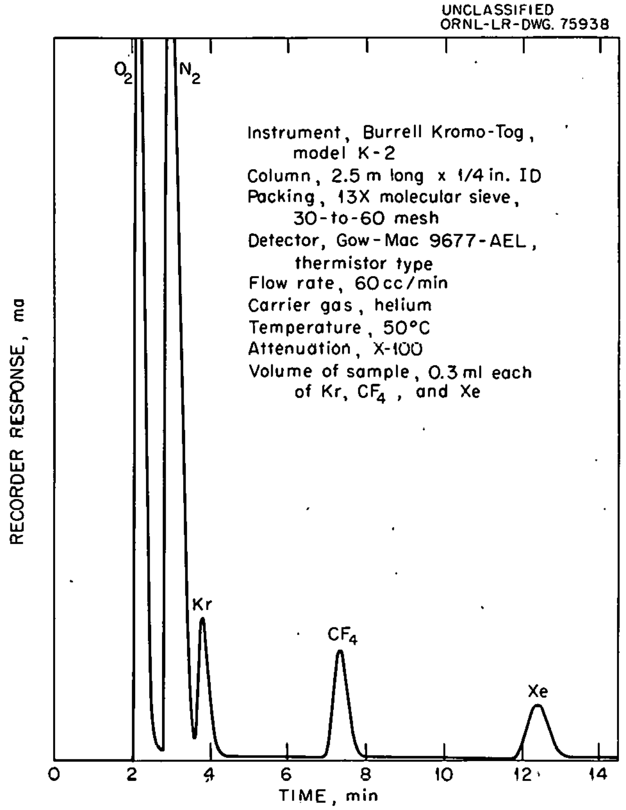

Fig. 5.7. Gas Chromatogram of Krypton, Xenon, and Carbon Tetrafluoride on 13X Molecular Sieve.

DETERMINATION OF OXYGEN IN HIGHER ALKALI METALS

Gerald Goldberg

The program to evaluate methods for the determination of oxygen in the higher alkali metals (potassium, rubidium, and cesium) was continued. Most of the work centered around the determination of oxygen in potassium, since this method is of prime importance to the Metals and Ceramics Division. After the amalgamation apparatus[11] was modified slightly (Fig. 5.8), the procedure was applied successfully, and with good precision, to replicate samples of potassium (and NaK) that contained from 10 to 50 ppm oxygen. The residue, after amalgamation, is dissolved in dilute HCl, and the potassium (or potassium and sodium) is determined by flame photometry, which is a less time-consuming method than the microtitration of the potassium hydroxide in an aqueous solution of the residue. Results obtained with the two methods showed little or no difference. The oxygen is calculated as K_2O.

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[11] J. C. White, A. S. Meyer, and Gerald Goldberg, "Determination of Oxygen in Higher Alkali Metals," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, p 41.

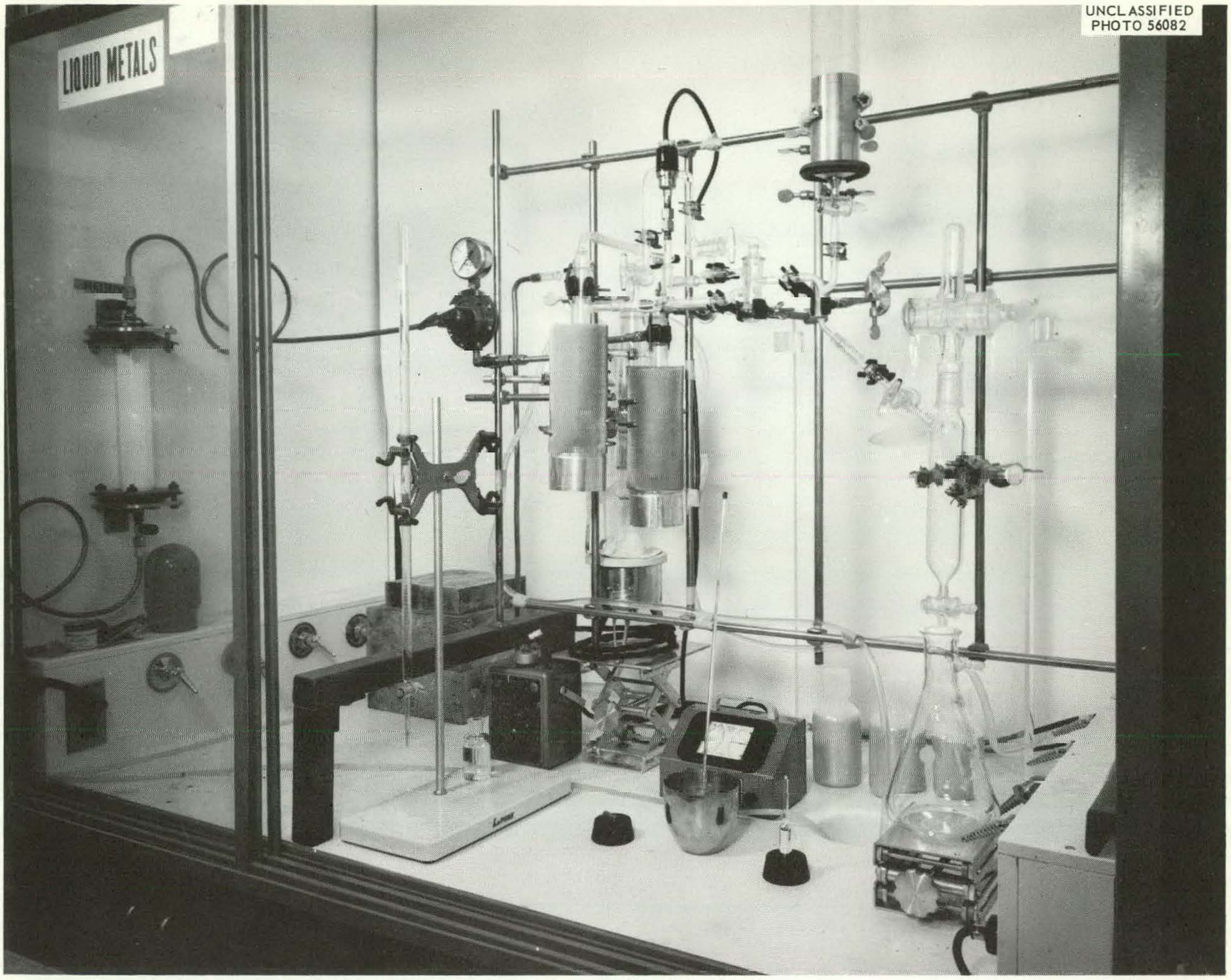

Fig. 5.8. Modified Amalgamation Apparatus for Determination of Oxygen in Alkali Metals.

To further substantiate the reliability of the amalgamation method and to determine whether the higher oxides of potassium are reduced to K_2O in the presence of excess potassium, samples of high-purity potassium together with known amounts of KO_2 were sealed in stainless steel capsules and were heated at elevated temperatures. Although there were indications that the KO_2 is reduced, the results were inconclusive because the corrosive potassium oxides attacked the stainless steel, and oxygen was lost to the corrosion products. In another test, niobium was substituted for stainless steel, and HgO was used as the spiking agent instead of KO_2. The results of this test were also inconclusive because of the large amount of niobium found in the residue after amalgamation; however, more oxygen was recovered. Essentially complete recovery of oxygen was obtained when K_2O was added to molten potassium in a stainless steel capsule, which was then cooled to room temperature. In other tests, K_2O or KO_2 was added to 5 to 6 g of high-purity potassium contained in an amalgamation reaction vessel. The oxides were recovered completely after the amalgamation; these results further substantiate the belief that none of the oxide is lost to the amalgam. Additional tests in which sealed capsules are being used are now in progress. The possibility of loss of oxygen to the amalgam will also be studied by vacuum distilling the amalgam from a nickel cup, which will then be examined for any residual oxide.

To determine whether the butyl bromide method is applicable to the determination of oxygen at a concentration of the order of 10 ppm in higher alkali metals, a modified version of the apparatus[12] was constructed. The sample can be added to the reaction vessel under vacuum or an inert atmosphere; the reagents are added directly from the chromatographic purification columns, which contain silica gel and types 4A and 5A molecular sieves. The apparatus was tested with 6-g samples of high-purity potassium. The large sample weight made the operation somewhat hazardous because of the extended reaction period. The values obtained for oxygen (i.e., 100 to 200 ppm) were higher than those obtained by the amalgamation method (i.e., 8 to 14 ppm). Because the amount of oxygen found decreased for each of several successive samples, it was concluded that contaminative moisture was being removed slowly from the chromatographic columns. Further tests will be made when the Metals and Ceramics Division can supply potassium metal in 1- to 3-g samples.

An extrusion apparatus was constructed for removing test portions of potassium contained within a $\frac{1}{2}$-in.-OD tubing. At present, this apparatus is in standby because it is not readily adaptable to the amalgamation procedure. It will be used if further development of the butyl bromide method is warranted.

Vacuum distillation is another method being considered for the determination of oxygen in potassium. Present plans are to vacuum-distill 5 to 10 g of potassium that contains a known amount of oxygen from nickel or molybdenum cups at 250°C and a pressure of 10^{-5} torr. The residues will be dissolved and examined for oxide and carbonate content.

At present, it is not planned to study the determination of oxygen in rubidium. Preliminary work on the determination of oxygen in cesium indicates that the existing amalgamation method[13] is not applicable.

DETERMINATION OF HYDROGEN IN ALKALI METALS

Gerald Goldberg

A simple method was developed for the determination of hydrogen (as the hydride) in sodium, potassium, and NaK. The sample to be analyzed is first treated according to the amalgamation procedure.[11] Deaerated water is then added under vacuum to the residue in the evacuated reaction vessel, which contains any hydride present in the sample. By means of a Toepler pump, the liberated hydrogen is pumped from the reaction vessel into an evacuated calibrated sample bulb through a magnesium perchlorate drying tube and a cold trap cooled by liquid nitrogen. The hydrogen is determined by gas chromatography; as little as 1 μg can be determined quantitatively.

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[12] J. C. White, W. J. Ross, and R. Rowan, Jr., "Determination of Oxygen in Sodium," *Anal. Chem.* **26**, 210 (1954).

[13] F. Tepper, S. J. Rodgers, and J. S. Greer, *Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, First Quart. Progr. Rept. Sept. 13, 1962*, MSAR 62-108.

DETERMINATION OF OXYGEN AND NITROGEN IN SALTS AND IN LITHIUM METAL BY HIGH-TEMPERATURE FLUORINATION WITH $KBrF_4$

Gerald Goldberg

Modification of the apparatus was necessary in order to increase the precision of the $KBrF_4$ method[14,15] in the range of 100 ppm of oxygen and/or nitrogen. A reactor was fabricated that has a $KBrF_4$ capacity at least five times that of the original reactor. It makes possible the analysis of samples that weigh as much as 2 g; 0.5 g was the limit of the smaller reactor. The increase in the ratio of liberated gas to blank resulted in better precision.

For the first time, both oxygen and nitrogen[16] were determined in the same test portion of lithium metal; test portions that weighed 100 to 200 mg were analyzed with no difficulty. The analysis of lithium has been a controversial issue because the amalgamation[11] and butyl bromide[12] methods normally used for the determination of oxygen in alkali metals are not applicable to lithium metal.

DETERMINATION OF FREE ALKALINE-EARTH METALS IN ALKALINE-EARTH METAL–ALKALINE-EARTH HALIDE SOLID SOLUTIONS

Gerald Goldberg

Samples of $Sr \cdot SrBr_2$ and $Ca \cdot CaF_2$ were analyzed for free alkaline-earth-metal content. The weighed sample was transferred, under inert atmosphere, to a reaction vessel of the type used in the amalgamation method.[11] The vessel was evacuated, and deaerated water was then added to it under vacuum. The reaction proceeded smoothly, hydrogen being liberated as a result of the reaction of the alkaline-earth metal with the water. By means of a Toepler pump the hydrogen was transferred to an evacuated calibrated sample bulb through a magnesium perchlorate drying tube and a cold trap cooled with liquid nitrogen. The amount of hydrogen liberated was determined by gas chromatography. The results obtained were in close agreement with anticipated results.

DETERMINATION OF OXYGEN BY THE MODIFIED LECO METHOD

F. J. Miller

Work has continued toward the development of a method of determining oxygen in fluoride salts by means of carbon reduction in an rf induction furnace. The apparatus was redesigned in order to reduce the blanks formerly obtained, to reduce the enclosed volume that is swept by the inert blanketing gas, and to achieve higher temperatures for the graphite capsule without loss of integrity of the quartz envelope. A

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[14] Gerald Goldberg, "Oxygen in Fluoride Salts and Refractory Metals, Potassium Tetrafluorobromide Manometric Method," Method Nos. 1 215894 and 9 00715894 (5-12-60), *ORNL Master Analytical Manual*; TID-7015, suppl 3.

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

[16] Gerald Goldberg, "Determination of Oxides and Nitrides in Lithium Metal by High-Temperature Fluorination with Potassium Bromotetrafluoride," *Anal. Chem.* **34**, 1343 (1962).

program has been carried on jointly with other members of the division who are attempting different approaches to the analysis.

The results already obtained for the oxygen content of fluoride salts have been valuable, especially for the purpose of comparisons. The increase in temperature that is expected to be achieved with the redesigned apparatus should yield more definitive data.

DETERMINATION OF OXYGEN IN FLOWING GAS STREAM

F. J. Miller

A commercial gas analyzer that is based on the principle of the Hersch cell was evaluated for the Reactor Chemistry Division. Further attention to detailed operation of such an instrument should result in reliable in-line operation of the instrument for measurement of parts-per-million concentrations of oxygen in a flowing gas stream.

6. Effects of Radiation on Analytical Methods

J. C. White

CHROMIUM(VI)–1,5-DIPHENYLCARBOHYDRAZIDE REACTION AND EFFECT OF GAMMA RADIATION ON IT

H. E. Zittel

The effect of gamma radiation on the reaction of Cr^{6+} with 1,5-diphenylcarbohydrazide (DPC), commonly used for the spectrophotometric determination of chromium, was studied. The mode of reaction between Cr^{6+} and DPC was clarified. An excess of Cr^{6+} oxidizes the colored intermediate; consequently, DPC can be titrated to a colorless end point with Cr^{6+}. Extraction studies in which Cr^{51} was used as a tracer were carried out on the Cr-DPC intermediate; it was proved that Cr^{3+} is not bound to the chromophoric group.

Under the conditions of the study, Cr^{6+} is reduced by gamma radiation to the extent of 2.5×10^{-9} mmole per ml of Cr^{6+} solution per roentgen. Both DPC reagent and the Cr-DPC intermediate are much less sensitive to gamma radiation than is Cr^{6+}. At levels of gamma radiation <1000 r, the effect of radiation introduces very little error in the method. A paper that describes this work was accepted by *Analytical Chemistry* for publication.

EFFECT OF GAMMA RADIATION ON ETHYLENEDIAMINETETRAACETIC ACID

H. E. Zittel

The effect of gamma radiation on ethylenediaminetetraacetic acid (EDTA) when used as a titrant was studied. The effects of varying EDTA concentration, pH, and radiation dose have been established. Within the limits studied, EDTA is destroyed to the extent of $\sim 1 \times 10^{-9}$ mmole per ml of EDTA solution per roentgen at all pH values and concentration ranges. The effect of gamma radiation on various organic end-point indicators commonly used for EDTA titration was studied. Radiation doses of $\sim 10^5$ r can be tolerated without effect on their end-point sensitivity. This work is described in an article submitted to *Analytical Chemistry* for publication.

EFFECTS OF GAMMA RADIATION ON THE THIOCYANATE–STANNOUS CHLORIDE SPECTROPHOTOMETRIC METHOD FOR MOLYBDENUM

Lucy E. Scroggie

The dose rate of the Co^{60} source to be used for studies of radiation effects was determined by use of ceric sulfate dosimetry; it was about 2×10^6 r/hr.

Prior to investigation of the effects of gamma radiation on the thiocyanate–stannous chloride spectrophotometric method for the determination of molybdenum,[1] the method was applied to known concentrations of molybdenum. The color of the molybdenum thiocyanate complex in butyl acetate is not very stable; this makes necessary the use of control solutions when the effects of radiation are being studied.

To determine whether ultraviolet adsorption spectrophotometry can be used to detect Mo^{3+} in irradiated solutions of Mo^{6+}, the ultraviolet spectra of aqueous solutions of Mo^{3+} and of Mo^{6+} were determined. The solutions of Mo^{3+} were prepared by reducing standard solutions of Mo^{6+} with a Jones reductor. Absorption maxima were found at 217 and 295 mμ for Mo^{6+} and Mo^{3+}, respectively; Mo^{3+} absorbs much less strongly than does Mo^{6+}.

Aqueous solutions of Mo^{6+} were irradiated in the presence and absence of air; ultraviolet absorption spectrophotometry was used to detect Mo^{3+} in the irradiated solutions. A solution of Mo^{6+} at a concentration of 10.0 μg/ml that was deaerated with helium and was given a gamma radiation dose of 5.2×10^5 r in a helium atmosphere contained Mo^{3+} at a concentration of 9.6 μg/ml after the irradiation. However, when an air-saturated solution of the same Mo^{6+} concentration was irradiated in air, the Mo^{3+} concentration of the solution after irradiation was only about 1 μg/ml. Since Mo^{3+} is oxidized in air, some of the Mo^{3+} formed as the result of the irradiation could have been oxidized back to Mo^{6+}. Some experiments were made to determine the dependence of the reduction of Mo^{6+} on total dose of gamma radiation. The results indicate that the amount of reduction is not a linear function of total dose of radiation and that perhaps several competing or concurrent reactions occur.

Some neutral and slightly acid aqueous solutions of potassium thiocyanate were irradiated, but it was difficult to determine microgram amounts of radiolytic products. The preliminary and rather erratic

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[1] T. C. Rains and L. J. Brady, "Molybdenum, Spectrophotometric Thiocyanate–Stannous Chloride Method," Method Nos. 1 215010 and 9 00715010 (5-10-57), *ORNL Master Analytical Manual*, TID-7015, sec 1.

results indicate that thiocyanate ion is extremely resistant to radiolysis. Duflo,[2] who is also studying the radiolysis of thiocyanate ion in neutral solution, reports that thiocyanate is stable to radiolysis.

The effects of radiation under the conditions of the extraction of molybdenum thiocyanate into butyl acetate are being studied.

PYROLYTIC GRAPHITE ELECTRODE

F. J. Miller

Potentiometry

A pyrolytic graphite electrode was investigated for use as an indicator electrode in acid-base titrations and in potentiometric redox titrations. Reproducible curves have been obtained in the potentiometric titrations of Fe^{3+} with Cr^{6+}. The locations of end points in acid-base titrations in both aqueous and nonaqueous systems were well defined and reproducible, even in dilute solutions. The pyrolytic graphite electrode should prove of value for potentiometric titrations of radioactive solutions in which the glass electrode is damaged, in nonaqueous titrations where the glass electrode becomes dehydrated, and in redox titrations in which noble-metal electrodes are subject to poisoning. The study of the pyrolytic graphite electrode will be extended to molten-salt systems.

A short communication that describes this work was presented for publication in *Analytical Chemistry*.

Voltammetry

The excellent results obtained for the potentiometric titrations made with the pyrolytic graphite electrode have encouraged the investigation of its use as a solid indicator electrode in voltammetry. The usable range of the pyrolytic graphite electrode is from -0.8 to $+1$ v vs the S.C.E. Determinations of metallic ions in 10^{-3} *M* concentrations were made in replicate with a relative standard deviation of 3%. Voltammetric determination of the following ions in either acid chloride or acid nitrate medium is feasible: Cu^{2+}, Ag^{+}, $UO_2{}^{2+}$, Sn^{4+}, Fe^{3+}, and Hg^{+}. The voltammetric determination of Fe^{3+} and $UO_2{}^{2+}$, present together in acid chloride medium, with the pyrolytic graphite electrode was demonstrated. A report of the work is being written for publication. Further application of the pyrolytic graphite electrode in voltammetry is planned.

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[2] M. Duflo, "Action des Rayonnements γ Sur Les Solutions Aqueuses de Thiocyanate de Potassium," *J. Chim. Phys.* 59, 655 (1962).

7. X-Ray and Spectrochemical Analyses

X-RAY AND SPECTROCHEMICAL ANALYSES (X-10)

M. T. Kelley
Cyrus Feldman

X-Ray Analysis

H. W. Dunn

X-Ray Fluorescence Microprobe. – The x-ray fluorescence microprobe has been used in the qualitative and semiquantitative analysis of 100- and 1000-μ-diam spots on Au-Cu welds, of clam shells (Fig. 7.1*A*), and of various grains and inclusions in alloys. Where standard alloys were available, x-ray intensities could be interpreted directly in terms of chemical concentrations. For example, with the aid of standard Re-W alloys, the malfunction of an Re-W thermocouple was traced to reduction of the rhenium concentration from the normal 30.0% to 25.4% in one section of wire (Fig. 7.1*B*).

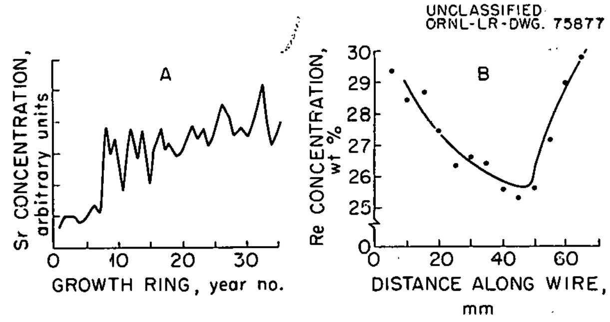

Fig. 7.1. Local Analysis of Clam Shell (*A*) and Re-W Thermocouple Wire (*B*) with the X-Ray Fluorescence Microprobe.

When standard alloys were not available (e.g., in testing the homogeneity of superconducting Zr-Nb alloys), the specimen was first scanned with a 100-μ-diam x-ray beam to locate the areas showing the highest and lowest Zr/Nb ratios. The impact point of the beam coincided with the cross hairs of an observation microscope. Small specimens ($\sim\leqq 50$ μg) were then removed from these areas with a microdrill (~ 125-μ diam). The drillings were dissolved and analyzed spectrographically. The concentration values thus obtained were correlated with the Zr/Nb x-ray fluorescence intensity ratios obtained from the corresponding areas to give an analytical curve. Zirconium concentrations in the spots analyzed were then determined by directing the x-ray beam at the various spots and observing the Zr/Nb x-ray intensity ratios. The specimens in this case were slices cut from a cast ring (Fig. 7.2). Spots were chosen on a cut surface of each slice as shown in the figure. Concentration values are shown in Table 7.1.

Application of Computer to X-Ray Absorption-Edge Analysis. – In the calibration of equipment for the determination of a given element by x-ray absorption-edge analysis, measurements of transmitted intensity are made immediately above and below the appropriate absorption edge on solutions that contain various known concentrations of the element in question.[1] Parameters derived from these data are used to determine the concentration of this element in unknown solutions. To derive these parameters, it is necessary to assume a trial value at each wavelength for a constant factor that sums up the influence of the dead time of the x-ray detector and other instrumental characteristics. The parameters so derived are tested by using them to calculate the composition of the standard solution as if it were an unknown. The parameter values that best reproduce the known concentrations are then adopted for use in analytical work. Since the calculation of the set of parameters corresponding to a given set of trial values of the constants is a long one, it is expedient to use the first set of parameters that meets the required standards of accuracy.

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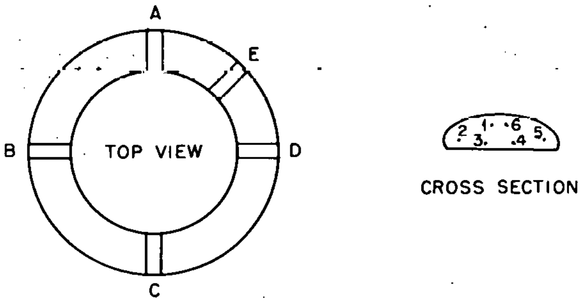

Fig. 7.2. Microdrilling Plan for Calibrating X-Ray Fluorescence Microprobe Standards.

Table 7.1. X-Ray Fluorescence Microprobe Analysis: Internal Variation of Zirconium Concentration in a Cast Zr-Nb Ring

Position	Zirconium (wt. %)				
	A	B	C	D	E
1	29.3	27.0	28.0	25.6	25.8
2	29.1	26.9	26.8	25.5	25.9
3	29.3	27.9	27.5	25.4	26.0
4	29.8	26.7	31.9[a]	29.8	26.2
5	27.1	27.3[a]	28.4	24.9[a]	28.7
6	29.4	26.8	28.3	25.0[a]	25.8

[a] Reference values, determined by spectrochemical analysis of drillings.

With the aid of H. P. Carter and Barbara A. Flores of the ORNL Mathematics Panel, a code was formulated to enable the IBM 7090 computer to calculate these parameters for a two-dimensional array of constants; the computer was requested to print out only those parameters that give the best possible fit to known data. A second code was devised to calculate concentration values from raw x-ray data.

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[1] H. W. Dunn, "X-Ray Absorption Edge Analysis," *Anal. Chem.* 34, 116 (1962).

Atomic Absorption Analysis

Determination of Mercury (Cyrus Feldman, R. K. Dhumwad[2]). – In the determination of mercury by atomic absorption analysis, the solution vapor aspirated by a Beckman burner is passed into an absorption tube of the design shown in Fig. 7.3. Light from a low-pressure mercury-vapor lamp is chopped and traverses the tube lengthwise; the degree of absorption of the Hg 2537 A line is then measured by means of a photomultiplier–tuned amplifier system. This system shows greater sensitivity for the detection of mercury ($\sim$0.2 μg/ml) than has thus far been claimed for systems involving moving vapors. The absorptivity shown by a given concentration of mercury is essentially unaffected by the presence of dissolved salts in as high a concentration as $\sim$1 mg/ml. It is often convenient, however, to isolate mercury by extracting it from acid solution into a solution of dithizone in methyl isobutyl ketone. This extract can be analyzed directly. The results obtained in comparison tests are shown in Table 7.2. Attempts to apply this absorption tube to the determination of elements other than mercury have indicated that difficulties may be encountered with memory effect. No memory effect was encountered in the case of mercury.

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[2] Temporary employee from Atomic Energy Establishment, Trombay, India.

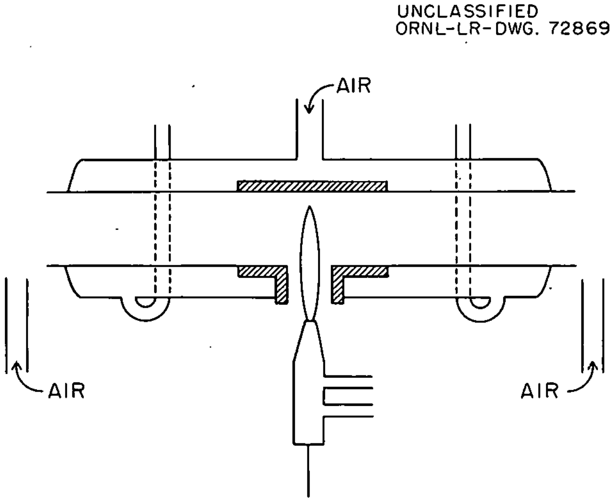

Fig. 7.3. Stainless Steel Absorption Tube for Determination of Mercury by Atomic Absorption.

Table 7.2. Accuracy of Mercury Values Obtained by Atomic Absorption Spectroscopy

Sample	Mercury Present (μg/ml)	Mercury Found (μg/ml)			
		Colorimetry	Atomic Absorption Spectroscopy		Neutron Activation Analysis
			Aqueous	Organic	
1	3.5		3.6	3.7	
2	20.0		20.2	20.7	
3	Unknown	14.9	15.1	14.9	15.7

Use of Demountable Hollow Cathode (Cyrus Feldman, S. R. Koirtyohann, T. S. Krishnan). – In order to make possible the determination of the maximum number of elements by atomic absorption analysis with a hollow cathode tube, a hollow cathode assembly similar to that described by Werner *et al.* [3] was constructed. The optical emission spectrum of a given metal was obtained either by fashioning the cathode entirely of that metal (Ni, Mg), by plating the desired metal onto the cathode (Zn, Cd on brass), or by soldering an appropriate foil to the cavity wall (Pb on brass). The cathode was cooled by a clamp-on water jacket. The power supply was a Jarrell-Ash model 82-135. The discharge was operated at 15 to 40 ma in a stream of tank argon or helium, adjusted with needle valves so that the steady-state pressure in the cathode was 2 to 4 mm. After a 20-min warm-up, these cathodes gave a signal stable to within ±1%. After several hours of use in helium, stability sometimes decreased but could be restored easily by buffing the internal surface of the cathode with diatomaceous earth. Cathodes remained stable for longer periods when used in flowing argon.

Most work on elements other than mercury was done by use of a sample-injection system similar to (but shorter than) that suggested by Fuwa and Vallee.[4] They used a 12-mm-diam, 150-mm-long quartz tube placed in the optical axis. A Beckman atomizer-burner was held with its tip approximately level with the bottom of the tube and 5 mm away from one end. The burner was tilted upward at an angle of about 30 degrees with the horizontal in order to direct the flame into the tube. Light from the hollow cathode source could thus be passed through the tube. A transverse blast of air at the exit of the tube diverted the hot gases upward, thus preventing damage to optical parts.

As in the case of mercury, the effect of dissolved solids on the absorptivity of the metals has been negligible. The quartz tube has shown no tendency toward memory effect but is less sensitive for mercury than is the T-tube illustrated in Fig. 7.3. Typical results obtained with demountable hollow cathodes and an end-fed quartz absorption tube are given in Table 7.3. In addition to applications in tissue analysis,

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[3] G. K. Werner *et al.*, "Further Investigations in the Spectro-Isotopic Assay Technique for Lithium," *J. Opt. Soc. Am.* 45, 202 (1955).

[4] K. Fuwa and B. L. Vallee, "Improved Instrumentation in Atomic Absorption Spectroscopy," presented at the International Conference on Spectroscopy, Washington, D. C., June 18–22, 1962.

Table 7.3. Typical Working Ranges and Conditions for Use of Demountable Hollow Cathodes In Atomic Absorption Spectroscopy

Metal Determined	Hollow-Cathode Current (ma)	Type of Solution	Limit of Detection (μg/ml)	Working Concentration Range (μg/ml)
Pb	15	Hexone	0.05	0.1 to 1.5
Zn	20 to 30	Aqueous solution of bone ash	0.005	0.01 to 0.20
Cd	20	Aqueous solution of bone ash	0.005	0.01 to 0.20
Mg	20 to 30	*p*-Dioxane–H_2O (1:1)	0.005	0.01 to 0.20
Ni	30 to 40	*p*-Dioxane–H_2O (4:1)	0.05	0.1 to 2.0

this technique has been used to determine lead in urine and in copper alloys, cadmium and mercury in aluminum, and nickel in MSRE fuel, and to make other trace analyses.

Spectrometric Determination of Carbon Tetrafluoride in Helium (Cyrus Feldman, T. S. Krishnan). – The fluorine line at 6856.02 A can be detected when microgram quantities of fluoride salts are placed in hollow cathodes and the discharge is operated in helium.[5] Therefore, when the need arose to determine carbon tetrafluoride and gaseous fluorine-containing species in helium, investigation of the use of a hollow cathode discharge was begun. Preliminary tests were made with the above-mentioned hollow cathode and He-CF_4 mixtures prepared by C. K. Talbott. These tests showed that the F 6856.02 line is easily visible at a 10-ppm concentration of CF_4. Work is under way to determine optimum operating currents, pressures, cathode materials, and other conditions.

Flame Photometry

Collection and Flame Photometric Determination of Cesium (Cyrus Feldman, T. C. Rains). – Although the sensitivity already attained in the determination of cesium by flame photometry (with a Beckman aspirator-burner, a grating monochromator, and a photomultiplier)[6] is sufficient for most purposes (0.05 μg/ml in aqueous solutions, ~ 0.02 μg/ml in organics), it is insufficient for the determination of cesium in the concentrations found in river water and animal tissue. A procedure was therefore developed for the chemical preconcentration of cesium prior to flame photometric determination.

The procedure is based on the unusually high efficiency of ammonium phosphomolybdate, $(NH_4)_3[PMo_{12}O_{40}]$, as an adsorbent of cesium.[6,7] In the analysis of water, the $(NH_4)_3[PMo_{12}O_{40}]$ was added to an 8-liter sample and then collected by adding Al^{3+} as a flocculant, heating to 60°C with an immersion steam coil, and allowing the floc to settle. The floc was dissolved in a solution of NaOH; the cesium was extracted into a solution of sodium tetraphenyl boron in methyl isobutyl ketone (Hexone). This extract was analyzed directly by flame photometry.

When tissue ash was analyzed, an aliquot of ash solution was transferred to a 50-ml centrifuge tube. The cesium was coprecipitated on several successive 50-mg portions of $(NH_4)_3[PMo_{12}O_{40}]$ in order to eliminate any coprecipitated potassium, which might interfere with the subsequent extraction. The $(NH_4)_3[PMo_{12}O_{40}]$ was collected by centrifugation, dissolved in NaOH solution, and treated as above. Recovery of added cesium from samples run through the entire procedure is shown in Table 7.4. The results obtained from the analysis of several samples typical of those received in the laboratory are given in Table 7.5.

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[5] F. T. Birks, "The Application of the Hollow Cathode Source to Spectrographic Analysis," *Spectrochim. Acta* 6, 169 (1954).

[6] J. van R. Smit, J. J. Jacobs, and W. Robb, "Cation Exchange Properties of the Ammonium Heteropolyacid Salts," *J. Inorg. Nucl. Chem.* 12, 95 (1959).

[7] J. van R. Smit, J. J. Jacobs, and W. Robb, "Cation Exchange on Ammonium Molybdophosphate – I," *J. Inorg. Nucl. Chem.* 12, 104 (1959).

Table 7.4. Recovery to Cesium Added to Water and Tissue Ash Samples

Cesium added, 50 μg

Sample	Cesium Recovered, Measured by			
	Flame Photometry		Tracer Method	
	(μg)	(%)	(μg)	(%)
Tap water (8 liters)	48.0	96	47	94
Fish-tissue ash	48.5	97		
Wood ash	47.5	95		

Table 7.5. Typical Cesium Concentrations Measured by the Ammonium Phosphomolybdate–Sodium Tetraphenyl Boron Flame Photometric Method

Sample	Cesium Concentration	Relative Standard Deviation (%)
Tap water	0.00002_6 μg/ml	
Fish-tissue ash	0.86 ± 0.07 μg/g[a]	8.2
U.S. Geological Survey granite G-1	$1.9_1 \pm 0.1_4$ μg/g[b]	7.2

[a] Nine aliquots of a stock solution, analyzed on different days.

[b] Four separate portions of granite powder.

Tissue Analysis

S. R. Koirtyohann Cyrus Feldman

About 1000 samples of tissue ash were analyzed by emission spectrometry, in support of the Trace Elements in Human Tissue Program of the Health Physics Division. The soft-tissue ash (740 samples) was analyzed for 23 elements and the bone ash (260 samples) for 18.

Development work continued along the following lines.

Precision and Accuracy. – The long-term precision of the emission spectrometric method used for the analysis of the soft tissue[8] was tested by repeatedly arcing several samples over a five-month period. The mean relative standard deviation, which includes any variability due to sampling, was about 10%. The accuracy of the determination of copper was checked by colorimetry and of Cd, Zn, and Pb by atomic absorption spectroscopy (see above, this chapter). The results obtained by other methods agreed with the emission spectrometric results to within less than 20% in 17 of 24 cases and to within 40% in the remainder.

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[8] S. R. Koirtyohann and Cyrus Feldman, "The Spectrographic Determination of Trace Elements in Human Tissue," *Analytical Chemistry in Nuclear Reactor Technology, Fourth Conference, Gatlinburg, Tenn., Oct. 12–14, 1960*, TID-7606, pp 51–63.

Bone Analysis. – A Quantometric method similar to that used for the analysis of soft tissues[8] was developed for bone ash. Standards were prepared by mixing 18 trace elements (in most cases, as the oxide) with $K_2S_2O_7$, fusing the mixture, and mixing the ground melt with $Ca_3(PO_4)_2$. The $Ca_3(PO_4)_2$ used for this purpose had to be essentially free of strontium. This material was prepared by precipitating calcium with 8-hydroxyquinoline as described by Mitchell,[9] ashing the precipitate, dissolving the residue, and precipitating the calcium as the phosphate.

The accuracy of the determinations performed with the Quantometric method was checked colorimetrically for iron and by atomic absorption spectroscopy for zinc. The difference between the results is generally less than 20% of the amount present.

Analysis of Plant Material. – For the Radiation Ecology Group of the ORNL Health Physics Division, methods were developed for the determination of trace elements in plant tissue. They are very similar to those methods used in the analysis of human tissue. More than 20 elements of interest can be determined in one sample with the expenditure of only 2 to 3 man-hours of work.

Ashing Losses. – Several experiments were run to determine whether any trace elements of interest are lost during the dry ashing of plant or animal tissue. The apparatus used for this work is shown schematically in Fig. 7.4. After leaving the 450°C ashing oven, exhaust gases from the furnace were filtered through quartz wool to remove fly ash and were then heated to ~ 700°C, with oxygen being added to complete the combustion of the vapors. The combustion products were cooled and passed through traps to catch any trace elements that might have been vaporized. Operation of the ashing muffle was not affected by the trapping system. Large samples could be burned in the ashing oven, with correspondingly high sensitivity for the detection of volatilized trace elements. Analysis of the trap solutions provided a direct measure of any loss.

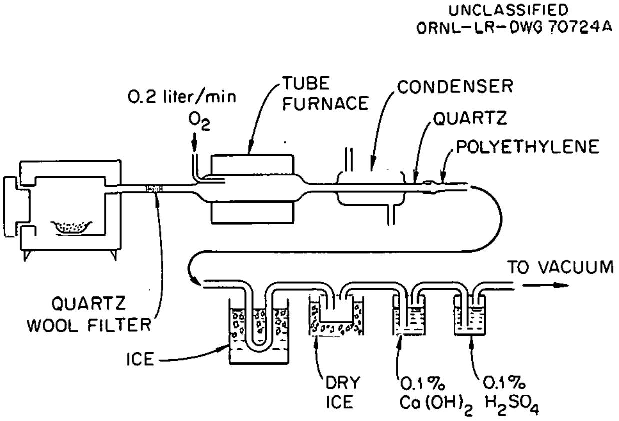

Fig. 7.4. Apparatus for Ashing-Loss Experiments.

The efficiency of the trapping system was tested by heating samples of H_3BO_3 and plant tissue simultaneously in separate dishes. The amount of boron recovered (nearly all from the Dry Ice trap)

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[9] R. L. Mitchell, "The Spectrographic Analysis of Soils, Plants and Related Materials," p 129 in *Commonwealth Bureau of Soil Science*, Technical Communication No. 44, Harpenden, England, 1948.

indicated a minimum trapping efficiency of 50%. The actual efficiency was probably higher than this, since part of the vaporized boron was undoubtedly absorbed in the ashing oven by the basic plant ash. By the same token, the loss of boron under actual ashing conditions would probably be less than 50%.

Analysis of the contents of the traps indicated that they contained, at most, small percentages of the trace elements known to be in the samples. The results are summarized in Table 7.6. In many cases, the element was not detected in the traps. In such cases, the limit of detection is given in terms of micrograms of trace element per gram of ash and is preceded by a "<" symbol. If the ash originally contained only a very small amount of the element, the limit of detection is comparatively high in terms of percentage of the original content.

Table 7.6. Volatilization of Trace Elements During Ashing of Tissue at 450°C

Element	Amount of Element Found					
	For Kidney (2 g of ash)			For Liver (6 g of ash)		
	In Ash	In Trap		In Ash	In Trap	
	(μg)	(μg)	(%)[a]	(μg)	(μg)	(%)[a]
Co				90	<12	<14
Cu	2,000	8	0.4	8,000	16	0.2
Ni	20	<3	<15	200	6	3
Cr	4	<1	<25	30	<2	<7
Pb	100	<12	<12	1,000	<24	<2.4
Al	170	20	12[b]	610	100	16[b]
Mn	260	1	0.4	1,200	4	0.3
Mo	80	<1.2	<1.5	580	<2.4	<0.4
Sn	1,500	<5	<0.3	90	<10	<11
Sr	20	<0.1	<0.5	8	<0.2	<2.5
Ba	120	<5	<4			
Ag	2	<0.4	<20	15	<0.8	<5
Zn	4,000	40	1	50,000	20	0.04
Cd	70	<4	<6	1,200	<8	<0.7
Fe	20,000	25	0.1	60,000	250	0.3

[a] % of total present in ash.

[b] Trap solution later found to contain aluminum.

Spectrographic Determination of Oxygen

R. E. Weekley

The experimental apparatus for the spectrographic determination of oxygen has been removed from the Y-12 area and relocated at X-10.

A direct-reading adapter was designed and fabricated for the Wadsworth-type spectrograph now being used. This adapter, which provides exit slit, mirror, and phototube positioning about three spectral lines of interest, is a direct replacement for the camera back normally used on this spectrograph.

In order both to compensate for the slower optical speed of the Wadsworth spectrograph and to permit the use of lower photomultiplier tube voltages (which reduces a major source of noise), the entire electronic system was modified and preamplifiers were added. Each of the preamplifiers uses a single transistor in the common emitter configuration. They are battery-operated, potted in Epoxy resin, and provide a voltage gain of about 48 db. At signal frequency of 1.8 kc, their input impedance is 330 ohms. The transfer function of the electronic system is now of the order of 10^{10} v of dc output per ampere (rms) of photocurrent. The day-to-day drift of the entire electronic system, including the photomultiplier tube, is less than 100 mv.

Both tantalum and tungsten counter electrodes of several different designs have been investigated for use in the excitation chamber. Because of fabrication problems and increased arc wandering with the metals, none was found to have any significant advantage over graphite counter electrodes.

Through the use of HgO as a comparison standard, the removal of oxygen from NBS standard steel samples has been shown to be quantitative.

Initial investigations into the determination of oxygen in Ti, Th, Zr, and Nb by use of platinum as a flux indicate that close control over the reaction parameters will be necessary in order to assure reproducible evolution of the contained oxygen.

Development work is still in progress on the determination of oxygen in MSRE fuel salt. Attempts to displace oxygen from the salt in the reaction capsule by use of CoF_3 at $\sim$600°C were unsatisfactory. Other ways of liberating oxygen at reaction temperatures higher than the 1200 to 1500°C previously achieved will be investigated in order to ensure reproducible reaction and evolution of the contained oxygen.

SPECTROCHEMICAL ANALYSES (Y-12)

C. D. Susano
J. A. Norris

Analog Computer for Direct-Reading Spectrometer

R. E. Weekley J. A. Norris

A four-by-four factorial experiment, designed by D. A. Gardiner of the Mathematics Panel, was used to test statistically the within-days and between-days variability of the combined Baird direct reader–computer system over its entire working range.[10] A total of 64 answers were computed for each of 16 channels. The variability, expressed as relative standard error at the 95% confidence level, was less than ±0.5% for the overall system.

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[10] R. E. Weekley and J. A. Norris, "Analog Computer for Direct-Reading Spectrometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 85–88.

The intercept system for the computer was changed from a fixed-point to a variable system by use of individual Helipots for each channel.

A new all-transistorized background-compensating system was designed and installed. This replaces the original system, which was installed in 1959.[11]

Spark Solution Analysis

J. A. Norris

By use of the rotating disk, high-voltage-spark solution technique, a study was made of the effect of varying the concentrations of Na, K, Al, Cu, and Zn on the ratios of the intensities of Y, La, Ce, Pr, Nd, Sm, and Lu to the intensity of Sr. The concentrations (μg/ml) of the test compounds were: Y_2O_3, 50; La_2O_3, 200; Ce_2O_3, 600; Pr_2O_3, 450; Nd_2O_3, 350; Sm_2O_3, 200; and Lu_2O_3, 15. The ranges of concentrations (μg/ml) of the added elements were from zero to those indicated as follows: Na, 960; K, 2080; Al, 2700; and Cu and Zn, 6700. The results showed no effect on the ratios within the precision of the method.

Determination of Ta/Nb Ratios

J. A. Norris

A dc-arc method was developed for determining Ta/Nb ratios in mixtures of tantalum oxides and niobium oxides. A 1-mg test portion was excited in a 10-amp dc arc, and the direct-reading spectrometer was used to record the line intensities of Ta and Nb. By use of the background-compensating system, a linear analytical curve of theoretical slope was obtained over the weight-ratio range of 0.02 to 1.0.

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[11] J. A. Norris and O. B. Rudolph, "Electronic Background-Compensating System for Photoelectric Spectrometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 65–66.

8. Mass Spectrometry

A. E. Cameron

J. R. Sites

A study of the UO_3^+ and UO_4^+ ions from $UO_{2.0}$, $UO_{2.1}$, and $UO_{2.2}$ material was made using electron bombardment ions at low temperatures from a platinum (nonoxidizing) filament.

A technique for sampling from sealed glass containers by means of an ultrasonic drill and a special vacuum-tight punch has been tested. Gases were also sampled from centrifuge cones sealed with rubber diaphragms by means of a hypodermic needle adapter.

The C^{13} contents of tagged methyl malonic and succinic acids were determined by use of the negative ions of the parent molecules.

The laboratory space that has recently become available will be used for an analytical service double-magnet mass spectrometer.

9. Optical and Electron Microscopy

M. T. Kelley
T. E. Willmarth
H. W. Wright T. G. Harmon

ELECTRON MICROSCOPY OF RADIOACTIVE MATERIALS

The development of methods and procedures suitable for the study of radioactive materials with the electron microscope has continued.

Thin-film-forming organic plastics other than Formvar[1] have been studied for use in encapsulating radioactive particles. Cellulose acetate butyrate, on examination, showed considerable promise. The introduction of butyryl groups into the cellulose acetate complex improves the moisture resistance of the polymer, thereby lessening the possibility that voids will appear in the thin film and thus cause loss of the captured particles when the film is floated off on water. It has been demonstrated[2] that cellulose acetate butyrate sheet (Triafoil BN) is an excellent material for the production of negative replicas from the surfaces of small particles. With slight modification, this technique can be adapted for use in the remotely controlled replication of radioactive particulates.

The use of electrostatic precipitation methods for the direct collection of submicron radioactive particles on electron microscope grids is being studied. Apparatus having the design features suggested by Craig[3] and Drummond[4] is being considered. Collection by such means could replace filter collection in certain ORNL experiments and thus eliminate several critical steps in the handling of dry radioactive particulates for electron microscopic observation. Sampling would be done in hot cells or glove boxes with provision for the remotely controlled insertion and removal of electron microscope grids.

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[1] T. E. Willmarth *et al.*, "Optical and Electron Microscopy," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 51–54.

[2] L. Moscou, "A Two-Step Replica Method in Electron Microscope Investigation of the Structure of Porous Aluminum Oxide Pellets," *Proc. Intern. Conf. Electron Microscopy, 4th, Berlin, 1958* 1, 444–46 (1960).

[3] D. K. Craig, *Interactions Between Radionuclides and Aerosols in the Respirable Size Range*, presented at the Sixth Annual Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 9–11, 1962.

[4] D. G. Drummond, "The Practice of Electron Microscopy," *J. Roy. Microscop. Soc.* **70**, 54 (1950).

INSTRUMENTATION

A device was purchased for vaporizing carbon and metals and for evaporating carbon and platinum simultaneously for shadowcasting according to the method of Bradley.[5] The device is far superior to the apparatus used heretofore in producing uniform homogeneous films.

RESEARCH ASSISTANCE

Research assistance in problems that required electron microscopy and electron diffraction of a wide variety of materials of interest in nuclear technology and other fields was given to research groups in the Chemistry, Reactor Chemistry, Chemical Technology, Physics, and Health Physics Divisions, and the Y-12 Development Division. Representative examples of the materials studied are: metallic silver whose formation was induced by irradiation of solutions of silver nitrate; sedimentary deposits from local river water; surfaces of platinum exposed to modulated molecular beams of helium and deuterium; steam-stripped and annealed thorium oxide gels; irradiated and nonirradiated beryllium oxide; crystals in the urania-thoria system; particulates from plasma-torch, exploding-wire, and Tesla-coil experiments; and films that contaminated the surfaces of solar reflectors. The particle-size-distribution data for aerosols produced in exploding-wire experiments and reported by Karioris, Fish, and Royster[6] were obtained from electron micrographs produced by members of this group. Five of the many electron micrographs taken for this study are reproduced in the publication by Karioris, Fish, and Royster. Typical electron micrographs from two other studies are shown in Figs. 9.1 and 9.2.

Assistance was also given to persons in the Physics and Chemistry Divisions in the vaporization and study of the following types of thin films: gold film used to provide surface conductivity on radiation detectors where the structure and thickness of the film were critical; thin films of metals (Cd, Pb, Al, Si, Mn, Ni, Fe, and Pt) or their oxides used to form metal–metal oxide laminations that were deposited as specified by J. W. T. Dabbs of the Physics Division; and thin films of Th, U, Cu, Ge^{70}, Ge^{72}, Ge^{74}, and Ge^{76} prepared for use as targets in the Van de Graaff generator.

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[5] D. E. Bradley, "Study of Background Structure in Platinum-Carbon Shadowing Deposits," *British J. Appl. Phys.* **11**, 506 (1960).

[6] F. G. Karioris, B. R. Fish, and G. W. Royster, Jr., "Aerosols from Exploding Wires," p 299 in *Exploding Wires*, vol 2 (ed. by W. G. Chace and H. K. Moore), Plenum Press, New York, 1962.

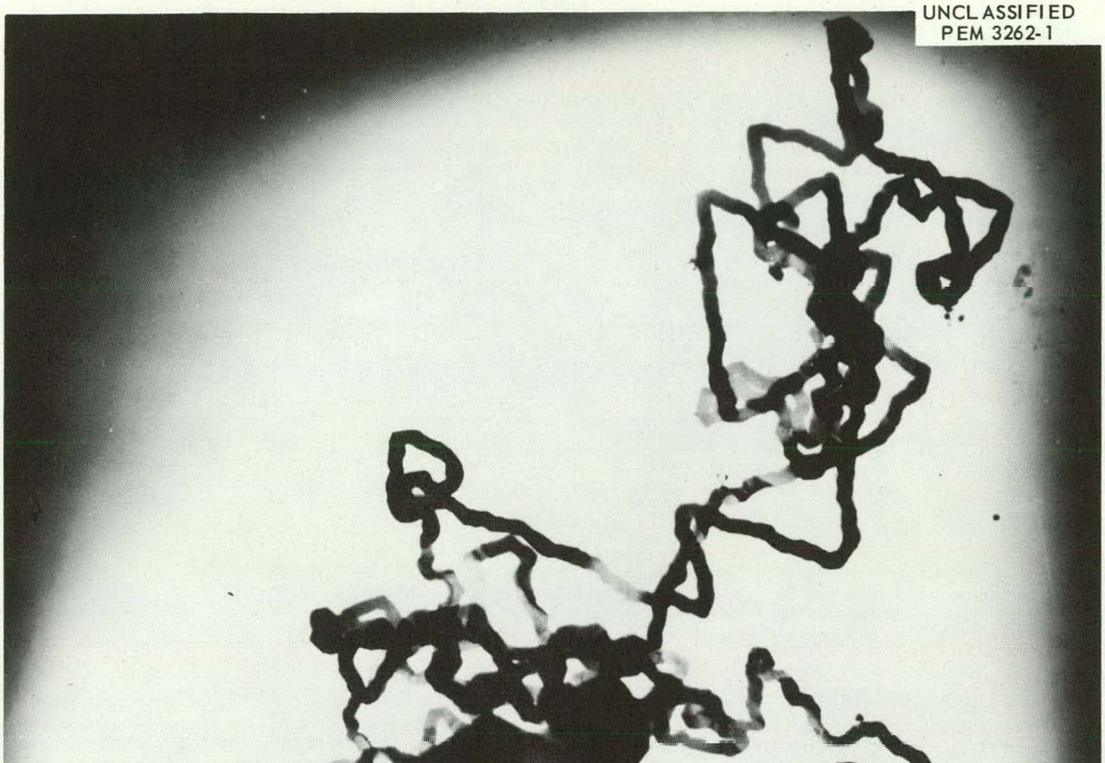

Fig. 9.1. Filament Growth from a Single Crystal of Silver Produced in a Silver Nitrate Solution by Irradiation from a Co^{60} Source. 16,000X.

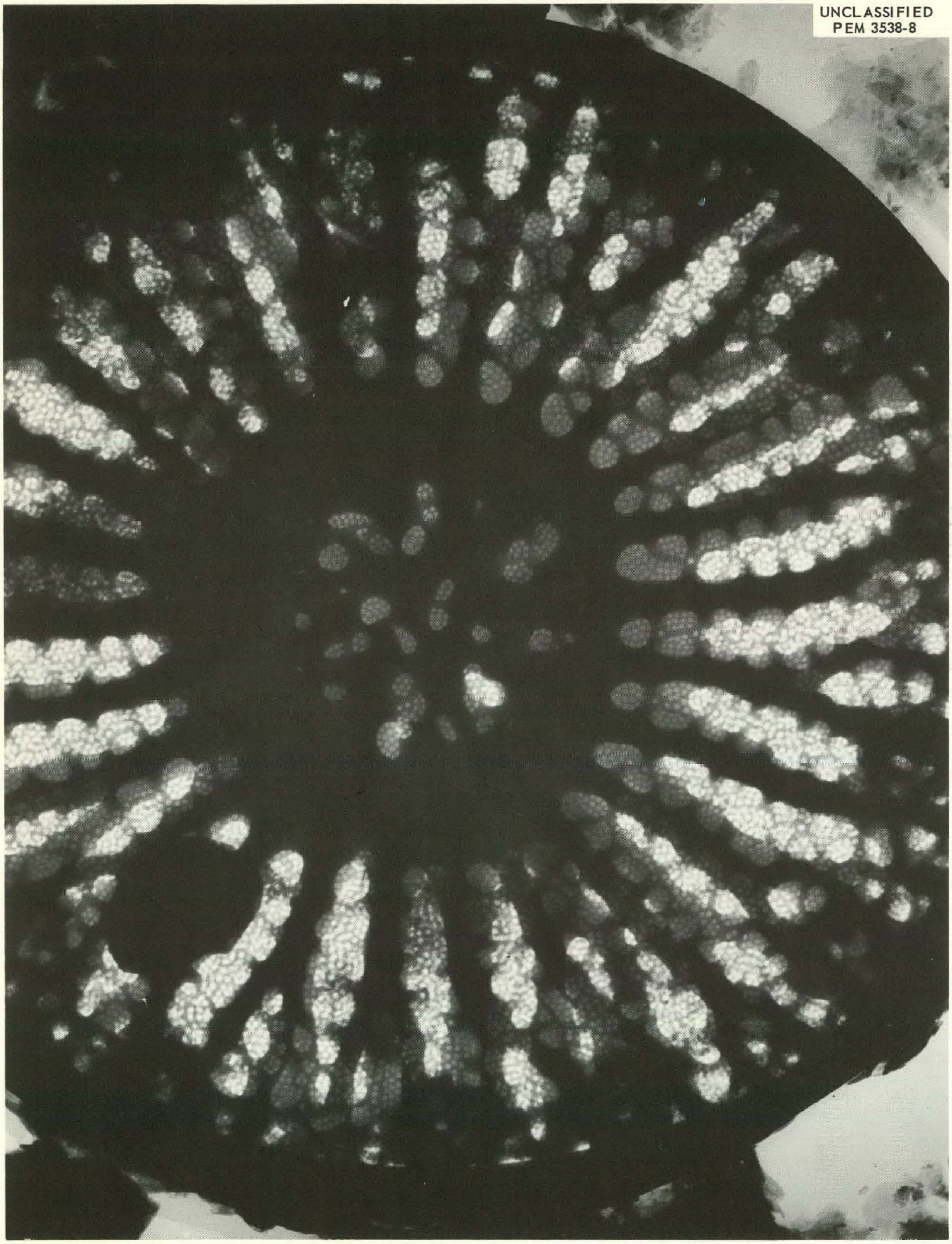

Fig. 9.2. Typical Diatom Form Found in Sediment of "K-25 River Water." 68,000X.

10. Nuclear and Radiochemical Analyses

J. C. White
W. S. Lyon

RADIOCHEMICAL STUDIES

Properties of Dialkyl Phosphorodithioic Acids in Extraction Systems

T. H. Handley

To obtain a better understanding of the reactions of dialkyl phosphorodithioic acids, $(RO)_2P(S)SH$, in solvent-extraction systems, the acid dissociation constants and partition coefficients of a number of dialkyl phosphorodithioates were determined in carbon tetrachloride, methyl isobutyl ketone, and *n*-amyl acetate. Also, the solubility of the di-*n*-butyl phosphorodithioate was determined in aqueous solutions of HCl and of NaCl, and the rate of decomposition of the reagent in carbon tetrachloride was measured. The values obtained were compared with those for the corresponding dialkyl phosphoric acids and for diphenyl phosphinodithioic acid. This work is being done jointly with Raquel H. Zucal[1] and J. A. Dean;[2] it is described in detail in a paper submitted for publication in *Analytical Chemistry.*

Complex Formation of Zinc with Dialkyl Phosphorodithioic Acids

T. H. Handley

Dialkyl phosphorodithioic acids were screened in acid media for their selectivity in liquid-liquid partition of metallic ions. The metal complexes have a very low solubility in water but can be extracted into a number of organic solvents. Little is known about systems that contain thiono and thiolo phosphorus groups. Hence, the principal objective in this investigation was to establish the dominant zinc species in the organic and aqueous phases under various conditions of hydrogen-ion concentration and reagent concentration and with different types of organic solvents. Zinc phosphorodithioate was selected as a representative of the group of metal phosphorodithioates that rapidly attain equilibrium in weak acid solutions without a concomitant salt or solvent effect. The overall extraction constant, the chelate formation constant, and the partition coefficient of the zinc complex were determined. Knowledge of these constants increases the usefulness and specificity of application of phosphorodithioic acids as extractants and permits prediction of the effects of masking agents on the extraction equilibrium without the necessity of screening each masking agent individually.

This work was done jointly with J. A. Dean[2] and Raquel H. Zucal.[1] A paper that describes this work was submitted for publication in *Analytical Chemistry.*

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[1] Present address, Argentina Atomic Energy Commission, Buneos Aires, Argentina.

[2] University of Tennessee, Knoxville.

Di-*n*-butyl Phosphorothioic Acid as an Extractant for Metallic Ions

T. H. Handley

Di-*n*-butyl phosphorothioic acid (5 w/v % in CCl_4) was evaluated as a reagent for extracting metallic ions from aqueous solutions of HCl or H_2SO_4. The results have been arranged in two periodic-table type charts as plots of log distribution ratio (*D*) vs log $[H^+]$. Of 32 metallic ions studied, 18 were found to extract in significant amounts. In general, those metallic ions that form insoluble sulfides have the highest *D*. The relative order of extraction of 11 metal di-*n*-butyl phosphorothioate complexes was determined. The effect of di-*n*-butyl phosphorothioic acid concentration on the *D* values for Ag^+, Hg^{2+}, Zn^{2+}, and In^{3+} was investigated. The influence of various organic solvents on the *D* values for Hg^{2+} and Zn^{2+} was studied. The limits of extraction for Ag^+, Hg^{2+}, and Pd^{2+} were in the parts-per-billion range. The nature of zinc di-*n*-butyl phosphorothioate as it exists in the aqueous and organic phases was investigated. A paper that describes this work was submitted to *Analytical Chemistry* for publication.

Extraction of Fluo-Anions with Tetraphenylarsonium Chloride

G. Goldstein

Tetraphenylarsonium chloride forms extractable ion-association compounds with many types of anions such as oxy-, chloro-, bromo-, iodo-, and thiocyanato- anions. Tests are in progress to determine whether fluo-anions also form such extractable compounds; some results are shown in Fig. 10.1. The ions Sb^{3+}, Sc^{3+}, Hf^{4+}, and Sn^{4+} were not extracted under the conditions indicated in Fig. 10.1. Variations in the sulfuric acid concentration from 0.36 to 6 *M* had no effect on the extractability of tantalum but caused the extractability of niobium to decrease. Radioactive tracers were used in these experiments because the solubility of the extractable compounds in $CHCl_3$ is limited. The solubility of the tantalum ion-dissociation compound, for example, is only about 6 μg/ml. Several ions are yet to be tested.

It appears that this extraction may provide an extremely selective means of separating small amounts of tantalum and may also be useful for studying fluoride complexation. Attempts are being made to prepare a pure sample of tetraphenylarsonium fluotantalate in order to study the exchange of Ta^{182} between this compound and the fluotantalate ion.

Valence States of Radioisotopes in Radioisotope Products

T. H. Handley G. Goldstein

Work was continued to determine the valence states of the radioisotopes in various ORNL radioisotope products. The results are presented in Table 10.1.

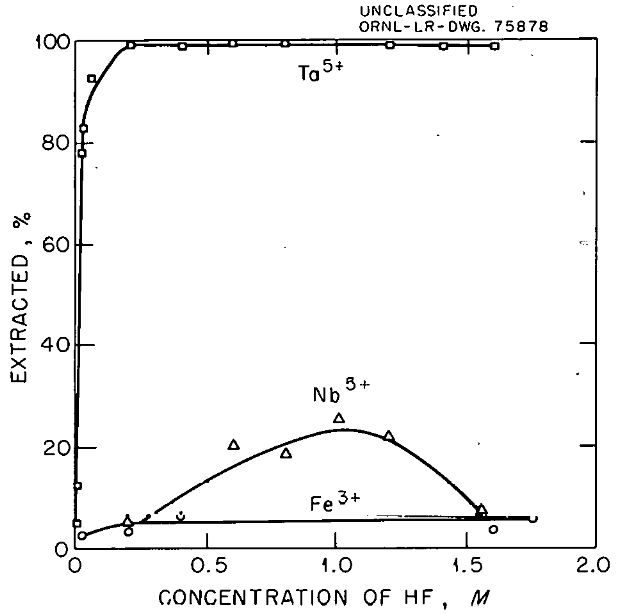

Fig. 10.1. Extraction of Fluo-Anions with Tetraphenylarsonium Chloride. Aqueous phase: 10-ml volume; $[H_2SO_4]$, 0.36 *M*; [TPAC], 4.5×10^{-3} *M*. Organic phase: 10 ml $CHCl_3$. Equilibration time, 5 min.

Table 10.1. Valence States of Radioisotopes in Some ORNL Radioisotope Products

Radioisotope Product	Valence-State Distribution	
	Component	(%)
As^{77}	As^{3+}	90
	As^{5+}	10
Sb^{124}	Sb^{3+}	10
	Sb^{5+}	90
Sb^{125}	Sb^{3+}	10
	Sb^{5+}	90
Os^{191}	OsO_4	5
	$OsO_4{}^{2-}$	60
	Others	35
Ir^{192a}	$IrCl_6{}^{2-}$	50
	$IrCl_6{}^{3-}$	25
	$IrCl_5(H_2O)^{2-}$	25

[a] Nonradioactive solution.

The isotopes As^{77}, Sb^{124}, and Sb^{125} were studied by extraction techniques essentially the same as those reported previously.[3]

Osmium-191 was studied by adding a portion of the As^{77} product to solutions of various acids and immediately extracting three times with an equal volume of CCl_4. Under these conditions, almost all the OsO_4 is extracted, and osmium in the lower valence states remains in the aqueous phase. Only about 5% of the radioactivity was extracted from 2.5 *M* H_2SO_4 solutions, but about 60% was extracted from 5 *M* HNO_3. This result indicated that 5% of the total osmium is present as OsO_4 and 55% as some easily oxidizable form, possibly $OsO_4{}^{2-}$. The balance of the osmium is most likely present in various hydrolyzed forms that are not easily converted to OsO_4.

To determine the valence states of iridium in Ir^{192} product, a nonradioactive solution of iridium (3×10^{-4} *M* $IrCl_6{}^{2-}$ in 0.1 *M* HCl) was prepared to simulate the isotope solution, and its absorption

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[3] F. F. Dyer and G. W. Leddicotte, "Studies of Valence States of Radioisotopes," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, p 75.

spectrum was measured. Over 60 days, the absorbance associated with the $IrCl_6^{2-}$ ion decreased, probably because of the reduction of $IrCl_6^{2-}$ to $IrCl_6^{3-}$. Absorption spectra of $IrCl_6^{2-}$ solutions were also measured. As the solutions aged, the absorbance shifted to the ultraviolet, an effect attributed to the formation of $IrCl_5(H_2O)^{2-}$. On the basis of these spectra, the amounts of each of these species present after 60 days were estimated.

Separation of Selenium from Tellurium by Liquid-Liquid Extraction

A. P. Grimanis[4] G. W. Leddicotte[5]

A chemical method was developed for the separation of submicrogram, microgram, and milligram amounts of Se^{4+} from Te^{6+} by extraction of Se^{4+} (apparently as $SeBr_4$) into benzene from either 1 *M* HBr–7 *M* $HClO_4$ or 1 *M* HBr–6 *M* H_2SO_4 solutions. It was established that the extracted species consists of selenium and bromine in a ratio of 1 to 4. Equilibrium is reached in less than 2 min. For both systems, more than 98% of the Se^{4+} is extracted, and less than 0.1% of the tellurium is coextracted. Other metallic ions tested were Ga^{3+}, Sb^{3+}, As^{3+}, Fe^{3+}, Cr^{3+}, Pa^{5+}, Au^{3+}, Cu^{2+}, Sn^{2+}, and Hg^{2+}. Of these, As^{3+} (99%) and Sb^{3+} (12%) were extracted. Less than 0.4% of each of the other metal ions was extracted. The solvents, toluene and xylene, were as effective as benzene.

Transuranium Chemistry: Separation of Americium from Other Elements

F. L. Moore

A new, simple, analytical radiochemical method for the determination of americium tracer (i.e., submicrogram amounts) involves the silver-catalyzed peroxydisulfate oxidation of trivalent americium to the sexivalent state. Fluoride is used to stabilize the americyl ion during a series of lanthanum fluoride scavenges. Excellent separation of americium tracer is effected from Cm, Bk, Cf, Pu, U, Th, Cs, Sr, Zr, Nb, Ru, Fe, Al, and the lanthanide elements. The method is useful in several analytical and process applications. Complete details are available in a report[6] and have been submitted for publication in *Analytical Chemistry.*

APPLICATION OF RADIOISOTOPES TO ANALYTICAL CHEMISTRY

Radiotracer Method for Fluoride

F. L. Moore

A novel radiotracer method was developed for fluoride ion. It is based on the highly selective extraction of the Ta^{182}-fluoro complex species. The system diisobutyl ketone–sulfuric acid provides

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[4] Nuclear Research Center, Greek Atomic Energy Commission, Athens.

[5] Present address, Union Carbide Nuclear Company, Tuxedo, New York.

[6] F. L. Moore, *Separation of Americium from Other Elements. Application to the Purification and Radiochemical Determination of Americium,* Sept. 25, 1962 (unpublished report).

optimum conditions for speed, high selectivity, adaptability to colored solutions, and high tolerance for oxidants and does not require critical control of pH or temperature. The Ta^{182} extracted into the organic phase is proportional to the fluoride-ion concentration of the aqueous phase over the range 40 to 200 $\mu g/ml$. Several useful applications of the method are described in detail in a forthcoming CF memorandum and in an article to be submitted for publication in *Analytical Chemistry.*

Determination of Alkaline-Earth Elements

S. A. Reynolds

The alkaline-earth elements are of importance in biology, in water technology, as components of building materials, and in fall-out problems. Simple, rapid, and reliable methods for the determination of these elements are, therefore, needed. The availability of gamma-active tracers (Ca^{47}, Sr^{85}, and Ba^{133}) from the ORNL Isotopes Division encouraged the study of isotope-dilution methods, used together with flame spectrophotometry for determining low concentrations and with titrimetry for high concentrations. Radiometric yield corrections are always applied.

Four types of samples are recognized: (1) Ca, Sr, and Ba low in concentration; (2) Ca high, Sr and Ba low; (3) Sr high, Ca and Ba low; and (4) Ba high, Ca and Sr low. The second type is most commonly encountered in natural materials. Methods are being developed for all cases.

Most of the data collected to date have been relative to individual steps in the required separation procedures, such as precipitation of a given element, and coprecipitation, or "carrying," of one of the elements by compounds of another.

Separation of Barium. – The determination of barium was studied first, since its concentration is usually lowest and it requires the greatest decontamination from the other elements. A modification of a method developed for radium was used for barium.[7] The following steps are included: add 50 mg Pb^{2+} and then citric acid; precipitate hot with H_2SO_4; wash $Pb(Ba)SO_4$ with concd HNO_3 and H_2O; dissolve $Pb(Ba)SO_4$ in ammonium EDTA; add 0.1 g of Dowex 50 and then acetic acid; stir 10 min; wash resin with H_2O; desorb Ba^{2+} in ammonium EDTA (10 min); and measure the barium by flame spectrophotometry. Precipitation of $PbSO_4$ from an acid solution of citrate serves to concentrate barium and to isolate it from many other substances. Dissolution of the precipitate in EDTA, with

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[7] A. S. Goldin, "Determination of Dissolved Radium," *Anal. Chem.* **33**, 406 (1961).

Table 10.2. Behavior of Alkaline-Earth Elements in Barium Sulfate Procedure

Alkaline-Earth Elements		Distribution (%)		
Identity	Weight Range (mg)	In SO_4^{2-} Waste	In Resin Waste	In Product
Ba	10^{-3} to 1	0.6 to 17	3 to 26	61 to 77
Sr	10^{-4} to 100	20 to 44		52 to 80
Ca	10^{-2} to 100	99 to 100		~0.5

subsequent decomposition of the Ba-EDTA complex by acetic acid, permits recovery of barium without lead. Washes of the original sulfate precipitate with concd HNO_3 and water resulted in tolerable losses of barium, but washes with dilute HNO_3 entailed large losses. If sufficient barium is present, the sulfate precipitates upon acidification of the EDTA solution. It was found in the present study that micro quantities are recovered by adsorption on a small amount of Dowex 50 cation-exchange resin. Adsorption on paper pulp was unsatisfactory for this purpose. Barium is separated from calcium by this procedure but not from strontium (Table 10.2), although better separation is indicated by recent incomplete experiments. The classical chromate method,[8] with $PbCrO_4$ as carrier, if required, serves for the latter separation (Table 10.3); further, if the level of barium is high (sample type 4), dissolution and titration of the chromate permits quantitative determination.

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[8] N. H. Furman (ed.), *Scott's Standard Methods of Chemical Analysis*, 6th ed., vol 1, pp 140–49, Van Nostrand, New York, 1962.

Table 10.3. Behavior of Alkaline-Earth Elements in Barium Chromate Procedure

Element		Distribution (%)		
Identity	Weight Range (mg)	In First Waste[a]	In Second Waste[a]	In Product
Ba	10^{-2} to 100	0.6 to 1.7	0.3 to 20	68 to 96
Sr	10^{-4} to 100	96 to 99	1 to 4	<0.07
Ca	10^{-2} to 100	99 to 100	1 to 2	<0.3

[a] Supernatant solutions from chromate precipitations.

Table 10.4. Coprecipitation of Barium with Calcium Oxalate

Present (mg)		Barium Coprecipitated (%)	
Ca	Ba	In First Precipitate	In Second Precipitate
10	0.001	85	58
	0.01	72	33
	0.1	68	30
	1	62	16
	5	50, 57	7, 5
	10	66	18
50	0.001	94	51
	0.01	89	37
	0.1	65	42
	1	62	24
	5	51	22
	10	70	26

Studies of Barium Oxalate. – The coprecipitation of barium with calcium oxalate could be of importance in some analyses. Further, there exist in the literature certain discrepancies as to the extent of coprecipitation of amounts of barium below several milligrams; opinions included "practically all,"[8] "incompletely,"[9] and "does not coprecipitate."[10] A series of experiments in which Ba^{133} tracer was used (Table 10.4) indicated that in the conventional double precipitation of CaC_2O_4 coprecipitation of barium is incomplete and that the apparent solubility of BaC_2O_4 depends on the amount of barium present (i.e., that both "carrying" and solubility are important). Centrifugation was used to isolate solid phases; therefore, only moderate precision was expected.

Approximate solubilities of BaC_2O_4 were measured under various conditions (Table 10.5). The solubility in water at 25°C is in good agreement with the accepted value, 10.87 mg/100 ml.[11] The increased

Table 10.5. Approximate Solubilities of Barium Oxalate

Composition of Media[a]						BaC_2O_4 Solubility (mg/100 ml)
$(NH_4)_2C_2O_4$ (*M*)	NH_4Cl (*M*)	NaCl (*M*)	NH_4NO_3 (*M*)	Ca (mg)	Mg (mg)	
b						$10._7$
0.008						12
0.04						7.9[c]
0.07						8.4[c]
0.07	0.16					7.9
0.07	0.65					12
0.07	1.2					17
0.07		0.17				9.0
0.07		0.65				15
0.07			0.06			7.5
0.07			0.22			8.5
0.07				10[d]		15
0.07				50[d]		14
0.07					10	8.0
0.07					25[d]	13
0.07					50[d]	22

[a] Temperature ~90°C, exceptfirst entry.

[b] H_2O, 25°C.

[c] Probably insignificantly different.

[d] Precipitation of calcium or magnesium occurred.

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[9] W. F. Hillebrand *et al.*, *Applied Inorganic Analysis*, 2d ed., p 614, Wiley, New York, 1953.

[10] L. C. Peck and V. C. Smith, "Removal of Manganese from Solutions Prior to Determination of Calcium and Magnesium," p 401 in *U.S. Geological Survey Professional Paper 424-D*, U.S. Govt. Printing Office, Washington, D.C., 1961.

[11] W. F. Linke, *Solubilities of Inorganic and Metal Organic Compounds*, 4th ed., p 330, Van Nostrand, Princeton, N.J., 1958.

solubility observed in the presence of NH_4Cl, NaCl, and during coprecipitation with calcium or magnesium is not surprising in view of a similar observation[11] with respect to KCl, KNO_3, $MnCl_2$, and uranyl oxalate.

Calcium and Strontium. – Recoveries of calcium and strontium were 81 to 92% by double precipitation as oxalates following removal of barium as chromate (Table 10.3). Analyses of NBS standard samples, reagents, river water, and river silt are in progress. Details of this research were presented orally.[12]

Determination of Beryllium by the Photoneutron Method

G. Goldstein

Equipment was designed and fabricated for determining beryllium by means of the $Be^9(\gamma,n)Be^8$ reaction. The design, based largely on British designs,[13] is shown in Figs. 10.2 and 10.3. The cross section for this reaction reaches a peak of about 1 mb at a gamma energy of 1.7 Mev. An Sb^{124} gamma source (branching $\sim$46% through the 1.7-Mev gamma) was prepared by activating 40 mg of Sb^{123} contained in a sealed quartz tube, which was located in an aluminum can. The source is positioned in a brass tube over which a second brass tube can slip. This second tube passes through and carries a quartz sample container, which holds about 5 ml of solution. Source and sample are both placed in an annular lead cylinder to attenuate the gamma radiation. The neutron-detector unit consists of five 2-in. $B^{10}F_3$ counter tubes arranged in a polyethylene moderator. The results of initial tests with an Am^{241}-Be neutron source indicate that the instrument is operating satisfactorily and with about 5% efficiency for neutrons of 4-Mev average energy. In tests with a 200-mr/hr Sb^{124} source, the counting rate due to gamma radiation could be eliminated by proper choice of pulse-height-discriminator voltage, with only a small loss in neutron counting rate.

Surface-Area Measurements

F. F. Dyer

Effort described previously[14,15] to measure the surface area of UO_2 powder by isotope exchange in an aqueous medium was continued. The powder is dispersed in the solution, U^{237} tracer is added, and the extent of exchange between the U^{237} atoms in solution and the uranium atoms in the powder is followed as a function of time in order to measure the surface area. An extensive study was made with UO_2 by use of 0.001 *f* $Na_4P_2O_7$ as the aqueous medium. The results were very erratic and did not give usable exchange curves. The use of this medium was therefore discontinued. Since previous

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[12] S. A. Reynolds, "Determination of Thorium and Alkaline-Earth Elements by Isotope Dilution," presented at the Sixth Annual Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962.

[13] G. W. C. Milner and J. W. Edwards, *The Determination of Beryllium by the Photoneutron Method*, AERE-R-2965 (June 1959).

[14] F. F. Dyer and G. W. Leddicotte, "Measurement of Surface Area of Uranium Oxide by Use of U^{237} Tracer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 47–48.

[15] R. L. Ferguson and G. W. Leddicotte, *Surface-Exchange Method for Determination of Surface Area of UO_2 Powder*, Aug. 6, 1959 (unpublished report).

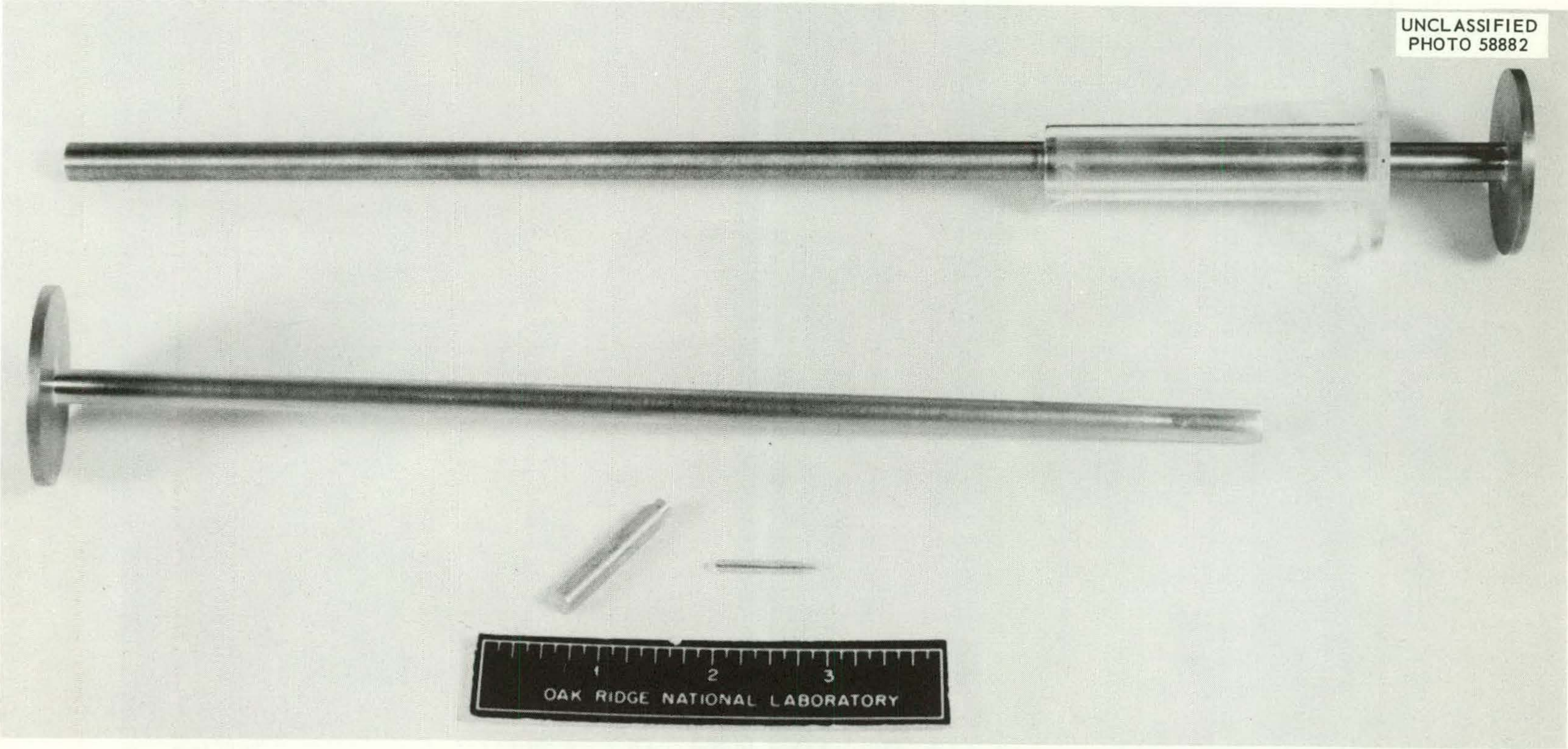

Fig. 10.2. Source, Container, and Sample-Loading Arrangement for the Determination of Beryllium by the Photoneutron Method.

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Fig. 10.3. Neutron-Detection Assembly for the Determination of Beryllium by the Photoneutron Method.

measurements indicated that slightly acid media may be more amenable to such measurements, additional experiments in such media are planned.

Because the results obtained with UO_2 were unsatisfactory, the method was applied to CaF_2. Calcium fluoride powder was dispersed in 0.001 / HNO_3, and the exchange of Ca^{45} ions in the solution with the calcium atoms on the powder was followed. This system gave exchange curves from which it was possible to calculate the surface area of the CaF_2. From a number of exchange measurements, the surface area of the CaF_2 was calculated to be 4.0 ± 0.8 m^2/g; by the BET nitrogen-adsorption method, it was found to be 15 ± 2 m^2/g.[16] Two additional measurements were made in which the powder was placed under vacuum before the solution was added to it. The surface areas calculated from these measurements were 7 and 8 m^2/g. Thus, it appears that reproducible measurements of the surface area of CaF_2 can be made in this manner, although the calculated values for surface area depend on what type of pretreatment the powder has received. The data do not, however, agree with those obtained by BET measurements.

Determination of Sulfate with Cr^{51}

W. J. Armento[17] C. E. Larson[18]

A new radiometric method was developed for the determination of sulfate. Barium chromate, labeled with Cr^{51} (27.8 d, gamma-emitter) and dissolved in dilute hydrochloric acid, is added in excess to a sulfate solution to precipitate barium sulfate. After addition of excess ammonium hydroxide to precipitate excess barium chromate, an aliquot of the supernate is counted in a well-type gamma-scintillation counter. The counting rate is linear with the concentration of sulfate present over a wide range of concentration. Most of the interferences of previous methods are avoided.

A communication that describes this work was accepted for publication in *Analytical Chemistry*.

CHEMISTRY OF PRESSURIZED-WATER IN-PILE LOOP OF THE OAK RIDGE RESEARCH REACTOR

T. H. Handley

The transport and deposition of corrosion products (crud) and long-lived radionuclides are important unsolved problems associated with the water chemistry of primary systems of the Pressurized Water Reactor (PWR). The crud fouls heat-transfer surfaces and impairs the operating reliability of mechanical systems exposed to primary water. The long-lived radionuclides, which originate from the neutron activation of corrosion products in the reactor flux, cause a long-term buildup of radiation throughout the primary system. In undertaking a study of the water chemistry of the pressurized-water loop of the ORR,

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[16] Measurements made by W. R. Laing of the Analytical Chemistry Division.

[17] Graduate student from Department of Chemistry, Georgia Institute of Technology, Atlanta, Ga.

[18] Union Carbide Nuclear Company.

the primary objective was to gain knowledge of the nature and behavior of water-borne radionuclides and crud in the hope that new methods for their control would be suggested.

Results obtained thus far provide strong evidence that in the neutral PWR system a large part of the low-level, longer-lived, water-borne radionuclides (principally Mn^{54}, Co^{58}, Fe^{59}, and Co^{60}) are present during normal loop operation as dissolved ionic material. Thus, tests in which cooled water samples were passed through a series of Millipore filters, used in order of decreasing porosity, showed a lower limit to crud particle size of $\sim 0.5\ \mu$, with virtually all remaining water-borne radioactivity passing through a 0.01-μ filter. This "nonfilterable" activity was absorbed reversibly by cellulose backing pads used in some filtration tests. Such radioactivity, when absorbed on chromatographic paper, was found in electromigration tests to move toward the cathode with a velocity expected for simple cations. If it is assumed that the specific activity for the dissolved material was the same as was found for the filterable crud, the resulting concentration of ionic material (calculated on the assumption that all the nonfilterable activity is present as simple ions) was in reasonable agreement with the ion concentration indicated from the observed conductivity of loop water.

Other results indicate that the dissolved radioisotopes exchange at an appreciable rate with the radioisotopes in the crud. This crud was shown by electron micrographs to be crystalline and by x-ray diffraction patterns to exhibit the structure of magnetite (Fe_3O_4), which is often a principal constituent of PWR crud. The apparent lower limit to particle size indicates that recrystallization occurs, which would result in exchange of radioactivity. The assumption of equal specific activities for the dissolved material and the the crud is consistent with such exchange.

Since Fe_3O_4 is the stable oxide of iron in such systems and is a principal constituent of crud, it may possibly be suitable as a high-temperature-filter ion-exchange medium. If this constituent of crud both supplies and exchanges with the ionic material in the high-temperature water, then the introduction of a bed of nonradioactivated Fe_3O_4 into the PWR coolant (pH ~ 7) system might, by the same process which contributes to the transport of activity, accumulate the dissolved activity without otherwise disturbing the chemical or nuclear behavior of the system. Accordingly, tests are in progress to examine the suitability of magnetite as such a high-temperature purification medium. This work is being done jointly with C. F. Baes, Jr.[19]

MEASUREMENT OF RADIOACTIVITY

Decay of Au^{199}

R. L. Hahn W. S. Lyon

The decay of 3.15-d Au^{199} was investigated because the elucidation of the decay scheme is in itself of interest and because this information is of use in the study of burnup of Au^{198} in nuclear reactors. Gold-199 has been studied previously;[20,21] however, improved techniques in gamma-ray

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[19] Reactor Chemistry Division.

[20] P. M. Sherk and R. D. Hill, "The Disintegration Scheme of Au^{199}," *Phys. Rev.* **83**, 1097 (1951).

[21] P. J. Cressman and R. G. Wilkinson, "Internal Conversion Coefficients of M1 Gamma Rays of Au^{199} and Au^{195}," *Phys. Rev.* **109**, 872 (1958).

spectrometry and in 4π-beta-gamma coincidence measurements are useful in the determination of the intensities of the gamma rays and the electron shell vacancies.

Gold-199 was produced by low-energy neutron irradiation of natural platinum; the Pt^{199} formed in the reaction was then "milked" by repeated extractions with ethyl acetate to obtain the Au^{199} daughter carrier-free.

The intensities, per Au^{199} disintegration, were observed to be 0.368 ± 0.011, 0.0774 ± 0.0022, and 0.0031 ± 0.0015 for the 0.158-, 0.208-, and 0.050-Mev gamma rays, respectively, and 0.219 ± 0.010 and 0.176 ± 0.005 for the *L*- and *K*-shell vacancies, respectively. These data and the relative conversion electron yields of Cressman and Wilkinson[21] were used to obtain the following empirical values for the internal conversion coefficients: in the *K* shell, 0.313 ± 0.013 and 0.790 ± 0.030 for the 0.158- and 0.208-Mev gamma rays, respectively, and in the *L* shell, 0.492 ± 0.029, 0.149 ± 0.017, and 8.5 ± 4.1 for the 0.158-, 0.208-, and 0.050-Mev gamma rays, respectively.

An article that describes this work was accepted for publication in *The Physical Review.*

Study of Separations of Isomers of Tellurium Isotopes

R. L. Hahn

The chemical separation of radioactive isomers of the same isotope was demonstrated some 20 years ago by DeVault and Libby[22] and by Segré, Halford, and Seaborg.[23] The conditions necessary for effecting such a separation are that (1) the main decay mode of the upper state is by isomeric transition to the lower state, (2) this isomeric transition has a large probability for internal conversion, (3) the half-life of the upper state is long compared with that of the lower state so that an equilibrium mixture of the isomeric activities can be obtained, and (4) two stable chemical forms of the isotope that do not undergo rapid exchange reactions can be prepared.

The tellurium isotopes of masses 121, 127, 129, and 131 satisfy the above requirements. Thus, for example, if an equilibrium mixture of the metastable- and ground-state activities of Te^{127}, with half-lives of 103 d and 9.3 h, respectively, is obtained and is oxidized to the Te^{6+} chemical form, it is found that a later separation of the Te^{4+} chemical form from the solution will yield a large fraction of pure 9.3-h Te^{127g}. However, previous work on isomer milkings[24,25] of Te^{127} and Te^{129} has led to discrepancies in the reported yields of separated daughter activities and in the interpretations of the observed phenomena.

In the present work the isomer separations of these tellurium isotopes are being reexamined with the aid of various counting techniques – for example, 4π-beta counting and differential gamma counting. It is expected that the results of these experiments will yield information about the internal conversion probabilities in these isotopes and about the chemical processes leading to the observed separations.

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[22] D. DeVault and W. F. Libby, "Decay of the 4.5-Hour Br^{80} Isomer," *Phys. Rev.* 58, 688 (1940).

[23] E. Segré, R. S. Halford, and G. T. Seaborg, "Chemical Separation of Nuclear Isomers," *Phys. Rev.* 55, 321 (1939).

[24] G. T. Seaborg, G. Friedlander, and J. W. Kennedy, "Mechanism of Nuclear Isomer Separation Process," *J. Am. Chem. Soc.* 62, 1309 (1940).

[25] R. R. Williams, Jr., "Nuclear Chemistry of Tellurium: Chemical Effects of Isomeric Transition," *J. Chem. Phys.* 16, 513 (1948).

Properties of Nuclear Levels in a Number of Odd-A Nuclei ($151 \leqq A \leqq 191$)

T. H. Handley

In order to obtain more evidence about the systematic behavior of nuclear energy levels in the deformed region, a number of neutron-deficient odd-mass-number (odd-A) activities were studied by means of internal-conversion-electron spectrographs. Some measurements were made with a scintillation counter. Level schemes are postulated for decays to the following odd-neutron nuclei:

$$\begin{gathered} \mathrm{Pm}^{151} \rightarrow \mathrm{Sm}^{151},\ \mathrm{Tb}^{151} \rightarrow \mathrm{Gd}^{151},\ \mathrm{Tb}^{153} \rightarrow \mathrm{Gd}^{153},\ \mathrm{Tb}^{155} \rightarrow \mathrm{Gd}^{155}, \\ \mathrm{Eu}^{157} \rightarrow \mathrm{Gd}^{157},\ \mathrm{Tm}^{163} \rightarrow \mathrm{Er}^{163},\ \mathrm{Tm}^{165} \rightarrow \mathrm{Er}^{165},\ \mathrm{Ho}^{167} \rightarrow \mathrm{Er}^{167}, \\ \mathrm{Re}^{183} \rightarrow \mathrm{W}^{183},\ \mathrm{Ir}^{185} \rightarrow \mathrm{Os}^{185},\ \mathrm{Ir}^{187} \rightarrow \mathrm{Os}^{187},\ \text{and } \mathrm{Ir}^{189} \rightarrow \mathrm{Os}^{189}. \end{gathered}$$

As a corollary experiment, data were also taken for the odd-proton nuclei populated in the decays $\mathrm{Pt}^{189} \rightarrow \mathrm{Ir}^{189}$ and $\mathrm{Pt}^{191} \rightarrow \mathrm{Ir}^{191}$. The proposed states were interpreted by means of the Mottelson and Nilsson predictions. Some conclusions may be drawn concerning such properties of these orbitals as moments of inertia, $M1/E2$ mixing ratios, and positions of the intrinsic excitations. Ratios of gamma-ray transition probabilities from the various states were determined. Previously published studies of odd-A nuclei in the region of odd-N numbers 99 through 107 are incorporated in the particle energy-level systematics. This work was done jointly with B. Harmatz[26] and J. W. Mihelich.[27] A paper on this subject was published in *The Physical Review*.

New Isotope Products

K^{43} (W. S. Lyon). – Calcium enriched in the isotope of mass 43 was irradiated in the ORR by members of the Isotopes Division in an effort to produce K^{43} by the reaction $Ca^{43}(n,p)K^{43}$. The radioisotope K^{43} is a 22-h activity, emits negatrons, and has a number of gamma-ray transitions; the intensities of the gamma rays are somewhat uncertain. Because of the preliminary nature of this experiment, no chemistry was performed on the sample; hence, data were obtained only by decay and gamma-ray measurements. The following radionuclides were positively identified in the K^{43} product:

Radionuclide	Activity (dis min^{-1} ml^{-1} $\times 10^{-3}$)
Ir^{19}	6.5 (gammas)[a]
Na^{23}	1.1
K^{43}	7.7
Ca^{47}	1
Zn^{65}	0.7
La^{140}	2.2
Lu^{177}	52

[a] Based on number of 200-Mev gamma rays; branching not known.

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[26] Electronuclear Division.

[27] University of Notre Dame, Notre Dame, Indiana.

The isotopes Na^{24}, Zn^{65}, La^{140}, Lu^{177}, and Ir^{192} are all probably neutron-capture products of contaminants present in the target materials; the presence of Ca^{47} is to be expected since the target was calcium. It appears obvious that a chemical separation should yield a K^{43} product of satisfactory quality. It is planned to separate K^{43} from the next preparation and to study its nuclear properties. Another problem brought to attention by this work, that is, the gamma branching in Lu^{177}, will be studied soon.

Br^{77} (W. S. Lyon). – In an experiment similar to that for the production of K^{43}, natural selenium was irradiated in the 86-Inch Cyclotron for 30 min, and bromine was extracted from the target. It was anticipated that Br^{77} would be a primary product resulting from both (p, n) and $(p, 2n)$ reactions on stable selenium nuclides. The amounts of three bromine nuclides found from gamma spectrometric studies and decay measurements were:

Radionuclide	Activity at Cyclotron "Off Time" ($\text{dis sec}^{-1}\ \text{ml}^{-1} \times 10^{-6}$)
Br^{76}	5.7
Br^{77}	0.38
Br^{82}	1.5

It is somewhat puzzling that the large amount of Br^{76} was present. The amount of each nuclide was calculated from gamma-branching data reported in the nuclear data compilation.[28] These literature data could be in error, but it is thought they are not in error by more than +25%. Interesting and useful areas of future study include the elucidation of the chemical states of bromine radioisotopes found, absolute gamma branching in the three bromine radionuclides formed, production of each nuclide as a function of proton energy, and relative (and perhaps absolute) cross sections for the production of the three bromine nuclides.

I^{123} (J. S. Eldridge). – A 49-mg sample of tellurium, enriched in isotope of mass 123 to 48.6% was bombarded with protons for 3 hr in the 86-Inch Cyclotron in order to produce I^{123} by the $Te^{123}(p, n)I^{123}$ reaction. The bombardment and processing of the target material were performed by members of the Isotopes Division.

Iodine-123 (13 h) decays by electron capture followed by the emission of a 0.16-Mev gamma ray. These properties indicate that this nuclide is potentially useful in medical investigations of thyroid disorders.

A solution of I^{123} in dilute sodium hydroxide was analyzed for I^{123} content by gamma-ray spectrometry. Iodine-124 and I^{126} were detected in the product by a similar spectrometric technique coupled with decay measurements. At discharge time, the I^{124} and I^{126} amounted to 3 and 1%, respectively, of the I^{123} content. The gamma-ray spectrum of this I^{123} product is shown in Fig. 10.4.

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[28] D. Strominger, J. M. Hollander, and G. T. Seaborg, "Table of Isotopes," *Revs. Mod. Phys.* 30, 585 (1958).

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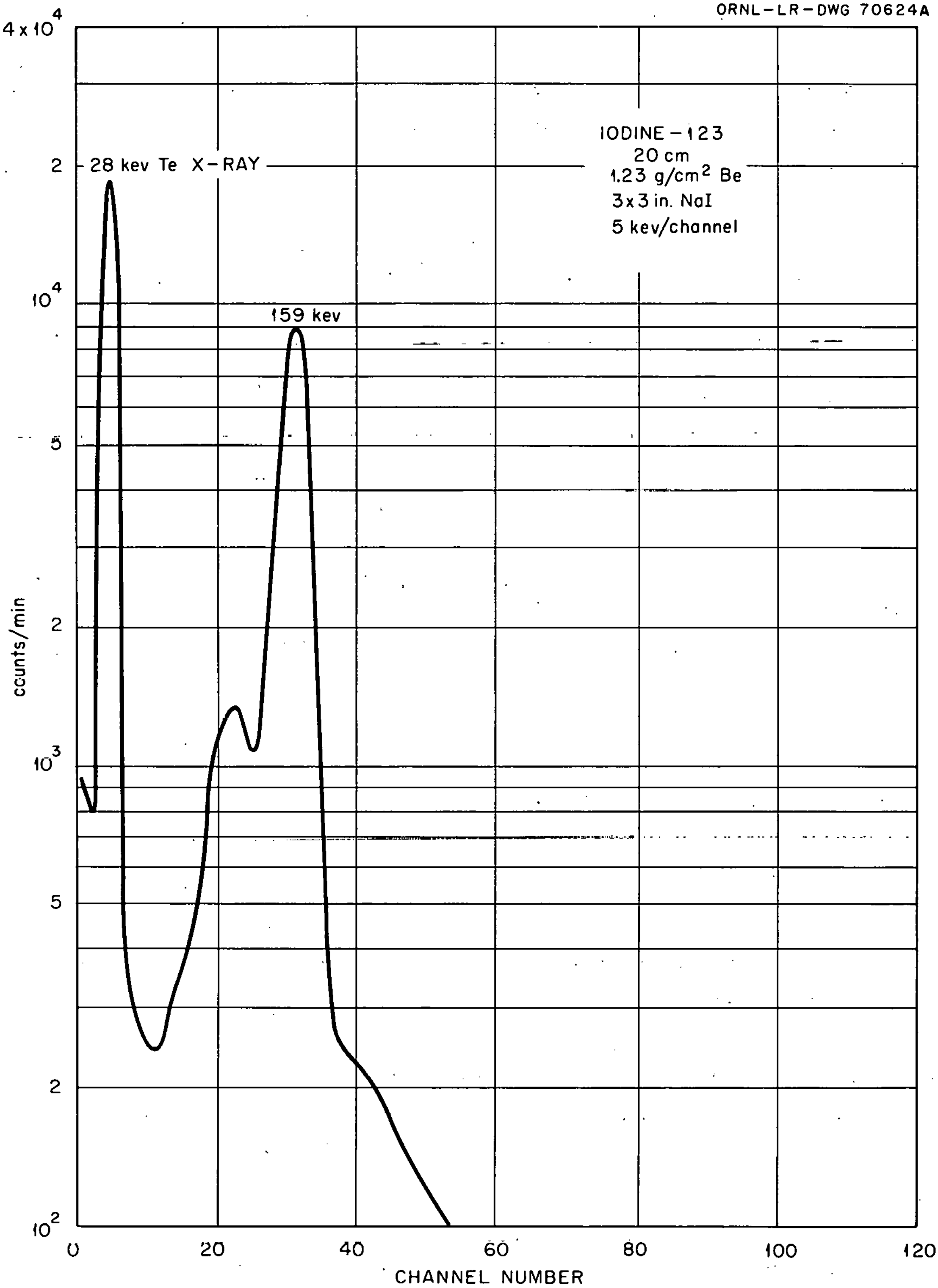

Fig. 10.4. Gamma-Ray Spectrum of I^{123} Product.

ELECTRONIC AND COMPUTER RESOLUTION OF GAMMA-RAY SPECTRA

Quantitative Analysis of Radionuclide Mixtures by Application of Computer Techniques to Gamma-Ray Spectra

G. W. Leddicotte[29] F. F. Dyer

A program was written for the IBM 7090 to allow quantitative determination of the radionuclides contained in a complex radionuclide mixture from its gamma-ray spectrum. The program was adapted from the work of Kuykendall *et al.*[30]

In analyzing a complex gamma-ray spectrum, the computer first selects the photopeak that possibly has the highest energy and then statistically confirms that the peak exists. The computer identifies the radionuclide that produces the photopeak by comparing the channel number of the photopeak with the

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[29] Present address, Union Carbide Nuclear Company, Tuxedo, New York.

[30] W. E. Kuykendall *et al.*, "The Application of Activation Analysis for Industrial Purposes," *TEES Quart. Progr. Rept., No. 3, Feb. 1, 1960,* Engineering Experiment Station, Texas Agricultural and Mechanical College System, College Station, Texas.

Table 10.6. Results of Radionuclide Assay of Neutron-Activated Stainless Steel by Computer and Complement-Subtraction Techniques

Sample	Absolute Disintegration Rate (dis/min)					
	Cr^{51}		Co^{58}		Co^{60}	
	C^a	$C\text{-}S^b$	C^a	$C\text{-}S^b$	C^a	$C\text{-}S^b$
	$\times 10^7$	$\times 10^7$	$\times 10^6$	$\times 10^6$	$\times 10^5$	$\times 10^5$
1	7.9	8.6	1.07	1.21	4.6	4.7
2	8.0	7.6	1.15	1.23	4.6	3.9
3	8.7	7.9	1.29	1.35	4.4	4.5
4	9.2	8.7	1.32	1.44	5.3	4.9
5	9.1	8.3	1.27	1.27	5.0	4.7
6	8.9	7.9	1.23	1.25	5.0	4.7
7	9.6	9.5	1.33	1.48	5.6	4.8
8	9.0	8.6	1.25	1.35	5.3	4.6
9	8.7	7.8	1.24	1.31	5.1	4.5
Av difference, %[c]	+16		−6		+11	

[a] C = computer result.

[b] C-S = complement-subtraction result.

[c] The positive and negative signs before the percent values designate whether or not the computer results are higher or lower, respectively, than the complement-subtraction results.

channel numbers of photopeaks of standard spectra that were taken with radionuclides of known disintegration rates under the same counting conditions as those used for the sample. The areas under the "unknown" and standard photopeaks are then computed and used to calculate the disintegration rate (or quantity) of the particular nuclide in the sample. The computer subtracts from the complex spectrum all spectral elements (photopeaks and Compton components) that are due to this "highest-energy nuclide." The computation is made according to the equation

$$C_{r,i} = C_{x,i} - (A_x/A_s)C_{s,i} ,$$

where $C_{r,i}$ is the count in channel i in the complex spectrum that remains after the subtraction of the identified gamma ray, $C_{x,i}$ is the original count in channel i in the complex spectrum, A_x is the area of the identified highest-energy photopeak in the complex spectrum, A_s is the area of the corresponding photopeak of the standard or library spectrum, and $C_{s,i}$ is the count in channel i of the library spectrum. After the subtraction is made, the process of finding, confirming, measuring, and subtracting the remaining photopeaks of lower energies in the complex spectrum is repeated until each photopeak has been measured.

This assay technique was applied to samples of neutron-activated stainless steel from which the Fe^{59} had been separated. The results are shown in Table 10.6 together with the results obtained for the same samples by use of the complement-subtraction technique. It is believed that the major error in the computer technique is caused by the difference in gain that results when spectra are taken of samples that contain different quantities of radionuclides. Gain shifts cause the channel numbers for photopeaks in complex spectra to be displaced slightly from the corresponding channel number of the library spectrum. Further work will be devoted to developing a computer program to correct spectra for gain shifts.

This work was done in collaboration with W. A. Gray and R. P. Savage[31] of the Central Data Processing Center of K-25.

Electronic Resolution of Gamma-Ray Spectra

J. S. Eldridge

A project is under way to investigate the applications and limitations of "spectrum stripping" as applied to the resolution of gamma-ray spectra. Studies are being made of the accuracy and precision attainable in resolving spectra by use of a commercial multichannel analyzer equipped with a device for summing or subtracting spectra within the analyzer itself. Results from these studies will be compared with results obtained with the complement-subtraction technique[32,33] and also with those from graphic-resolution techniques.

It is anticipated that, in conjunction with these studies, standard spectra of a large number of radionuclides will be collected from calibrated sources. These spectra will be made available to other

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[31] Present address, Tennessee Polytechnic Institute.

[32] D. G. Olson, *Quantitative Gamma-Ray Spectrometric Analysis of Nuclide Mixtures: Consecutive Standard Sources Nullification*, IDO-14495 (Nov. 17, 1959).

[33] W. Lee, "Direct Estimation of Gamma-Ray Abundances in Radionuclide Mixtures," *Anal. Chem.* 31, 800 (1959).

investigators as a paper-tape library. Computer resolution of complex gamma-ray spectra will then be applied as a further means of simplifying measurements of mixtures of gamma-emitting nuclides.

APPLICATIONS OF GAMMA-RAY SPECTROMETRY

Analysis of Radioactive Gases by Gamma-Ray Spectrometry

W. S. Lyon　Gerald Goldstein　J. S. Eldridge

Members of the Radiation Engineering Section of the Reactor Division were assisted in setting up, calibrating, and using a gamma-ray spectrometer for the analysis of short-lived fission gases. Duplicate analyses were performed simultaneously at the ORR building by persons in the Reactor Division and in Building 4500 by members of the Radiochemistry Group. Gas samples received in small glass vials were analyzed for Kr^{85m}, Kr^{87}, Kr^{88}, Xe^{133}, and Xe^{135}. Some uncertainty in the reported gamma branchings in Kr^{88} led to a brief study of the relative gamma intensities in the decay of this nuclide. After the method was standardized, the analyses were performed by the Radioisotopes-Radiochemistry Laboratory.

A method for the assay of Ar^{37} (34 d) radioisotope product was developed. Argon-37 is an electron-capture nuclide with K x rays of 2.6-kev energy. The internal bremsstrahlung spectrum is measured by use of a 3 × 3 in. NaI crystal and a multichannel analyzer and is integrated; an average photopeak energy is used to determine total photons. The disintegration rate is calculated by using the theoretical bremsstrahlung-to-electron capture ratio of 4×10^{-4},[34] which has been confirmed experimentally by Miskel and Perlman.[35]

Small amounts of Kr^{85} in the presence of large amounts of Xe^{133} continue to be measured by gamma-ray spectrometry in which a tantalum absorber is used to remove a large fraction of the Xe^{133} x rays and low-energy gamma rays.

Use of High-Level Gamma-Ray Spectrometer System

J. S. Eldridge

The high-level gamma-ray spectrometer system described previously[36] was evaluated further and was used in the examination of in-pile slurry loops.

A 52-mc source of Co^{60} was examined in the high-level system in order to provide calibration factors and to delineate the extent of collimation available in the system. In addition, the determination of the

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[34] H. Primakoff and F. T. Porter, "Atomic Excitation and Ionization Accompanying Orbital Electron Capture by Nuclei," *Phys. Rev.* **89**, 930 (1953).

[35] J. A. Miskel and M. L. Perlman, "Double Vacancies in the K Shell Associated with K-Electron Capture in A^{37}," *Phys. Rev.* **94**, 1683 (1954).

[36] J. S. Eldridge, "A High-Level Gamma-Ray Spectrometer System," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 58–59.

spectra of this pure material in the overall system will aid in the evaluation of future in-pile loop inspections. In Fig. 10.5 the gamma-ray spectrum of the 52-mc source of Co^{60} in the high-level spectrometer is compared with the spectrum of a 0.23-μc source in an intermediate-level system. There is essentially no difference between the spectra of Co^{60} obtained in the two systems, with the exception that the backscatter peak at channel 16 is higher in the intermediate-level system.

The gamma spectra of an intact thoria slurry loop, the dismantled filter from this loop, and some slurry removed from the filter are shown in Fig. 10.6. The peak at channel 38 is due to Zr^{95}-Nb^{95} fission product;

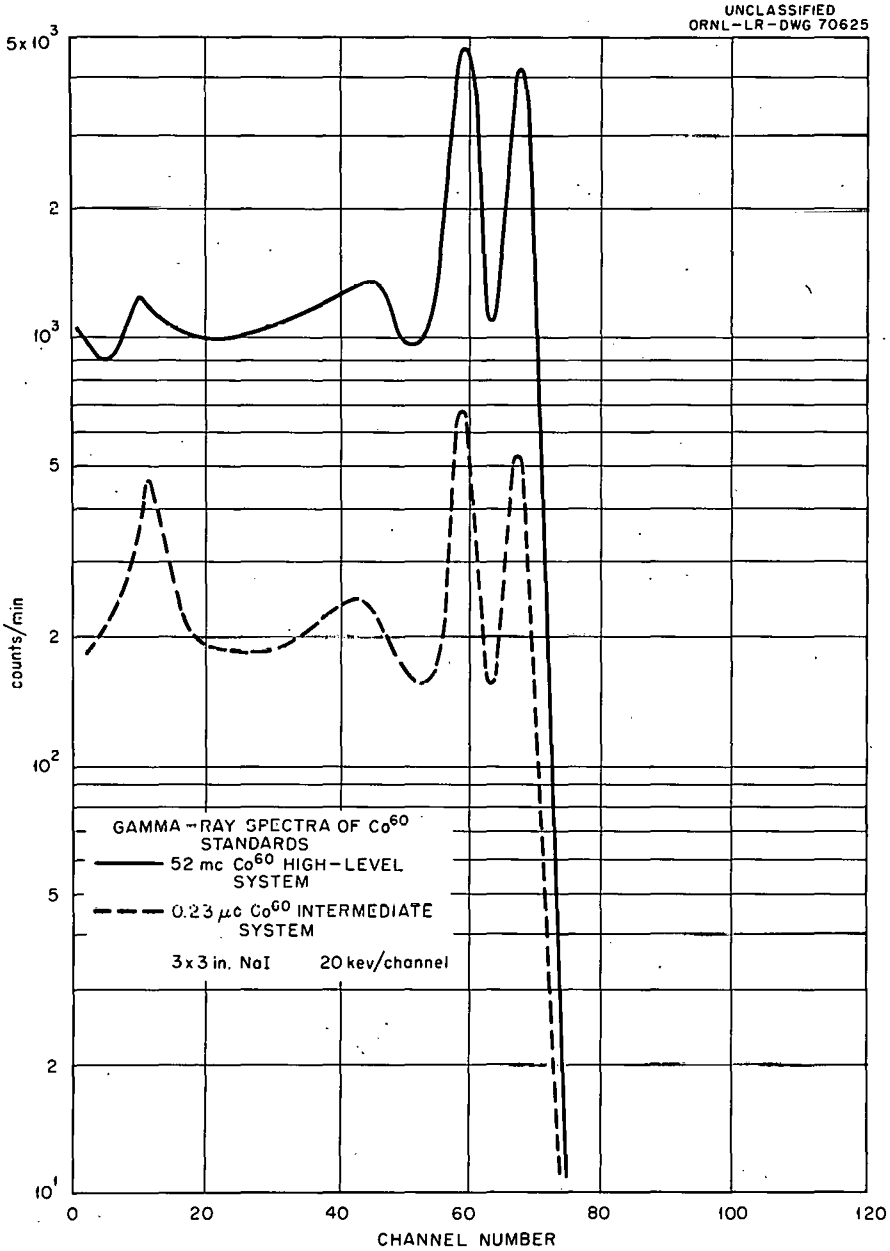

Fig. 10.5. Gamma-Ray Spectrum of 52-mc Co^{60} Source Compared with That of a 0.23-μc Co^{60} Source.

that at channel 16 is due to Pa^{233} and Cr^{51}. The double peaks in the region of channels 60–65 are due to Co^{60} induced in the stainless steel of which the loop and filter were made. The results of this comparison of spectra show that it is possible by use of gamma spectrometry to scan a large specimen, such as a 7-ft-long in-pile loop, and to detect areas of slurry and fission-product deposition. The development of this system was completed.

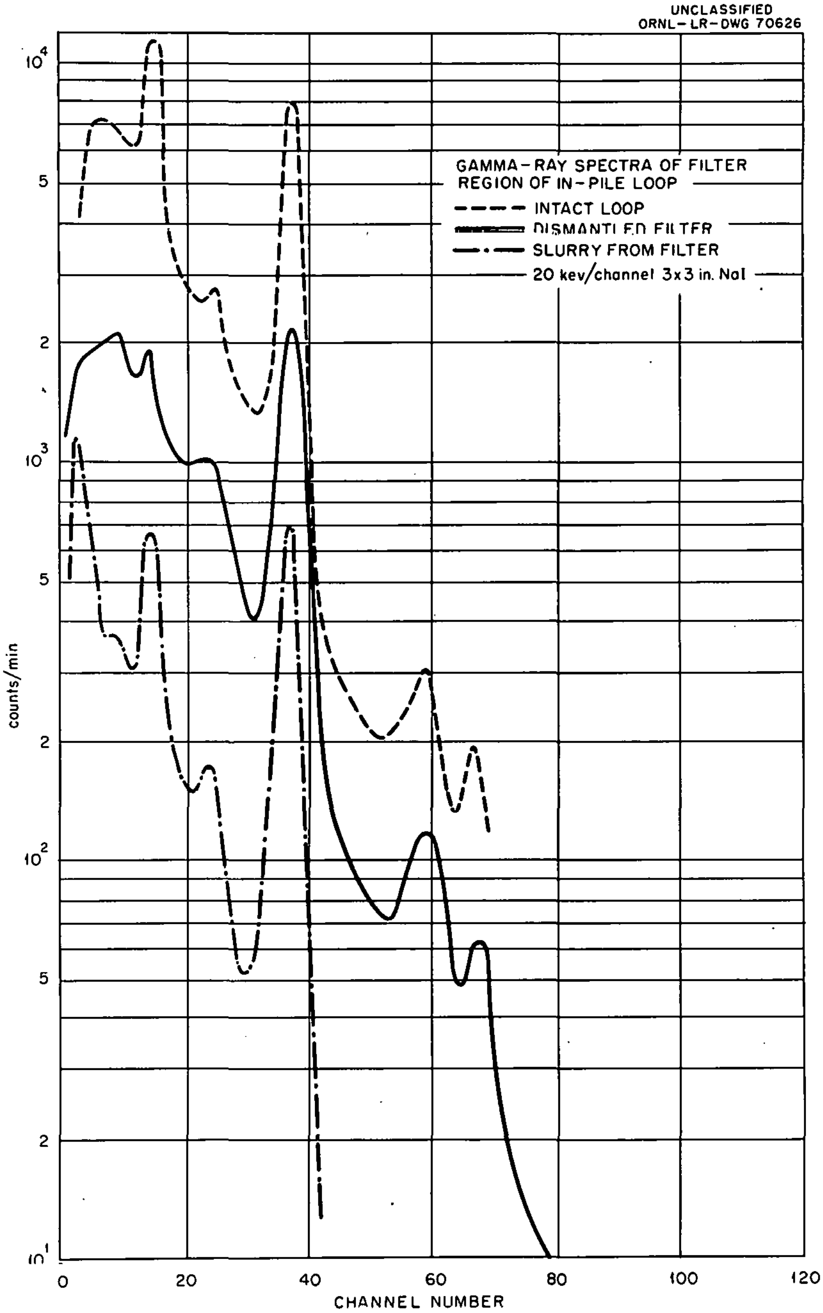

Fig. 10.6. Gamma-Ray Spectra of Thoria Slurry Loop Components.

Applications of Gamma-Ray Spectrometry in Reactor Problems

J. S. Eldridge

Gamma-ray spectrometry has continued to be useful for a variety of nondestructive assays.[37] Some examples of its application in reactor problems follow. Examination of HRT blanket-corrosion specimens revealed the presence of Sb^{125} formed by the activation and decay of tin present in the Zircaloy-2 alloy of the specimens. Samples of fuel salt and graphite from the MSRE showed a concentration of $Ru^{103,106}$ in surface layers of the salt. A sample of gas collected from one of the MSRE capsules showed the presence of Te^{129m}. The presence of fluorine in the gas indicated that the Te^{129m} was probably present as TeF_6. Studies of the characteristics of the isomers of Te^{129} have indicated that there is possibly an unreported beta branching in the 33-d isomer. Further study of the decay of this isomer is planned.

NEUTRON GENERATOR

Installation and Use of the 150-kv Cockcroft-Walton Neutron Generator

J. E. Strain

The Texas Nuclear Corporation 150-kv Cockcroft-Walton accelerator was installed in a shielded location in Building 3017. A vacuum-operated rabbit transport system was designed and installed; this system transfers samples in 0.6 sec from the position of irradiation to the 3 × 3 in. NaI(Tl) detector of a multichannel analyzer. Neutron production, flux monitoring, rabbit transfer, and initiation of counting are controlled by an automatic sequence timer that permits precise control of short time intervals. The electrical circuitry, rabbit transport system, and method of beam pulsing are described in a report.[38]

The generator has been used to evaluate shielding and to analyze a variety of samples for oxygen. The existing system makes possible the quantitative determination of as little as 100 ppm of oxygen in graphite. Oxygen has been determined successfully in a variety of materials (Table 10.7); no interferences were observed except fluorides, which produce N^{16} (7.35 s) through an $F^{19}(n,\alpha)N^{16}$ reaction.

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[37] J. S. Eldridge *et al.*, "Applications of Gamma Spectrometry," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 57–58.

[38] J. E. Strain, W. J. Hampton, and G. W. Leddicotte, *The ORNL Analytical Chemistry Division's 150-kv Cockcroft-Walton Generator*, ORNL TM-362 (Sept. 10, 1962).

Table 10.7. Results of Determination of Oxygen by Means of the 150-kev Cockcroft-Walton Accelerator as a Source of 14-Mev Neutrons

Compound Analyzed	Oxygen (wt %)	
	Theoretical	Found
Graphite	None	–20, 8, 8, 20, 20, 45, 62, 65 (ppm)
$(NH_4)_2SO_4$	48.5	46.0, 47.8, 48.4, 50.0, 52.2
SiO_2	46.1	43.7, 45.4, 46.0, 46.8, 48.8
AgS_xO_y		17.8, 18.3, 19.3, 19.6, 20.2

There is no moderator in the vicinity of the irradiation position; therefore, only fast-neutron (14.3-Mev) reactions are observed. The (*n*,2*n*), (*n*,*n*′), (*n*,α), and (*n*,*p*) reactions are now being studied.

NEUTRON SOURCE

Applications of Isotopic Neutron Sources

J. E. Strain

Eight Am^{241}(0.6 g)–Be(6 g) neutron sources were fabricated in order to evaluate their usefulness in neutron-activation analysis. To determine the arrangement of neutron sources that will permit the irradiation of the largest possible sample at a uniform neutron flux, neutron-flux distribution measurements were made on a series of geometrical arrangements in a large water moderator. The most satisfactory arrangement and its flux distribution are shown in Figs. 10.7 and 10.8, respectively. This source array was then transferred to a solid paraffin moderator for use.

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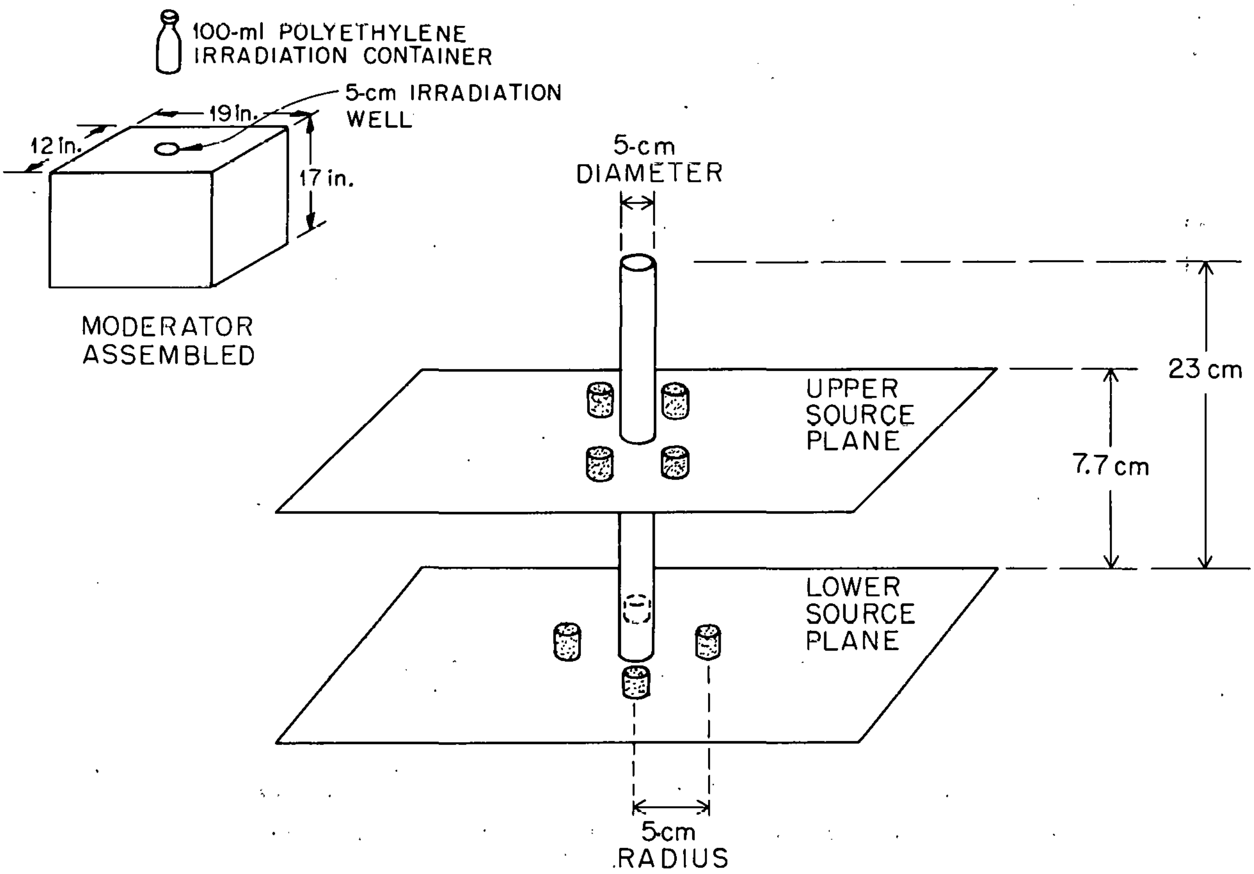

Fig. 10.7. Arrangement of Am^{241}-Be Neutron Source in Paraffin Moderator.

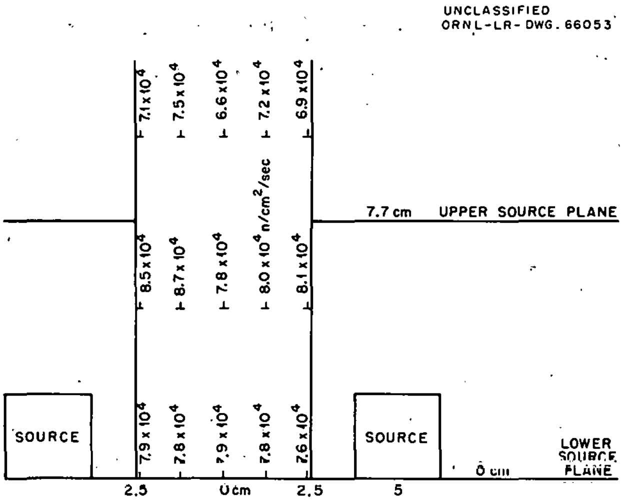

Fig. 10.8. Thermal-Neutron-Flux Distribution in Eight-Source Array. (Eight Am^{241}-Be neutron sources arranged around a 5-cm irradiation well. Source plane separated by 7.7 cm and 45° offset. Sources placed symmetrically at 5-cm radii in 12 × 17 × 19 in. paraffin block.)

Procedures of irradiation and counting were developed for rapid analysis. Examples of the determinations made are given in Table 10.8. Also, Hastelloys A, B, C, and D were distinguished from each other, and nine different types of stainless steel were identified.

Additional uses of the Am^{241} sources included determination of gadolinium in organic scintillators by neutron absorption techniques and qualitative determination of the distribution of uranium in Rover fuel element samples by 60-kev gamma radiography.

Table 10.8. Examples of Applications of Isotopic Neutron Sources

Sample		Element Determined	Duration of Irradiation (min)	Limit of Quantitative Measurement (wt %)
Material	Size (g)			
Soils[a]	50	Si	6	1
		Al	6	1
		Mn	15	0.01
Zr metal	2	Hf	1	0.005

[a] More than 40 soil samples were analyzed.

PARTICLE-SIZE-DISTRIBUTION ANALYSIS

L. C. Bate

Particle-size-distribution analyses were made on samples of ThO_2, UO_2, UO_3, and U_3O_8, as well as on ThO_2 slurries that had been irradiated in a loop of the ORR for as long as a month. Water and/or water-glycerin were used as settling mediums, depending on the estimated particle size of the sample.

The particle-size distributions of several aluminum samples were determined. In these, the radionuclides induced from impurities in the aluminum were used to measure the particle-size distribution. In the measurement of a sample of porcelain, the presence of Cu^{64} was observed. This constituent was used to determine the particle-size distribution. The neutron activation–sedimentation method[39,40] was used. Samples of Ce_2O_3 were analyzed by similar techniques.

Samples of ThH_4 and ThO_2 were submitted for particle-size-distribution analysis. Because ThH_4 reacts with water, a nonaqueous medium was needed for the measurement. Ethyl alcohol was found to be satisfactory. The samples will be mixed, ThH_4 converted to thorium, and the distribution redetermined.

METHODS DEVELOPMENT IN ACTIVATION ANALYSIS

General Applications of Neutron-Activation Analysis

W. T. Mullins

General applications of the method of neutron-activation analysis are indicated by the information given in Table 10.9. In almost every case, the development of a procedure was required; an example is the determination of tantalum and silicon in a series of zirconium-cadmium alloys of various cadmium contents. Cadmium absorbs more neutrons than does zirconium; therefore, in order to correct for this difference, a sample of cadmium-free zirconium was irradiated along with the samples. By determination of the specific activity of the zirconium-cadmium alloys and of the cadmium-free zirconium, a conversion factor was determined.

Comprehensive Scheme for Neutron-Activation Analysis

W. J. Ross

A program was initiated to extend neutron-activation techniques to the determination of essentially all the natural elements. The initial work required the development of rapid and comprehensive methods based on irradiation of samples in the neutron flux of a reactor, identification of the induced radionuclides, and determination of these nuclides by gamma-ray spectrometry. The resulting methods have been used to determine as many as 67 elements in beryllium and aluminum matrices.

Nondestructive techniques were used wherever possible, that is, activation of the sample followed by analysis with a multichannel pulse-height analyzer without intermediate chemical treatment. By use of multiple samples, the experimental conditions were varied in such a manner that the gamma energies of as many as 30 isotopes were measured nondestructively in beryllium samples that contained elements such as Al, Mn, Cu, and Sc, for which the method is very sensitive (Table 10.10). More extensive analyses are possible when the gamma energies of other isotopes for which the method is less sensitive are

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[39] L. C. Bate and G. W. Leddicotte, "Particle-Size Distribution in Thorium Oxide. Neutron Activation—Sedimentation Method," Method No. 5 10200 (10-10-61), *ORNL Master Analytical Manual;* TID-7015, suppl 4.

[40] L. C. Bate *et al.*, "Particle-Size-Distribution Analysis," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1958,* ORNL-2662, pp 11–12.

Table 10.9. Unusual Samples Analyzed by Activation Analysis

Sample		Elements Determined
Type	Number Analyzed	
Aluminum oxide	3	P
Asbestos material	4	Cr, Fe, Na, Sc, Th, Zn
Beryllium	22	Sc
	4	Sc, Th, U
	6	Si
	9	Si, Th, U
Beryllium fluoride	4	Sc, Th, U
Beryllium oxide	1	Si
Feed stuffs	6	Mn
	19	Se
Filter paper	3	Si
Fission products	8	Na
	1	Na, Sr
Germanium	3	Si
Gold film on aluminum foil	2	Au
LiF-BeF mixtures	24	Zr
Lithium chloride	3	K, Na
Nitric acid solution	2	Cl
Niobium	3	Si
ORR water	2	Cr, Cu, Fe, Na, Ni
Polyethylene bottle	3	Au, Br, Cu, Mn, Na
Potassium fluotantalate	3	Si
Rabbit-tissue ash	1	Au
Silicon	4	Au
	4	Mn
Sodium-potassium	1	Rb
Stainless steel	6	Co, Ni
Tantalum	3	Si
Water	2	Cl, Na
	5	K
	12	Mn
Zircon	1	Th
Zirconium	3	Si
Zirconium-cadmium	4	Si, Ta
Zirconium-gallium	2	Fe, Ni
	1	Si

Table 10.10. Results of Analysis of Beryllium by Nondestructive Methods

Duration of Irradiation	Decay Time	Radioisotope Detected		Approximate Limit of Quantitative Measurement[a] (μg)
		Identity	Half-Life	
10 sec[b]	2 m	Mn^{56}	2.6 h	0.06
	8 m	In^{116m}	54 m	0.005
	5 m	Dy^{165m}	75 s	0.001
1 min[b]	2 m	Al^{28}	2.3 m	0.02
	9 m	Ti^{51}	5.8 m	0.5
	1.1 m	V^{52}	3.8 m	0.001
	0.7 m	Nb^{94m}	6.6 m	0.001
	4 m	Rh^{104}	44 s	0.005
	1 h	Eu^{152}	9.3 h	0.01
	5 m	Th^{233}	22 m	0.02
10 min[b]	10 m	Ga^{72}	14 h	0.1
	16 m	Sr^{87m}	2.8 h	0.2
	14 m	Ba^{139}	83 m	0.05
	15 m	U^{239}	24 m	0.02
10 min[c]	20 h	K^{42}	12.5 h	7
	21 h	Mo^{99}	66 h	1
	24 h	Sb^{122}	2.8 d	0.1
	21 h	La^{140}	40 h	0.2
	21 h	Pr^{142}	19 h	3
	25 h	Nd^{147}	11 d	5
	23 h	Sm^{153}	47 h	0.001
	21 h	Gd^{159}	18 h	1
	21 h	Ho^{166}	27 h	0.03
	21 h	Tm^{170}	127 h	1
	21 h	Yb^{175}	4.2 d	0.5
	21 h	Lu^{177}	6.8 d	0.01
16 hr[d]	27 h	Na^{24}	15 h	0.5
	30 h	Sc^{46}	84 d	0.8
	25 h	Cu^{64}	12.9 h	0.2
	27 h	Ga^{72}	14.1 h	4
	30 h	Br^{82}	35.7 h	1

[a] Amount of element necessary to produce 200 counts/min in peak channel when separated from a 3 × 3 in. crystal by a 0.5-in.-thick polyethylene absorber.

[b] ≦1-mg sample required. Flux of 6×10^{13} neutrons cm^{-2} sec^{-1}.

[c] ≦100-mg sample required. Flux of 6×10^{13} neutrons cm^{-2} sec^{-1}.

[d] Flux of 8×10^{11} neutrons cm^{-2} sec^{-1}; 1-g samples used.

not screened by such constituents. Because of the similarities in their nuclear properties, many radioactive isotopes formed by neutron activation cannot be differentiated by varying experimental parameters (neutron flux, duration of irradiation, decay, and counting). Therefore there exists a limit to the number of naturally occurring elements that can be determined from a single gamma spectrum. Such a limitation can be overcome to various degrees by performing chemical separations on the sample after irradiation.

A tentative method has evolved from this initial work whereby submicrogram or microgram amounts of 62 elements can be determined in less than 16 man-hours. The method consists in the following steps: (1) nondestructive determination of 11 elements (Table 10.11) through irradiation of a small sample (~ 10 mg) in a rapid-transit system and at a flux of 10^{13} neutrons cm^{-2} sec^{-1}, followed by gamma spectrometric measurement of short-half-life isotopes after a decay of only 1 or 2 min; (2) determination of halides (at the following limits of quantitative measurement: I, 0.2 μg; Br, 0.3 μg; and Cl, 3 μg) by irradiating samples in a flux of 10^{11} neutrons cm^{-2} sec^{-1} for 20 min and separating the volatile halides by distillation from H_2SO_4 media; (3) determination of 50 elements in the fractions of another sample (1 g) after (*a*) the sample has been irradiated for 16 hr (overnight) in a neutron flux of 10^{11} neutrons cm^{-2} sec^{-1} and allowed to decay for 24 hr and (*b*) five simple and rapid chemical separations have been carried out (Fig. 10.9). Resolution of distinct gamma energies is possible for all except the rare-earth-element fraction without further chemical treatment. The chemical yields are established by means of synthetic solutions and exceed 80% except for As, Os, Ir, and Hg, for which yields are usually 30 to 50%.

The radioactive isotopes are identified with the aid of a catalog of the gamma activities compiled from data taken for comparators under the same experimental conditions. The concentration of each element is determined from a corollary list of experimentally determined sensitivities. The concentrations of neon, xenon, and krypton can be determined empirically from the known concentration of argon and the natural abundance of these gases. If time is of minor importance, the sensitivities for most of the elements can be enhanced by irradiating the sample for longer periods of time.

Table 10.11. Sensitivity of the Method for Short-Half-Life Isotopes

Radioisotope		Approximate Limit of Quantitative Measurement[a] (μg)
Identity	Half-Life	
Mg^{27}	9.55 m	7
Al^{28}	2.3 m	0.1
Ar^{41}	1.83 h	1
Ti^{51}	5.8 m	2
V^{52}	3.77 m	0.005
Mn^{56}	2.58 h	0.06
Sr^{87m}	2.8 h	5
Rh^{104}	42 s	0.02
Dy^{165m}	1.25 m	0.0004
Eu^{152}	9.3 h	0.007
In^{116}	54 m	0.004

[a] 10-sec irradiation in a flux of ~6 × 10^{13} neutrons cm^{-2} sec^{-1} and a 120-sec decay. Peak channel contains 200 counts/min when the sample is separated from a 3 × 3 in. NaI(Tl) crystal by a 0.5-in. polyethylene absorber.

This work is being continued in an effort to make the method more quantitative either by increasing the efficiency of the separation procedures or by developing alternate schemes, especially for use in the analysis of radioactive matrices.

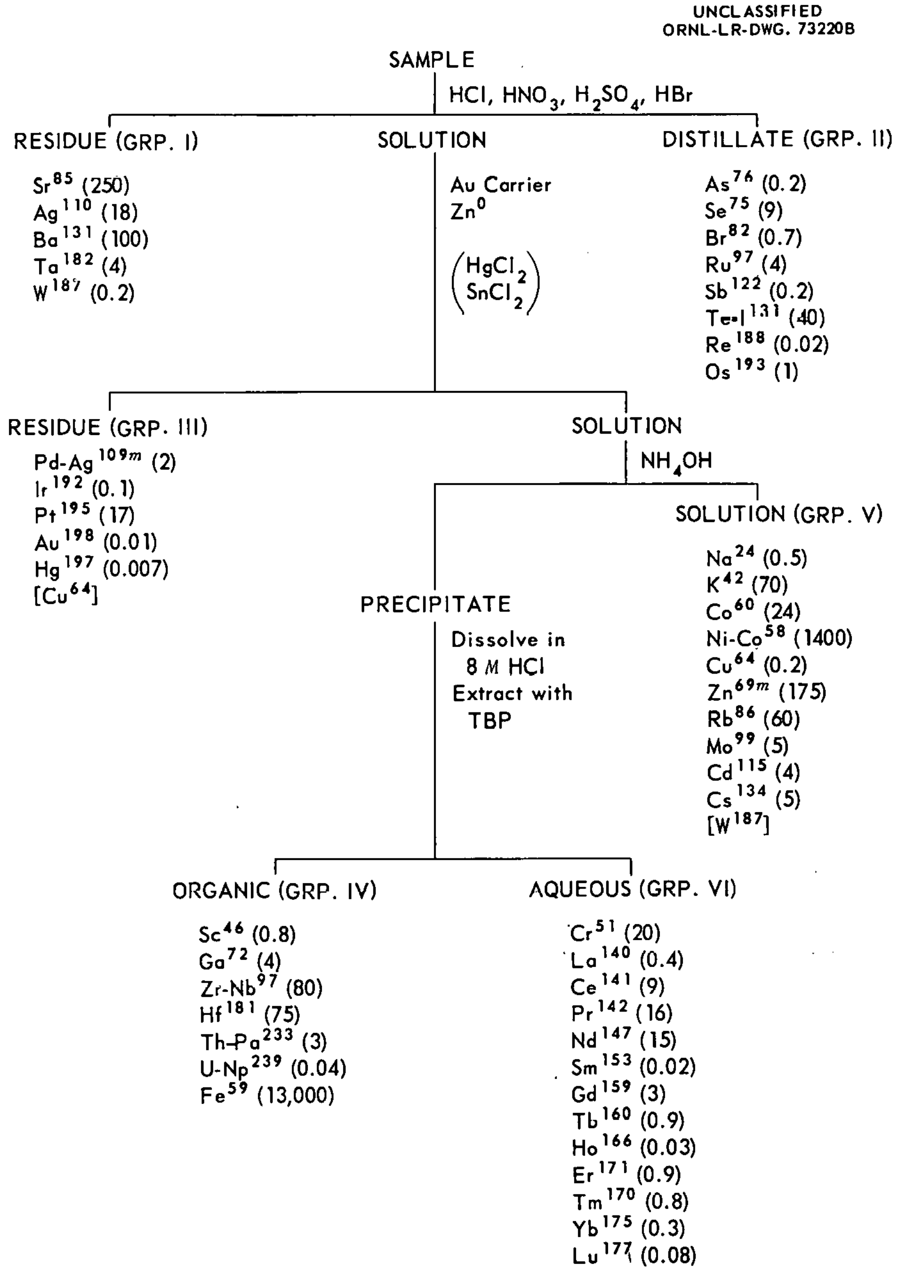

Fig. 10.9. Procedure and Sensitivities for the Radiochemical Analysis of Irradiated Beryllium Samples. (Duration of irradiation, 16 hr; flux, 8×10^{11} neutrons cm^{-2} sec^{-1}; decay period, 28 hr.)

Applications of Activation Analysis and Stable Tracer Methodology to Measurement of Water Flow

Y. Wellwart[41] L. C. Bate W. T. Mullins J. Stokely[42] G. W. Leddicotte[43]

Investigation of the feasibility of using stable isotopes as tracers in conjunction with activation analysis in studying flow patterns of water was undertaken. A study was made of the flow of water through a pressurized system equipped with a valve to prevent backflow. Stable manganese and potassium were added to the system as tracers. During the test operation, samples were removed from the system, irradiated, and processed for Mn^{56} (2.6 h) and K^{42} (12.4 h). This work has been reported.[44]

The water flow through the turbine of a hydroelectric generator was studied by use of stable indium tracer. The In^{116m} (54 m) product of the $In^{115}(n,\gamma)In^{116m}$ reaction was measured. The limit of quantitative measurement of the method is 0.1 nanogram (i.e., 1×10^{-10} g) of indium.

The potential of the use of stable isotopes as tracers in conjunction with activation analysis has not been fully determined, since only a limited number of stable isotopes have been studied in this function.

ANALYTICAL APPLICATIONS OF ACTIVATION TECHNIQUES

Determination of Sulfur by Neutron-Activation Analysis

W. J. Ross

A neutron-activation method was developed for determining sulfur. It is based on the formation of S^{35} by neutron irradiation of S^{34} and subsequent measurement of the 0.167-Mev beta activity of the induced S^{35}. A series of chemical separations are performed to remove all extraneous activities and thus to isolate S^{35} so that its weak-beta energy can be compared with that of an S^{35} standard by means of a Tri-Carb liquid scintillation counter. When an irradiation of 1 week in a flux of 10^{11} neutrons cm^{-2} sec^{-1} is used, the activity of 1 μg of sulfur is sufficient to yield $\sim$120 counts/min.

The method was calibrated by analyzing NBS samples of limestone (0.27% S) and steel (0.09% S) and was observed to exhibit a positive bias of $\sim$10%. It has been tested on fluoride salts of Na, Li, Be, Zr, Th, and U for use as a referee method for other analytical methods for sulfur. Fair agreement of results is obtained between the activation analysis method and the spectrophotometric methylene blue method[45] for samples that contain > 100 ppm of sulfur. However, in the lower ranges of sulfur concentration the radiochemical method gives higher results than does the methylene blue method. Additional work is being done to test the reliability of the method and to develop a faster procedure for isolating the S^{35}.

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[41] Israel Atomic Energy Commission, Soreq Research Establishment, Rehovoth, Israel.

[42] Graduate student from Clemson College, Clemson, S.C.

[43] Present address, Union Carbide Nuclear Company, Tuxedo, New York.

[44] Y. Wellwart *et al.*, "Stable Isotope Trace-Activation Analysis Methodology: Use in Water Flow Studies," presented at the 14th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962.

[45] J. C. White, "Sulfur in Inorganic Compounds, Spectrophotometric Methylene Blue Method," Method Nos. 1 218110 and 9 00718110 (3-15-55), *ORNL Master Analytical Manual;* TID-7015, sec 1.

Delayed-Neutron Counting

F. F. Dyer

The method of delayed-neutron counting was used to determine U^{235} in zirconium oxide and in neutron-irradiated uranium oxide. The method is especially useful for determining U^{235} in materials that have been previously neutron irradiated and that are highly radioactive (e.g., uranium oxide). Since no chemical processing is needed, these types of samples can be analyzed for uranium with minimum exposure of the analyst to radiation. Under certain conditions of irradiation and counting, the limits of quantitative measurement of U^{238} and Th^{232} were determined to be about 10^4 counts per milligram of each nuclide. These sensitivities can probably be extended by a factor of 10. Cadmium-ratio measurements made by delayed-neutron counting on uranium samples of various U^{235}-to-U^{238} ratios have demonstrated that the method is suitable for determining the isotopic composition of uranium without prior knowledge of the total quantity of uranium in a sample. This technique should be applicable to samples that contain uranium in which the U^{235} content varies from 10 to 10^4 μg per gram of total uranium. A formal report that describes the delayed-neutron-counting method for uranium determination was published;[46] the method was also written for inclusion in the *ORNL Master Analytical Manual.* In addition, an article that describes this method and presents the results obtained with it is being prepared for publication in the open literature.

Activation of Carbon Disulfide

R. L. Hahn

A method was devised whereby liter quantities of carbon disulfide are used to detect low-intensity fluxes of million-electron-volt neutrons via the $S^{32}(n,p)P^{32}$ reaction. After exposure to the neutron flux, the carbon disulfide is distilled at 45°C from the irradiation flask; then with the aid of conventional radiochemical techniques,[47] the P^{32} in the flask is removed and measured. The method was developed primarily for use in thermonuclear machine experiments.

Determination of Oxygen in Molten-Fluoride Salts by Neutron-Activation Analysis

L. C. Bate

Traces of oxygen in nonradioactive fused salts from the MSRE (e.g., $LiF\text{-}BeF_2$ and $LiF\text{-}BeF_2\text{-}ZrF_4\text{-}NaF$) were determined by neutron-activation analysis based on the neutron reactions $Li^6(n,\alpha)t$ and $O^{16}(t,n)F^{18}$. The normal Li^6 content of each test sample was sufficient to produce the flux necessary for the $O^{16}(t,n)F^{18}$ reaction. Following each irradiation, the test samples were processed radiochemically to obtain the F^{18} (112 m) for the radioactivity measurements. The fluoride ion of each specimen

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[46] F. F. Dyer, J. F. Emery, and G. W. Leddicotte, *A Comprehensive Study of the Neutron Activation Analysis of Uranium by Delayed-Neutron Counting,* ORNL-3342 (July 27, 1962).

[47] W. T. Mullins and G. W. Leddicotte, *The Radiochemistry of Phosphorus,* NAS-NS-3056 (March 1962).

was high enough in concentration to be used as a "carrier" of the F^{18}. The chemical yield of each experiment was determined titrimetrically. Typical data obtained are presented in Table 10.12, together with data taken with the $KBrF_4$ method.[48]

The limit of measurement of this method is about 1 μg. Rigid sampling procedures are required and are now being studied.

Table 10.12. Results of Determination of Oxygen in Molten-Fluoride Salts by Neutron-Activation Analysis

Sample		Oxygen Concentration (ppm)	
Type	Number	Activation Analysis	$KBrF_4$ Method
LiF(66%)–BeF_2(34%)[a]	1	690 ± 40	
LiF-BeF_2-ZrF_4-NaF[b]	1	407	518
	2	471	371
	3	450	300
	4	517	651
	5	534	657
	6	550	439
	7	567	414

[a] Eight determinations, made at two different times.

[b] In this series, each of the two analyses was done on a single portion from each test specimen. Test specimens from different sources.

Determination of Stable Trace Elements in Radioactive Materials

W. T. Mullins J. F. Emery G. W. Leddicotte[43]
L. C. Bate F. F. Dyer A. P. Grimanis[49]

The analytical procedures normally used in the neutron-activation analysis of nonradioactive samples are, in many cases, applicable to materials that are already radioactive. The radioactivity of such materials can vary from a small quantity of natural radioactivity to curie quantities of previously induced radioactivity. Both radiochemical and nondestructive (gamma scintillation spectrometry) methods of analysis have been used.

The fact that these samples are already radioactive before they are irradiated for purposes of neutron-activation analysis makes necessary certain specific processing procedures in order to ensure compliance with radiation-safety regulations, as well as to assist in the determination of the induced radioactivity.

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[48] G. Goldberg, "Oxygen in Fluoride Salts and Refractory Metals, Potassium Tetrafluorobromide Manometric Method," Method Nos. 1 215894 and 9 00715894 (5-12-60), *ORNL Master Analytical Manual;* TID-7015, suppl 3.

[49] Nuclear Research Center, Greek Atomic Energy Commission, Athens.

Table 10.13. Typical Examples of the Neutron-Activation Analysis of Radioactive Materials

Neutron flux, 6×10^{11} or 7×10^{13} neutrons cm^{-2} sec^{-1}

Matrix Material		Sample Size	Element Determined			Limit of Quantitative Measurement (μg)
Identity	Approximate Level of Radioactivity		ND[a]	RC[a]	Concentration (ppm)[b]	
Metallic Tc^{99}	*c*	10 mg	Na		2100	0.007
			As		194	0.02
			Au		1	0.002
Graphite	1 mr/hr	100 mg	U^{235}		40 to 430	~0.01
Reactor cooling water	10 mr/hr sample	10 ml	Cu		2×10^{-4}	0.003
			Mn		4×10^{-5}	0.001
			Co		0.07	0.05
			Na		0.04	0.01
			Cl		0.25	0.1
			Al		0.04	0.01
			Cd		0.029	0.2
			Ba		0.002	0.05
				Ni	<1	
				U^{235}	4×10^{-6}	0.001
				U^{238}	0.0011	0.1
Sr^{90} solution	Variable	Variable	Na		1 to 1000	4
				Na	1 to 1000	4
				Ba	<1	0.05
$LiF\text{-}BeF_2\text{-}ZrF_4\text{-}ThF_4\text{-}VF_4$	Natural	25 mg		Th	Few	0.2
				Cr	0.2 to 1120	0.7
ThO_2	5 r/hr	0.5 g	Y		20	0.1
Co-Al alloy wire	<1 mr/hr	25 to 100 mg	Co		1000 to 5000	0.005
$Co\text{-}Al_2O_3$	<1 mr/hr	25 to 100 mg	Co		1000 to 5000	0.005
I^{131} solution	100 mr/hr	1.0 ml	I		0.5	0.1

[a] ND = nondestructive determination; RC = radiochemical determination.

[b] A range of values for concentration indicates that a number of samples were analyzed.

[c] Only radioactivity from Tc^{99}, a beta emitter, was present.

The procedures used depend markedly on the type of sample, the level of radioactivity of the sample prior to the neutron activation, and the conditions under which the irradiation is to be made. Dilution or a preprocessing of the materials before reinsertion into a reactor sometimes can help to control the amount of radioactivity that is handled in the analysis. For example, portions of $Sr^{89,90}$ solutions are diluted at least 20 times before the irradiation is made. In the case of the determination of yttrium in irradiated thorium oxide, the stable element must be separated chemically before the irradiation, since the half-life of the Y^{89m} (the induced radionuclide that is measured) is too short (16 s) to permit chemical separations to be made after the irradiation.

Typical examples of the neutron-activation analysis of radioactive materials are given in Table 10.13.

Determination of Pa^{231} in U^{232} Radioisotope Product Solutions

J. E. Strain

A method was developed for determining Pa^{231} in U^{232} radioisotope product solutions. The method is based on gamma spectral techniques that consist in recording a gamma spectrum of the sample before neutron irradiation for use as a background spectrum, irradiating the sample for 10 sec in the ORR HN-3 facility, allowing a 16-hr decay, and analyzing the final gamma spectrum of the sample. The difference between the integrated counts of the two spectra in the energy region of 0.8 to 1.0 Mev is used as a measure of the Pa^{231} present in the sample. The limit of quantitative measurement of the method for determining Pa^{231} in U^{232} is 0.6 wt %.

Determination of Arsenic by Neutron-Activation Analysis

A. P. Grimanis[49] G. W. Leddicotte[43]

Radioisotope methodology was used to develop a rapid extraction procedure for separating arsenic from other elements by means of the system benzene–1 *M* HBr–7 *M* $HClO_4$. More than 99.5% of the As^{3+} present is extracted into benzene in less than 2 min. At the indicated optimum molarities of perchloric and hydrobromic acids, the behavior of 36 other elements was investigated. With the exception of Ge^{4+} and Se^{4+}, which behave like As^{3+}, only Sb^{3+} extracts to any extent (13%). Less than 0.5% of each of the other elements is extracted. This separation technique has been included successfully in activation-analysis methods for determining submicrogram and microgram amounts of arsenic in copper alloys and in organic materials. As little as 0.1 μg of arsenic can be determined. The extraction procedure should be useful in other types of methods and also applicable to the separation of milligram amounts of arsenic.

SURVEY AND IDENTIFICATION APPLICATIONS OF ACTIVATION ANALYSIS

Use of Neutron-Activation Analysis in the Identification and Comparison of Physical Evidence for Enforcement Purposes

L. C. Bate M. J. Pro[50]
J. F. Emery G. W. Leddicotte[43]

The feasibility of using radioactivation analysis in enforcement work was studied. The objectives were to determine whether activation-analysis data can be used to distinguish between samples submitted for physical evidence and to identify the origins of such samples.

Six black automobile lacquers were neutron irradiated for different time intervals and were assayed nondestructively by gamma scintillation spectrometry. From the gamma spectral measurements, it was possible to distinguish five types of samples; two of the six samples appeared to be identical. In addition, soil and soot physical-evidence samples from a typical enforcement case were treated similarly. The results indicated that the several soot samples were similar, as were the soil samples. It appears that the determination of the elemental composition of a sample by activation analysis can be used successfully to compare and, in some cases, to identify physical-evidence samples. Results obtained in this study have been reported.[51]

The feasibility of applying neutron-activation analysis to narcotic law-enforcement requirements was demonstrated. Commercially prepared barbitals and meperidine hydrochlorides were examined and their sources of manufacture were identified. The possibility exists of using activation analysis successfully in the control of the distribution of manufactured drugs and in the identification of illicitly prepared drugs.

Applications of Neutron-Activation Analysis in Oceanography

W. T. Mullins J. F. Emery
L. C. Bate G. W. Leddicotte[43]

Neutron-activation analysis is an important means of obtaining systematic knowledge about the abundance of trace elements in oceanographic samples. The procedures needed for irradiating and processing the test samples and the equipment required are now available. Applications of activation analysis in oceanography are indicated in Table 10.14.

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[50] Alcohol and Tobacco Tax Laboratory, Internal Revenue Service, Treasury Department, Washington, D.C.

[51] L. C. Bate, M. J. Pro, and G. W. Leddicotte, *Identification and Comparison of Physical Evidence for Law Enforcement Purposes by Neutron Activation Analysis*, ORNL TM-363 (Sept. 11, 1962).

Table 10.14. Applications of Activation Analysis in Oceanography

Sample	Elements Determined	
	Identity	Concentration Range (µg/g or µg/l)
Sea water	Au	10 to 506
	As	0.03 to 5.2
	Ba	1 to 10
	Cs	0.021 to 0.026
	Rb	1.0 to 1.4
	Sr	8000 to 8300
	U	0.03 to 5.3
Clays, sediment ash	In	$\leq$0.001
	Ir	$\leq$0.0005
	Sc	0.06 to 1.0
	U	1.4 to 4.7
Sea weed	Cs	0.008 to 0.02
	Rb	0.04 to 19
Marine sediment cores	Cs	0.08 to 32
	Rb	0.07 to 30
Marine organisms	Ba	1 to 10
	Sr	1 to 10
Marine sediments and oceanic rocks	Co	2 to 39
	Ni	9 to 289
Marine biological ash	As	0.05 to 5.4
	Au	0.003 to 0.009
	Mo	.17
	Re	0.009 to 0.07
	V	1 to 262
	W	0.009 to 0.46

Comparison of Some Materials and Containers Used in Pharmaceutical Manufacture

S. B. Poey[52] G. W. Leddicotte[43]

Neutron-activation analysis was used in a preliminary comparative assessment of some of the materials and containers used in the manufacture of pharmaceuticals. Manganese, copper, and sodium were determined in water distilled in stainless steel and Pyrex and in water distilled twice from Pyrex containers. The amounts of these elements leached from stainless steel, Pyrex, and polyethylene storage containers have also been determined with distilled and doubly distilled water. The manganese,

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[52] Institut Teknologi, Bandung, Indonesia.

copper, and sodium contents of polyethylene bottles were determined. The same techniques were used to determine some of the impurities in adrenaline and vitamin C.

Determination of Trace Elements in Raw Opium by Neutron-Activation Analysis

J. F. Emery

The program[53] to correlate the composition of raw opium with its source country and area of growth is being continued. From some 270 samples received, about 100 have been selected for activation analysis. The samples include those collected over several years from particular areas. This method of collection will permit the constancy of trace-element uptake to be determined as a function of time.

Identification and Comparison of Documents for Law-Enforcement Purposes

J. F. Emery

A preliminary study was made to determine the feasibility of using radioactivation analysis to "fingerprint" typed or written documents by trace elements in the writing inks, typewriter print, and carbon-paper print. Segments cut from the text of the typed or written document, together with adjacent segments of blank paper, were irradiated for 5 min in the pneumatic tube facility of the ORR. Gamma-ray spectra were made of each test specimen. The trace-element content of the test specimens is shown in Table 10.15. The results of these studies indicate that it is possible, in some instances, to make comparisons among and to identify documents by radioactivation analysis. Since most writing inks are probably sodium salts, a longer irradiation and the decay of Na^{24} are required for their satisfactory analysis. In future studies, these requirements will be taken into consideration, and autoradiography will perhaps also be used.

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[53] J. F. Emery *et al.*, "Trace Elements in Raw Opium," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 67–68.

Table 10.15. Results of Activation Analysis of Prints and Inks

Sample			Elements Detected
Material	Brand	Exhibit[a]	
Typewriter print	1	3a	Mo, Sb
	2	6a	Mo
Carbon-paper print	3	3b	Sb
	3	6b	Sb
	4	3c	Sb[b]
	4	6c	Sb[b]
Writing ink	5	5a	Na
	6	5b	Na
	7	5c	Na
	8	5d	Na

[a] Designation used at source of sample.

[b] Antimony content estimated to be half that of brand 3.

FLUX MEASUREMENTS

F. F. Dyer

Measurement of Thermal and Resonance Neutron Flux by Use of Two Bare Monitors

The epithermal or resonance neutron flux in a nuclear reactor (usually considered to have a $1/E$ distribution) is normally measured by the activation of a suitable monitor enclosed in a cadmium shield. The resonance flux ϕ_r per unit natural-logarithmic interval of energy is given by the equation

$$\phi_r = R_r/I_0 \ ,$$

where R_r is the reaction rate per atom of the monitor enclosed in cadmium, and I_0 is the resonance integral of the monitor evaluated from the cadmium cutoff energy.[54] The thermal (Maxwellian) neutron flux ϕ_{th} is obtained from a knowledge of ϕ_r and the reaction rate of a bare (uncovered) sample of the monitor and is given by the equation

$$\phi_{\mathrm{th}} = \phi_r(CR - 1)I_0/\sigma_{\mathrm{th}} \ ,$$

where CR is the cadmium ratio, and σ_{th} is the thermal-neutron-capture cross section. The cadmium ratio is defined by the equation

$$CR = R_t/R_r \ ,$$

where R_t is the reaction rate per atom of the bare monitor sample.

Values for ϕ_{th} of sufficient accuracy can be obtained by use of monitors that are relatively insensitive to the epithermal neutron flux (i.e., monitors for which the ratio I_0/σ_{th} is small) without the need to make irradiations in cadmium covers. In certain cases, however, it is desirable to measure ϕ_r in reactor facilities in which it is impractical to use cadmium covers. Such measurements can be made by use of two or more monitors according to the methods of Ben-David and Huebschmann[55] and of Weale *et al.*[56] The reaction rates R_1 and R_2 of two bare monitors can be expressed as

$$R_1 = \phi_{\mathrm{th}}\sigma_{1,\mathrm{th}} + \phi_r I_{1,0} \ ,$$
$$R_2 = \phi_{\mathrm{th}}\sigma_{2,\mathrm{th}} + \phi_r I_{2,0} \ ,$$

where the subscripts 1 and 2 refer to monitors 1 and 2. If one of the monitors is sensitive primarily to the thermal neutron flux and the other to the resonance neutron flux, the reaction rates can be measured (by assay of the radionuclides formed), and the two preceding equations can be solved simultaneously to yield values for ϕ_{th} and ϕ_r.

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[54] R. W. Stoughton and J. Halperin, "Heavy Nuclide Cross-Sections of Particular Interest to Thermal Reactor Operations: Conventions, Measurements, and Preferred Values," *Nucl. Sci. Eng.* **6**, 100 (1959).

[55] G. Ben-David and B. Huebschmann, "Neutron Flux Measurements Using Dysprosium Detectors," *Reactor Sci. Technol.* **16**, 291 (1962).

[56] J. W. Weale *et al.*, *Neutron Flux Measurements in the Core on LIDO*, AERE R/R 2620 (July 1958).

This technique has been used to obtain values of ϕ_{th} and ϕ_r in hydraulic tube No. 1 of the ORR by use of thin foils of cobalt-aluminum and gold-aluminum alloys. In addition, values of ϕ_{th} and ϕ_r were also obtained by irradiations of samples of these foils with and without cadmium covers. The results are shown in Table 10.16. The use of gold for such measurements is limited to short-period irradiations because of the short half-life (64.8 h) of Au^{198} and the fact that Au^{198} has a large neutron-capture cross section and "burns up" to form Au^{199}. Other monitor combinations are now being investigated that will allow this technique to be used to measure ϕ_{th} and ϕ_r when irradiations are carried out for long periods of time in thermal neutron fluxes greater than 1×10^{14} neutrons cm^{-2} sec^{-1}.

Table 10.16. Thermal and Resonance Neutron Flux in Hydraulic Tube No. 1 of the ORR

Method of Measurement	Neutron Flux (neutrons cm^{-2} sec^{-1})	
	Thermal, ϕ_{th}	Resonance, ϕ_r
	$\times 10^{14}$	$\times 10^{14}$
Bare samples of Co(0.154%)-Al and Au(0.109%)-Al alloys[a]	1.88	0.108
Cadmium ratio:		
Co-Al alloy	1.84	0.127
Au-Al alloy	1.71	0.122

[a] Values calculated by equations for R_1 and R_2.

Quantitative Analysis of Radionuclides in Neutron-Irradiated Stainless Steel

Type 302 stainless steel contains a number of stable nuclides that are useful as neutron-flux monitors. Three nuclides (Cr^{50}, Fe^{58}, and Co^{59}) make excellent monitors of thermal neutron flux via the reactions $Cr^{50}(n,\gamma)Cr^{51}$, $Fe^{58}(n,\gamma)Fe^{59}$, and $Co^{59}(n,\gamma)Co^{60}$, respectively. In addition, two nuclides (Fe^{54} and Ni^{58}) serve well as monitors of fast neutron flux via the reactions $Fe^{54}(n,p)Mn^{54}$ and $Ni^{58}(n,p)Co^{58}$, respectively. The half-lives of the radionuclides formed in these reactions, as well as the corresponding cross sections, are fairly accurately known. If the steel is irradiated for a few weeks and allowed to decay one week or more, all other radionuclides are present in negligible amounts. For neutron-flux monitoring, the steel is normally used in the form of wire of length from a few inches to a few feet. To obtain data for neutron-flux calculations, it is necessary to determine the absolute disintegration rate of one or more of the above-mentioned radionuclides in the wire. Usually, the wire is cut into segments of equal length (~ 1 in.) and weight so that the spatial distribution of the neutron flux to which the wire was exposed can be obtained. If a number of wires, each a foot or more in length, are to be processed, the number of radionuclide determinations can become very large (five times the combined lengths of the wires in inches). A simple radiochemical method was developed that makes possible the rapid determination of each of the radionuclides in these wire segments with a relative standard deviation of about 10%. To avoid the necessity of weighing each wire segment, a jig was attached to a pair of diagonal wire cutters to allow a wire to be cut into 1-in.-long segments with a relative standard deviation of about 1%. The wire segments are then dissolved in aqua regia, and the solution is diluted to a known volume. An aliquot that contains about 10^5 to 10^6 dis/min of each radionuclide is taken and made about 6 *M* in HCl. The iron, including the Fe^{59}, is extracted into ether. The remaining radionuclides (Cr^{51}, Mn^{54}, Co^{58}, and Co^{60}) can be mounted suitably and assayed by gamma-ray spectrometry. The Fe^{59} in the ether phase can also be mounted suitably and assayed.

The complement-subtraction method[57,58] was used to determine the Cr^{51}, Co^{58}, and Co^{60} in about 500 stainless steel samples. Determinations were made by taking a gamma-ray spectrum of a sample and successively subtracting the Co^{60}, Co^{58}, and Cr^{51} components of the spectrum by use of separate standards of each of these nuclides of known disintegration rates. The absolute disintegration rates of these radionuclides in the samples were calculated from the known disintegration rates of the standards and the times required to subtract the corresponding photopeaks of these radionuclides from the gamma-ray spectra of the test samples.

This work was carried out at the request of V. O. Haynes of the Reactor Division.

LIQUID SCINTILLATION DEVELOPMENT

Gerald Goldstein

Two programs involving the use of liquid scintillators are currently in progress.

In one program, various types of liquid scintillators have been prepared for counting fast neutrons in the presence of gamma radiation by pulse-shape discrimination. A 1-g/liter solution of 1,4-*bis*-[2-(5-phenyloxazolyl)]-benzene (POPOP) in 1-methylnaphthalene(80 vol %)–toluene(20 vol %) shows good pulse-shape discrimination and fast recovery time but poor pulse height for neutrons. A xylene solution containing 4 g of *p*-terphenyl per liter and 0.4 g of POPOP per liter has good pulse height and recovery time but poor pulse-shape discrimination. This work is being done jointly with V. V. Verbinski of the Neutron Physics Division.

In the other program, work is continuing on the development of a large glass-loaded liquid scintillator.[59] A method of purifying commercial 1-methylnaphthalene by chromatography on "acidic" grade alumina was developed. 1-Methylnaphthalene solutions containing 1 g of POPOP or dimethyl POPOP per liter were

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[57] L. C. Bate and G. W. Leddicotte, "Complement Subtraction Method of Gamma-Ray Spectrometry for Quantitative Analysis of Complex Mixtures of Radionuclides," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959,* ORNL-2866, p 33.

[58] W. Lee, "Direct Estimation of Gamma-Ray Abundances in Radionuclide Mixtures," *Anal. Chem.* **31**, 800 (1959).

[59] W. S. Lyon, "Liquid Scintillators by Use of Glass Loading," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961,* ORNL-3243, p 57.

found to be excellent liquid scintillators under gamma excitation.[60] The primary difficulty in glass-loading these solutions is caused by the Christiansen filter effect.[61] Essentially, a glass-liquid mixture transmits radiation at the wavelength at which the refractive indexes of the two components are the same and scatters radiation of other wavelengths. In Fig. 10.10 are shown the refractive indexes of 1-methylnaphthalene and several commercial flint glasses as a function of wavelength. In Fig. 10.11 the transmittance of a typical glass-loaded 1-methylnapthalene is presented along with the fluorescence spectrum of POPOP. For a glass-loaded scintillator to be satisfactory, these two spectra must overlap. The transmission spectrum of the glass-loaded solution can be adjusted by diluting the 1-methylnaphthalene with toluene, but there is a decrease in transmittance. A second problem is the preparation of glass particles without surface scratches, stains, or internal defects. Transmittance measurements of glass-loaded solutions that contained particles prepared from large glass blocks by hammering, by grinding done commercially, and by scraping with a diamond bit showed 65% maximum transmittance for the ham-

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[60] W. S. Lyon and G. Goldstein, "Liquid Scintillators Using 1-Methylnaphthalene," to be submitted for publication.

[61] E. D. McAlister, "The Christiansen Light Filter," *Smithsonian Inst. Misc. Collections* **93,** No. 7 (1935).

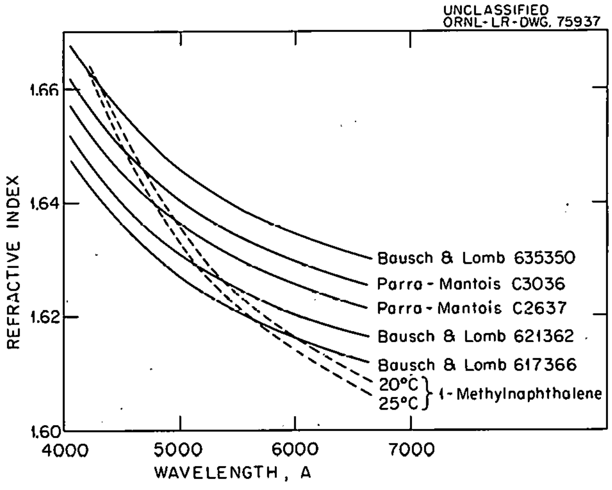

Fig. 10.10. Refractive Index of 1-Methylnaphthalene and of Some Flint Glasses.

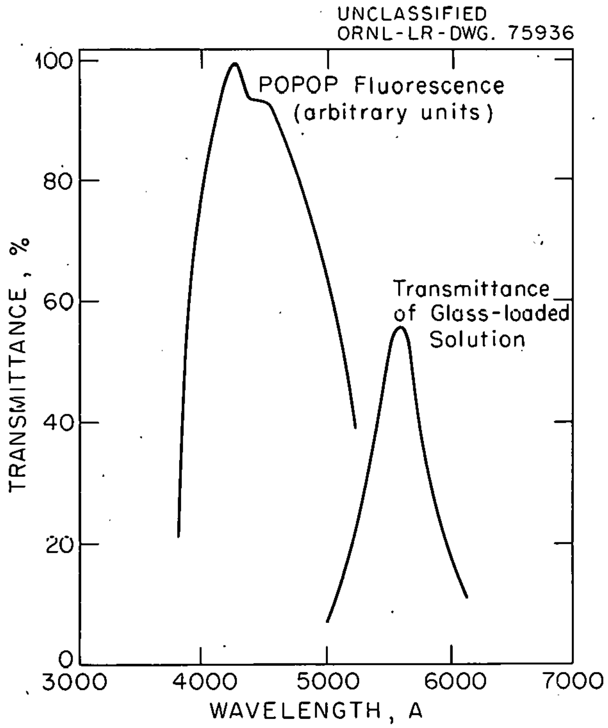

Fig. 10.11. Fluorescence of POPOP and Transmittance of a 1-g/liter Solution of POPOP in 1-Methylnaphthalene Loaded with Bausch and Lomb No. 617366 Glass.

mered particles, 50% for the ground, and 10% for the scraped. Samples of various types of flint glass are now being obtained, and methods of preparing suitable particles are being studied. This work is being done jointly with R. L. Macklin of the Physics Division.

11. Inorganic Preparations

M. T. Kelley
D. E. LaValle
R. B. Quincy, Jr.

The major portion of the work was devoted to the preparation of anhydrous salts in fused or sublimed form.

For the Spectroscopy of Ionic Media Group of the Metals and Ceramics Division, numerous preparations of the eutectic mixture KCl-LiCl in bulk and in specific geometric forms were made. In addition, 100-g quantities of alkaline-earth-metal chlorides and smaller quantities of iron-group chlorides were provided.

For the High Temperature and Structural Chemistry Group of the Chemistry Division, numerous preparations in 150-g quantities of the anhydrous alkaline-earth-metal and rare-earth-metal halides were continued. The chlorides and bromides were prepared routinely by methods described in previous reports: for the alkaline-earth-metal salts, fusion and passage of the appropriate halide gas through the melt, followed by filtration through fritted fused-silica disks; for the rare-earth-metal salts, preliminary dehydration by any of various well-known methods, followed by sublimation.

The iodides, however, presented problems. The alkaline-earth-metal iodides were amenable to preliminary dehydration by the usual methods, but the rare-earth-metal iodides had to be synthesized from the elements in a static evacuated system. Because the iodides attack quartz and platinum at high temperatures, the problem of final purification was solved only by resorting to sublimation in a molybdenum system enclosed in quartz.

For the Nuclear Physics and Neutron Diffraction Group of the Physics Division, only minor activity was continued in the preparation of rare-earth-metal compounds. The deuterides of terbium, holmium, and erbium were prepared. Attempts to prepare HoS free from Ho_2OS_2 have been unavailing, probably because of original oxide contamination in the metal. Attempts to prepare the subcarbides Ho_3C and Er_3C always resulted in products having more than a single phase. The major work has been devoted to the preparation and treatment of alloys. Numerous alloys of yttrium with rare-earth metals were prepared. Also, a system was set up that is capable of measuring the hydrogen absorbed or evolved by some Pd-Fe alloys at atmospheric pressure and at various temperatures. The unstable hydrides of nickel[1] and chromium[2] were prepared by electrolysis.

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[1] B. Baranowski and M. Smialowski, "Charging of Nickel Films with Hydrogen Evolved Electrolytically in the Presence of Catalytic Poisons," *Intern. J. Phys. Chem. Solids* 12, 206 (1960).

[2] M. J. Trzeciak, D. F. Dilthey, and M. W. Mallett, *Study of Hydrides*, BMI-1112 (July 12, 1956).

The work for the Nuclear Physics and Low Temperature Group of the Physics Division consisted mainly in the preparation of a series of alums of the type $NH_4Al(SO_4)_2 \cdot 12H_2O$, in which it was attempted to replace up to 75 mole % of the Al with Fe, as an experiment preliminary to the use of Fe^{57}. The introduction of the Fe in the amounts desired has not quite been achieved. Other preparations for this group were a Cd-Au alloy and the ionic compound CsAu.

The program for the preparation of high-purity K_2O for the High Temperature Materials Group of the Metals and Ceramics Division has been terminated for the time being with the preparation of a product of better than 98% purity. A series of lithium niobates was also prepared for this group.

For the Radiation Chemistry Group of the Chemistry Division, about 100 g each of Li^6BrO_3 and Li^7BrO_3 were prepared by passing $KBrO_3$ through an acidic cation exchange resin and collecting the $HBrO_3$ in the appropriate lithium hydroxide prepared from the metal isotope.

The investigation of the chemistry of rhenium and technetium for the Inorganic and Physical Chemistry Group of the Chemistry Division was resumed, with emphasis on attempts to prepare lower fluorides of rhenium. The compound $ReBr_3$ was fused in NH_4HF_2, and a green complex salt was isolated. Repeated fusions of the green complex greatly reduced the bromide content but did not eliminate it completely. Fusion of $ReBr_3$ in KHF_2 and extraction of the excess KF with methanol yielded a gray complex salt insoluble in water. The complex salt $(NH_4)_2ReF_6$ was prepared by ion exchange from K_2ReF_6, which was prepared and described last year.[3] The decomposition of $(NH_4)_2ReF_6$ in vacuum at 180°C, in HF at 250°C, and in argon at 250°C always led to unidentified substances that contained some fluorine but no metal, whereas the analogous technetium compound behaved differently.[3]

In the high-purity preparations program for the Insulating Crystals Group of the Solid State Division, pure MgO was prepared;[4] the product contained <10 ppm (in most cases, <5 ppm) of any impurity. Preliminary work was also done in the preparation of high-purity TiO_2. Crystal-bar titanium metal that contained as the two chief impurities 50 ppm of Mg and 500 ppm of Zr was dissolved in HCl, the solution was passed through an anion exchange resin, titanium was precipitated with NH_4OH, and the precipitate was ignited at 450°C. An evaluation of this product has not yet been completed.

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[3] M. T. Kelley and D. E. LaValle, "Inorganic Preparations," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961,* ORNL-3243, pp 77–78.

[4] R. B. Quincy, Jr., *Preparation of High-Purity Magnesium Oxide,* ORNL TM-302 (Aug. 15, 1962).

12. Organic Preparations

J. C. White
P. F. Thomason
H. L. Holsopple, Jr.

Organic compounds were prepared and purified on request from the Chemical Technology, Analytical Chemistry, Chemistry, and Biology Divisions. These compounds either were not readily available from commercial sources or were available in impure form only and required purification. A summary of this program follows.

COMPOUNDS PREPARED

Arsenazo III

Sixty grams of 1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis[(azo-2)-phenylarsonic acid], which is a chromogenic reagent called arsenazo III, was synthesized for use in the determination of thorium. This compound, a bis-diazo dye based on chromotropic acid and *o*-aminophenylarsonic acid, was found by Savvin[1] to give a marked color reaction with thorium in low concentrations. A method of synthesis was used in which *o*-nitroaniline was diazotized and reacted with sodium arsenite in alkaline solution to form *o*-nitrophenylarsonic acid. This product was then reduced with ferrous chloride and sodium hydroxide to form *o*-aminophenylarsonic acid, after which arsenazo III was prepared by the azo addition of diazotized *o*-aminophenylarsonic acid and chromotropic acid. Detailed methods for the preparation of these intermediate compounds, together with modifications of Savvin's synthesis to form arsenazo III, will be described in a formal report.

n-Alkylbenzenes

Two normal alkylbenzenes, *n*-hexyl- and *n*-heptylbenzene, were synthesized for Chemical Development Section C of the Chemical Technology Division. These compounds were prepared by reacting bromobenzene and sodium with *n*-hexylbromide or *n*-heptylbromide, as required. The resulting product was separated by distillation at atmospheric pressure and was then purified by distillation over sodium under reduced pressure. Approximately 670 g (47% yield) of *n*-hexylbenzene and 150 g (59% yield) of *n*-heptylbenzene were obtained from several batches. The results of elemental analysis and measurements of physical characteristics were in good agreement with theoretical and literature values (Table 12.1). The details of this work are reported elsewhere.[2]

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[1] S. B. Savvin, "Analytical Use of Arsenazo III," *Talanta* 8, 673 (1961).

[2] H. L. Holsopple, *Synthesis of* n-*Hexyl- and* n-*Heptylbenzene*, ORNL TM-254 (June 14, 1962).

Table 12.1. Composition and Physical Characteristics of Two *n*-Alkylbenzenes

Property	*n*-Hexylbenzene		*n*-Heptylbenzene	
	Theoretical[a]	Found	Theoretical[a]	Found
Carbon, mole %	88.8	88.5	88.7	88.2
Hydrogen, mole %	11.2	11.3	11.3	11.6
d_4^{20}	0.860	0.850	0.859	0.848
n_D^{20}	1.488	1.484	1.486	1.482
BP, °C	226	225 to 227	244	243 to 245
Flash point (Cleveland open-cup), °F		208		203

[a] These values are those given by Francis in his compilation of physical properties of 379 alkylbenzenes [see A. W. Francis, "Properties of Alkylbenzenes," *Chem. Rev.* 42, 107 (1948)]. They are selected mean values based on the preponderance of agreement of several observations.

Organophosphorus Compounds

The Chemical Technology Division requested the preparation of a number of organophosphorus compounds for use in studies of their behavior as diluents and solvent-extraction reagents. One of these, di(*sec*-butyl)phenylphosphonate, is useful in the separation of uranium and thorium. Unfortunately, its metal salts have limited solubility in the ordinary aliphatic diluents. It is desired to determine whether substitution of an alkyl group for a hydrogen of the benzene ring will result in increase in solubility. Consequently, a quantity of di(*sec*-butyl)phenylphosphonate having an alkyl group (butyl to octyl, branched or unbranched) on the benzene ring is being synthesized. Also, attempts are being made to synthesize pure mono- and dialkylphosphoric acids from nonylphenol, octylphenol, and phosphorus pentoxide as starting reactants. Other compounds of interest yet to be synthesized are some methyl phosphonic acids, branched-chain hydroxamic acids, and substituted phenols (e.g., 2-heptyldecylphenol and 2,4-di-2-ethylhexylphenol).

COMPOUNDS PURIFIED

Diphenyl Ether

Nearly 4 liters of diphenyl ether was purified by distillation under vacuum. In this system, possible contamination from grease on ground-glass joints was avoided by use of very thin Teflon sleeves to lubricate the joints.

Diphenylcarbohydrazide

Twenty grams of diphenylcarbohydrazide was purified by crystallization from hot ethyl alcohol.

Tetramethylammonium Hydroxide

One hundred grams of solid tetramethylammonium hydroxide was recovered from a 10% aqueous solution by use of the freeze-dry technique for removal of liquid.

1-Methylnaphthalene

Two 50-ml quantities of 1-methylnaphthalene were distilled into containers especially designed to be removed and sealed under vacuum. This material was for use in studies being acrried out by the staff of the Bulk Shielding Facility.

1,4-Dioxane

One liter of pure 1,4-dioxane was prepared for the Biology Division. Two liters of technical 1,4-dioxane was boiled for 7 hr under reflux with 0.1 *M* HCl to decompose ethylene acetal. A stream of air was passed through the condenser to remove acetaldehyde. The product was treated with KOH, allowed to dry over sodium metal, and distilled. The constant-boiling fraction was collected at 101°C.

Di(2-ethylhexyl)phosphoric Acid

Four liters of di(2-ethylhexyl)phosphoric acid was purified for use by the Chemical Technology Division. The purification consisted essentially in hydrolyzing the poly- and pyrophosphates present by refluxing the technical-grade material with 2 *M* HCl, conversion of the dialkyl acid to the sodium salt, and extraction of the inert materials (hydrocarbons, trialkyl phosphates, and alkyl alcohols) in a continuous petroleum ether extractor. At this point, a phase that contained the sodium salt separated out. It was partitioned with ethylene glycol to remove the mono(2-ethylhexyl)phosphoric acid, washed several times with 6 *M* HCl and water, and treated with activated carbon and anhydrous sodium sulfate.

Part II. Analytical Development

J. C. White
P. F. Thomason

13. Ionic Analyses

Hisashi Kubota

DETERMINATION OF THORIUM AND URANIUM IN GRANITE

R. F. Apple J. R. Lund Hisashi Kubota

The analytical schemes available for the determination of thorium and uranium in granites follow two definite patterns. One is acid attack of the rock, which removes many of the unwanted components by volatilization and selective dissolutions. The other is alkaline attack, whereby the bulk of the unwanted material is dissolved and the desired substances are kept insoluble. Either approach is time-consuming because repeated treatments are necessary.

A scheme of analysis for thorium in granite was developed that combines both approaches and reduces the time required for analysis from 4 to 1½ days. The sample is sintered with sodium peroxide for 90 min at 450°C; the sinter is cooled and is then suspended in water. The suspension is centrifuged, and the solid residue is treated with an $HClO_4$-HF mixture. After removal of all traces of fluoride, the residue is dissolved in nitric acid and the thorium is extracted with tri-*n*-octylphosphine oxide (TOPO), stripped from the organic phase into 1 *M* H_2SO_4, and determined spectrophotometrically.

In the analysis for thorium, most of the uranium, as the carbonate complex, remains in the supernate following the centrifugation. Since the uranium is determined fluorometrically, only one-tenth of the supernate is acidified and extracted with TOPO. For the fluorometric determination, this extract is combined with a similar fraction of the original thorium extract. A small negative bias was observed when the results obtained by this procedure were compared with values obtained previously by other methods.

ARSENAZO III AS A CHROMOGENIC REAGENT FOR THORIUM

R. F. Apple

The synthesis and application of arsenazo III have been reported.[1] In view of the claim that this reagent has great sensitivity for thorium (molar absorptivity of 130,000), the reagent was synthesized and tested for use in the analysis of granite.

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[1] S. B. Savvin, "Analytical Use of Arsenazo III," *Talanta* 8, 673 (1961).

The color is developed in a medium that is 3 to 9 *M* in HCl. For the type of samples most generally encountered, that is, one in which some uranium or zirconium is present, 6 *M* is the most useful concentration. At this acid concentration, the molar absorptivity of the thorium–arsenazo III complex is about 80,000 at 662 mμ. No separation from equimolar quantities of uranium or zirconium is necessary. Nitrate and fluoride must be absent; however, a thousandfold excess of sulfate, phosphate, or oxalate is tolerable.

Arsenazo III is very useful for the determination of 1 to 10 μg of thorium in 0.1 to 1 g of granite and has been used in many programs. It is hoped to extend its use to the determination of uranium and zirconium.

DISSOLUTION OF HIGH-FIRED, RADIOACTIVE, REFRACTORY MATERIALS

R. F. Apple Hisashi Kubota

Procedures were developed for the dissolution of several types of reactor material that had been exposed to very high temperatures and levels of radiation, thereby acquiring refractory properties. The materials themselves contained so much radioactivity that the dissolutions had to be performed entirely in hot cells. The dissolution procedures were as follows. Thorium oxide was refluxed with 13 *M* HNO_3–0.1 *M* NaF. Material not affected by this treatment was dissolved by an ammonium bifluoride fusion. The mixture ThO_2-UO_2-BeO was fused with ammonium bifluoride, and the melt was dissolved in sulfuric acid. Uranium carbide, coated with pyrolytic graphite, was treated with perchloric acid that contained a small amount of chromic acid. After the dissolution was complete, the chromium was volatilized as the chromyl chloride to prevent its interference with subsequent analyses. Strontium titanate was solubilized by ammonium bifluoride fusion.

Ammonium bifluoride is a very versatile reagent that can be used in a hot cell without special equipment. These procedures were satisfactory for dissolving materials that had been heated to about 3000°C.

This work was described in a paper presented orally.[2]

DETERMINATION OF LITHIUM IN BERYLLIUM OXIDE

J. R. Lund

In order to learn the fate of the lithium that was produced by the $Be^{10}(n,\alpha)Li^7$ reaction, lithium was determined in beryllium oxide that had been exposed to various levels of neutron irradiation. Since lithium can be detected in the presence of a large amount of beryllium by a flame photometer that has a very sensitive optical system, the main problems were the dissolution of the refractory material and the removal of radioactive elements to prevent the contamination of the photometer environment.

Beryllium oxide was dissolved in any one of the following media: phosphoric acid, perchloric acid, perchloric-nitric acids, and molten ammonium bifluoride followed by an acid dissolution. In view of the separations that have to be made, the perchloric acid with or without nitric was preferred. Ammonium bifluoride was found to contain a small amount of lithium.

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[2] Hisashi Kubota and R. F. Apple, *Dissolution of Irradiated High-Fired, Refractory, Nuclear Materials*, presented at the Sixth Annual Conference in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962.

The bulk of the radioactive elements was removed by a lanthanum fluoride precipitation. Some of the more radioactive species thus removed were Co^{60}, Sc^{46}, Zr^{95}-Nb^{95}, Ce^{141}, Co^{58}, and Mn^{54}.

DETERMINATION OF MICROGRAM QUANTITIES OF CARBON IN STEEL

J. R. Lund

The lower limit to the determination of carbon on the Leco apparatus is about 20 μg. An investigation, now suspended, was made to determine the carbon content of steels of about 10-ppm carbon content. It was proposed to take advantage of the great sensitivity of a gas chromatograph for the final determination of the carbon as carbon dioxide. The gas chromatograph can detect the carbon dioxide equivalent of 1 μg of carbon with good accuracy and precision. Problems that still remain are to effect complete combustion of the carbon in the material and to minimize the blank.

DETERMINATION OF CARBON AND NITROGEN IN NaK

J. R. Lund

Samples of NaK that were contained in sealed glass tubes were introduced into specially fabricated reaction flasks that contained anhydrous *n*-hexane overlaid by argon. After the sample tube was crushed, *n*-butyl bromide was added slowly until the NaK reacted completely. Water was then added, and the solution was heated. The released ammonia, formed from the nitrogen, was carried over by an argon stream into a sulfuric acid trap and was determined by the sodium phenoxide spectrophotometric procedure. The solution was filtered through a pretreated asbestos mat, and the carbon was determined on the Leco apparatus.

AMPEROMETRIC CUPFERRON TITRATION OF ZIRCONIUM

J. G. Surak[3] Hisashi Kubota

An amperometric titration of zirconium in which cupferron is the titrant and a D.M.E. is the end-point detector is described by Olson and Elving.[4] It has the outstanding advantage over many other titrimetric methods for zirconium that the titration is carried out in a strong acid medium and is unhindered by the presence of fluorides. The procedure originally described,[4] however, is slow and requires many repeated operations. Both the procedure and sensing system were modified to make the titration a continuous operation and thus to eliminate many of the operations formerly required.

The titrant is fed in at a steady rate with an infusion pump. The electrode system is a stirred mercury pool and a platinum wire. The graph of the current that passes through this electrode pair vs titrant delivered shows an abrupt rise when the end point is passed. Best results are obtained when the mercury pool is maintained at −0.55 v relative to the platinum wire electrode and a drop of 0.1% gelatin solution is added.

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[3] Temporary employee from Marquette University, Milwaukee, Wis.

[4] E. C. Olson and P. S. Elving, "Amperometric Titration of Zirconium," *Anal. Chem.* **26**, 1747 (1954).

It is planned to adapt this titration to the determination of zirconium in radioactive materials in the hot cells.

This work will be described in a paper to be presented at the 144th National Meeting of the American Chemical Society in Los Angeles.

DETERMINATION OF PHENOLS BY NONAQUEOUS TITRIMETRY

Corinne C. White

Phenols form bonds with cesium under basic conditions, a property that is being exploited in an attempt to extract radioactive cesium from waste-processing solutions. The economics of this extraction depends on the efficiency of the extraction, as well as on the degree of loss of extractant per pass. The loss of several substituted phenols from the organic to the aqueous phase was determined. Nonaqueous acidimetry was found to be an ideal method for determining the loss. The following conditions were satisfactory. The titrant tetrabutylammonium hydroxide was prepared by reacting tetrabutylammonium iodide with silver oxide in a methanol-benzene medium.[5] Acetone was the titration medium used for the more acidic phenols, and pyridine for the less acidic ones. The titration cell was a Lingane H-cell in which a fritted disk and agar plug separated the medium from the S.C.E. used as reference. The indicator electrode was a conventional glass electrode that was reconditioned daily by soaking in water. The precision normally attained in the titration of ~1 mg of a substance was attained easily.

A bromination procedure was also studied. The recovery and precision were good; however, the experimental parameters had to be maintained very carefully in order to ensure reproducible values. Bromination is useful for some special applications but has no advantages over the titrimetric procedure for this particular problem.

ANALYSES MADE ON REQUEST

Hisashi Kubota R. F. Apple J. R. Lund
Lucy E. Scroggie Corinne C. White

Some analyses and operations that were done on request are listed below. Precise analyses of acid and halide solutions were performed for the Chemistry Division. A scheme of analysis was devised to determine all the products of the high-temperature reduction of calcium sulfate and magnesium sulfate. The Cr^{3+} content of a chromic acid plating bath was determined spectrophotometrically following anion-exchange separation of the Cr^{3+} and Cr^{6+}. The identity and concentration of iron complexes in some dissolver solutions were determined. The vapor pressure of Cosmoline 1094, a pump oil, was determined between 150 and 300° F, and the mixture of more volatile components was analyzed. A polarographic method was developed for determining mercury in gold foils used as neutron dosimeters. Work is continuing on the analysis of the decomposition products from the gamma irradiation of Dowex 50.

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[5] R. H. Cundiff and P. C. Markunas, "Tetrabutylammonium Hydroxide as Titrant for Acids in Nonaqueous Solutions," *Anal. Chem.* **28**, 792 (1956).

DISPOSAL OF RADIOACTIVE WASTE SOLUTIONS IN NATURAL SALT

Hisashi Kubota

The study of the disposal of radioactive waste solutions in natural salt is a part of the waste disposal program of the Health Physics Division. The work is reported bimonthly in the *Waste Treatment and Disposal Progress Report.*

It was found that salt samples from the salt mines in Kansas fracture when heated to 260 to 300°C and that this fracturing is accompanied by a release of steam. Field experiments have shown that unmined salt also fractures. The amount of water released is being measured quantitatively in order to determine the maximum credible damage that could be inflicted on waste-disposal operations. Salt from mines in areas other than Kansas is being tested in a similar manner.

ABSORPTION CELL ATTACHMENT FOR WELCH DENSICHRON REFLECTION UNIT

F. J. Miller[6]

Assistance was given to members of the Radioisotope-Radiochemistry Laboratory in setting up methods that require the use of the absorption-cell attachment with the Welch Densichron reflection unit. These methods are for the determination of heavy metals, total reducing agents, manganese, and nitrate in I^{131} product solutions.

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[6] Reactor Projects Group.

14. Infrared Studies

C. A. Horton

Infrared spectrometric methods were used in several analytical problems. Some of the studies and results are listed below.

INORGANIC COMPOUNDS

In pellets of potassium bromide, potassium pertechnetate was found to have principal absorption bands at 910, 900, 355, 335, and 325 cm^{-1}; potassium perrhenate at 924, 910, 900, 363, 317, and 305 cm^{-1}; and potassium permanganate at 915 and 400 cm^{-1}. The visible-ultraviolet absorption bands of such pellets were considerably sharper than were those for spectra of aqueous solutions. The saturated heavy-water solution of each of these three compounds showed single broader bands centered at 907, 917, and 907 cm^{-1} respectively.

Cesium bromate that had been irradiated with gamma rays in an inert atmosphere at controlled temperature did not show the unidentified bands which were observed previously in somewhat similar studies of alkali-metal bromates. The studies were made on bromates that had been irradiated with gamma rays in glass vials that contained air. The bromate concentration, however, decreased during all irradiations.

Several crystals of Li^7F that were examined showed no evidence of extraneous absorption bands, such as hydroxyl groups. The cutoff frequency depended primarily on the thickness of the crystals. The visible, near-infrared, or infrared spectra of irradiated crystals of silicon showed only slight evidence of absorption bands due to crystal defects.

ORGANIC COMPOUNDS

Radiation-induced composition changes were studied for a few reagents. The spectra of the decomposition products of ethylenediaminetetraacetic acid and of tri-*n*-octylphosphine oxide, both of which had been subjected to gamma irradiation, were compared with the spectra of the unirradiated compounds.

The spectrum of 3-methyl-6-aminopurine was compared with published spectra of other amino and imino purines, as well as with newly observed spectra of 7-methyladenine, 9-methyladenine, 6-methylaminopurine, 6-dimethylaminopurine, 3-methyl-6-dimethylaminopurine, and isoguanine. These data, coupled with p*K* data obtained by B. C. Pal,[1] ultraviolet absorption spectra, and electrophoresis data, confirm that 3-methyl-6-aminopurine exists in the amino form rather than the imino form previously postulated.[2,3]

The functional groups were identified in several types of samples. Low-volatility organic products obtained when uranium carbides are treated with water were found to contain methyl, methylene, carbonyl, and carboxylic acid groups. An oil collected in a trap at the ORR was identified as a slightly degraded pump oil. Fuming nitric acid boiled with graphite contained a mixture of organic compounds, which have not yet been separated for identification. The differences in composition of several plastic floor tiles and of four rubber samples were determined by use of the new attenuated-total-reflectance technique. The infrared spectrum of diphenylcarbazide was obtained for the first time and also that of the oxidation product obtained from it in the presence of Cr^{3+}. A crystalline material, expected from its ultraviolet spectrum to be a benzoate or similar compound, was identified as benzoic acid. A preservative recovered from a spillage of a shipment of a radioactive substance was identified as isopropylbenzene; it contained traces of an aliphatic ester and water. The organic by-products of the reaction of a perchloro-olefin with metal oxides were examined both before and after they were treated with water. The principal bands observed were carbon-chlorine and carbonyl types; no carbon-hydrogen types were observed. The following were identified in impurities isolated from α-methylnapthalene by adsorption on alumina and subsequent elution: carbonyl groups, monosubstituted benzene, and α-substituted napthalene.

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[1] Research participant in the Biology Division from Chemistry Department, Tuskegee Institute, Tuskegee Institute, Ala.

[2] G. B. Elion, "Some New *N*-Methyl Purines," p 39 in *Ciba Foundation Symposium on the Chemistry and Biology of Purines* (ed. by G. E. W. Wolstenholme and C. M. O'Conner), J. and A. Churchill, London, 1957.

[3] B. C. Pal and C. A. Horton, "Structure of 3-Methyladenine and Methylation of 6-Dimethylaminopurine," to be published.

SEMIQUANTITATIVE AND QUANTITATIVE STUDIES

Qualitative studies of undiluted and diluted hydroxamic acids were made. Quantitative estimates of hydroxamic acids in tributyl phosphate–dodecane mixtures were made. The relative proportions of ortho-, meta-, and paradiethylbenzene in commercial mixtures of these compounds were estimated. The amounts found, along with an extraneous compound in one batch, correlated with the behavior of the batches when they were used as diluents in an extraction process.

Quantitative studies in the 1100- to 1400-cm^{-1} region were made on mixtures of di(2-ethylhexyl)-phosphoric acid and its sodium salt in nonane. For mixtures that were 25 to 35% sodium salt, the absorbances for the 1230-cm^{-1} bonded-phosphoryl vibration and for the 1215- to 1220-cm^{-1} band (attributable to either unbonded phosphoryl or POO$^-$ ion absorptions) were minimum. For mixtures that were 20% sodium salt, the absorbance for the 1270-cm^{-1} band (attributable to the POO$^-$ group) was maximum. These findings correlate with the fact that maximum extraction of strontium was attained when the mixture was 25 to 30% sodium form.

The cyclohexane content of cyclohexanol-cyclohexene mixtures and the formation of other compounds in certain such mixtures were studied.

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Part III. Service Analyses

A summary of the service analyses made by the laboratories of the Analytical Chemistry Division is given in the table below.

Summary of Analytical Service Work

	Av No. in Group		Number of Results Reported																												
			For ORNL																			For Others									
Group Making Analyses	Scientists	Technicians	Analytical Chemistry	Biology	Chemical Technology	Chemistry	Electronuclear	Engineering and Mechanical	Health	Health Physics	Instrumentation and Controls	Isotopes	Metals and Ceramics	Neutron Physics	Operations	Physics	Reactor	Reactor Chemistry	Solid State	Thermonuclear	Inspection Engineering	Armour Research	AEC	G.E.	K-25	Miscellaneous	TVA	Tullahoma Air Force Base	University of Tennessee	Y-12	Total
Infrared Spectral Analyses[a]	1	1	100	240	2,200	250		16		18			24		10	25	75	55	25										120	60	3,218
Ionic Analyses[a]	4	1	26		1,287	176				50			202			10	4	435													2,190
Low-Radiation-Level Radiochemical Laboratory	2	2	9		538					3,450		28		85	185					2							10			27	4,334
Mass Spectrometry Analyses[a]	10	7	36	126	2,607	20	17					9,817	2,465		8	35	4,386	4,226	1112	52						2092				343	27,342
Nuclear Analyses[a]	8	3	2		228			232		12		28	98	25	271	5	893	199	1202	1				59						4	3,259
Optical and Electron Microscopy[a]	3	2	30		480	165				125	10	65	185	5	485	130	30	845										5		160	2,720
Process Analyses																															
General Analyses Laboratory	10	13	81		40,374	423				410		55	5,803	123	822	94	1,239	1,226	307	222											51,179
General Hot Analyses Laboratory	10	16			12,422					90		2,250	350		8,638		81	1,818	302			14		8							25,973
High-Level Alpha Radiation Laboratory	3	3			11,626					11		428	1	6				4	3											1055	13,134
Materials Testing Laboratory	5	11	17		16,409	168	5		2	26		75	843	86	113	33	1,035	3,301	11		10									6	22,140
Radioisotopes-Radiochemistry Laboratory	6	15	9	6	6,193	16				883	6	11,049	999	290	8,529	35	1,875	12,530	783	7				178		22				114	43,524
Radiochemical Analyses[a]	5	1	17		218	24	26			252		121	177	44		16	56	611	302						10						1,874
Gas-Cooled Reactor Project[a]	7				2,345	85						6	70				262	237													3,005
Spectrochemistry Laboratory[a]	2	2	29	104	738	112	1			991		14,140	1,860	72		122	660	3,560	42	78	18									3190	25,717
Reactor Engineering Service Laboratory[a]	1	4	2		842					465		7	314	14			2,083	9,547	18	36	29		532							112	14,001
X-Ray and Spectrochemical Analyses[a]	10	3	50		3,513	987		34	3370	19,923		63	998		411	75	93	3,759	366							399					34,041
Total	87	84	408	476	102,020	2426	49	282	3372	26,706	16	38,132	14,389	750	19,472	580	12,772	42,353	4473	398	57	14	532	245	10	2513	10	5	120	5071	277,651

[a] These groups also do research and development work; therefore, in these groups the average number of persons may be greater than the number of persons who have done service work.

15. Quality Control

C. D. Susano

C. K. Talbott Bobby J. Ginocchio

During the 12-month period from July 1961 through June 1962, the Statistical Quality Control program was extended. The permissible limits of variation were made smaller, and the number of "blind" quality control samples was increased. These changes were instituted specifically to control more rigidly the precision and accuracy of the methods of analysis, to develop a greater awareness of inadequacies in the methods, and to provide a means of evaluating such inadequacies. As a consequence, a larger proportion of the results are outside the so-called 2S limits, the 95% confidence level. It appears that the limits of some methods, particularly those involving remote analytical techniques in hot-cell applications and those utilized in the determination of low concentrations, will have to be liberalized. For some of the colorimetric methods where the 2S limit has been of the order of 4%, this limit should possibly be raised to 5 or 6%. Although this change seems rather large on a relative basis, it is of no real significance on an absolute basis. These remarks also apply to the coulometric and fluorometric procedures for the determination of uranium.

Some 3800 control tests were made during the period, compared with approximately 2900 for the preceding period. The distribution of these control tests by laboratory is shown in Table 15.1. A compilation that shows the distribution by methods is presented in Table 15.2.

Table 15.1. Distribution by Laboratory of Control Tests for July 1961 Through June 1962

Laboratory	Number of Control Results		Quality Level (%)[a]	
	Total	Outside Fixed Limits	1961	1962
General Hot Analyses	1239	181	89	85
High-Level Alpha Radiation	60	19		68
General Analyses	1671	146	94	91
Materials Testing	514	63	94	88
Reactor Engineering Service	279	15	96	95
	Total 3703	Total 424	Av 93	Av 85

[a] Percent of control data inside fixed limits.

Table 15.2. Distribution by Methods of Control Results for July 1961 Through June 1962

Type of Method	Constituent	Number of Control Programs	Number of Control Results
Colorimetric (spectrophotometric)	Aluminum	1	48
	Beryllium	1	10
	Chloride	1	6
	Chromium	3	102
	Copper	1	1
	Iron	3	212
	Manganese	1	30
	Nickel	3	103
	Thorium	3	569
	Uranium	5	1150
		22	2231
Coulometric	Uranium	2	428
		2	428
Fluorometric	Uranium	3	536
		3	536
Gravimetric	Carbon	3	177
	Copper	1	3
	Molybdenum	1	3
	Nickel	1	26
	Silicon	1	21
		7	230
Potentiometric	Uranium	1	96
		1	96
Volumetric	Aluminum	1	38
	Chromium	1	32
	Lithium	1	7
	Nitrate	2	93
	Phosphorus	1	19
	Sodium	1	1
	Sulfate	1	13
	Sulfur	1	33
	Thorium	1	3
	Uranium	1	3
		11	242
Total		46	3763

16. Low-Level Radiochemical Laboratory

M. T. Kelley
C. L. Burros

The Low-Level Radiochemical Laboratory reported 4334 results. Approximately 80% of these were for the Health Physics Division in connection with their ecological, waste-disposal, and area-monitoring programs. Samples were of the same types as those analyzed in past years.

17. Mass Spectrometric Analyses

A. E. Cameron
J. R. Sites

The Analytical Mass Spectrometry Laboratory reported over 27,300 results on some 3300 samples. About a third of these samples were separated stable isotopes of 42 elements: B, C, Ne, Mg, Si, Cl, Ar, K, Ca, Ti, Cr, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr, Mo, Ru, Ag, Cd, In, Sn, La, Ce, Nd, Sm, Gd, Dy, Er, Yb, Lu, Hf, Ta, W, Re, Os, Hg, Tl, and Pb.

Two sets of irradiated cadmium sulfide samples were analyzed in support of tests at the Idaho Operations. A set of uranium fuel samples were checked for the Power Reactor Development Company.

Submitted samples varied in size from 1 cc of fission-product krypton at a pressure of 1 cm Hg to a trailer of helium at a pressure of 2000 lb.

The Analytical Mass Spectrometry Laboratory continued to analyze samples derived from thermal diffusion experiments and production of staple isotopes, fission gases recovered from capsule tests, fission-product krypton and xenon for the Isotopes Sales Department, samples from MSRE capsule tests for hydrogen and carbon tetrafluoride, and uranium in various forms submitted for inventory and from burnup experiments. Cylinders of He, Ar, N_2, and H_2 were certified.

18. Spectrochemical Analyses Laboratory

C. D. Susano
Zell Combs J. A. Norris

More than 1800 samples were analyzed in the Spectrochemical Analyses Laboratory, and some 25,700 results were reported. Approximately 40% of the samples originated in the Isotopes Division and included the stable isotopes of Li, B, Mg, Si, Cl, Ca, Ti, Cr, Fe, Ni, Zn, Br, Rb, Sr, Zr, Mo, Ru, Pd, Cd, Sn, La, Ce, Nd, Sm, Gd, Er, Yb, Lu, Hf, Ta, W, Os, Tl, and Pb. The Process Improvement Group of the Electromagnetic Separations Department submitted samples of B^{10}, Ca^{46}, and La^{138} taken from experimental collections for the determination of beam-retention values. Other samples included 204 samples of mixed oxides of tantalum and niobium for the Ta/Nb ratio; 187 mollusk shells for Sr, Ba, Mg, Na, and Mn; and 347 samples of beryllium metal and its compounds.

19. Process Analyses

L. T. Corbin

The number of analyses performed this year increased by 12%, and the number of personnel remained the same. The largest increase was in radiochemical analyses. This increase in performance was due mainly to new equipment installed in these laboratories. A brief statement of new developments in each laboratory follows.

HIGH-LEVEL ALPHA RADIATION LABORATORY

J. H. Cooper

The major portion of the analytical service work of the High-Level Alpha Radiation Laboratory was for the Chemical Technology Division in conjunction with the preparation of U^{232} and with the Transuranium Chemical Process. Uranium-232 was determined by alpha-pulse-height analysis of a variety of process solutions that contained many alpha-particle emitters. In the transuranium program, microcurie amounts of Am^{241} were determined in millicurie amounts of Cm^{242} by alpha counting the Am^{241} after it was separated from the Cm^{242}. Americium was oxidized by persulfate, and curium was precipitated with lanthanum fluoride. Results obtained by this method were in agreement with those obtained by high-resolution pulse-height analysis.

The High-Level Alpha Radiation Laboratory aided in the study of plutonium polymerization by analyzing solutions that contained plutonium in various states of oxidation. The amount of plutonium in each oxidation state was determined by coulometric titration.[1] Concentrations of plutonium polymer in solutions of ionic plutonium were also determined.

Plutonium in the parts-per-billion range was determined radiometrically in samples of purified uranium from the Volatility Pilot Plant. Pulse-height analysis was necessary to correct for the traces of U^{234} alpha radiation that carried through the analysis.

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[1] W. D. Shults, *ORNL Procedures for Controlled-Potential Coulometric Titration of Plutonium*, ORNL TM-366 (Sept. 14, 1962).

GENERAL ANALYSES LABORATORY

W. R. Laing

A number of new methods and modifications of existing methods were put into service. Among the new methods are those for determining cobalt in stainless steel by nitroso-R-salt following the separation of cobalt on a column of activated alumina[2] and for the microtitration of cobalt with ferricyanide following a separation on Dowex 1. Uranium carbides and thorium carbides were analyzed for free carbon. Bars of pyrolytic graphite that contained from 0.5 to 1000 ppm of uranium in concentration increasing from one end of the bar to the other were sectioned (see "Jig for Precisely Sampling a Graphite Bar," in Chap. 1 of this report), the sections were burned, and the residues were analyzed for uranium. Microtitration procedures for the determination of nitrite in scrubber solutions and for the determination of magnesium in sea water were developed and are in use. An EDTA electrolyte was used for the polarographic determination of germanium.[3] EDTA was also used as the titrant for aluminum in solutions that contained both thorium and uranium; either eriochrome black T or dithizone was used as the indicator. Several hundred 10-mg punchings of U-Al alloy, each of which contained about 1 mg of U, were analyzed coulometrically for uranium with a relative standard deviation of 0.5%.

Included in the methods that were modified are those for the continuous-flow determination of surface area, the conductometric determination of carbon, yield stress measurement, and the spectrophotometric determination of nitrate in the presence of nitrite.

A Leco Oxygen Determinator and equipment for pore-size distribution were placed in service.

The total number of results reported was 51,179.

GENERAL HOT ANALYSES LABORATORY

C. E. Lamb

A program was initiated to investigate various phases of the chemical analyses to be required on startup of the MSRE. A mock-up of a hot cell was assembled in Building 4500S for the evaluation of techniques, methods of analysis, and equipment proposed for use with the MSRE salt samples under conditions of remotely controlled operations. A Mixer/Mill was purchased and modified for use in pulverizing and homogenizing the MSRE fuel salt samples.[4] An assembly for dissolving the fuel salt and for collecting the hydrogen evolved during the dissolution was fabricated and tested in the cell mock-up.[5] A servo-controlled pipetter, polarographic assembly, and filter photometer were obtained for use in evaluating some of the methods of analysis.

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[2] R. C. Shank *et al.*, *Annual Report of ICPP Analytical Section for 1961*, IDO-14588 (May 31, 1962).

[3] F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, Van Nostrand, Princeton, N.J., 1958.

[4] M. J. Gaitanis, C. E. Lamb, and L. T. Corbin, *Homogenization of Molten-Salt Reactor Project Fuel Samples*, ORNL TM-291 (July 5, 1962).

[5] J. C. White *et al.*, *Determination of Trivalent Uranium in Fluoride Salt Mixtures by the Modified Hydrogen Evolution Method*, ORNL-2043 (Feb. 28, 1956).

Several new methods were tested in the hot cells of the High-Radiation-Level Analytical Facility. They included methods for the measurement of attrition rates of irradiated ThO_2 pellets, spectrophotometric determination of thorium by use of arsenazo III (see "Arsenazo III as a Chromogenic Reagent for Thorium," in Chap. 13 of this report) and by titration with EDTA,[6] titration of aluminum with EDTA using eriochrome black T indicator, and determination of the melting point of salt samples from the fluoride volatility process.

A precise method to determine the volume percent of di-*sec*-butyl phenylphosphonate (DSBPP) in diethylbenzene was needed to meet the requirements of the Kilorod Program of the Chemical Technology Division. By means of standard solutions of DSBPP in diethylbenzene, plots of DSBPP concentration vs density, acid equilibration rate, and dielectric constant were prepared. The curves indicated that measurement of the dielectric constant is the most sensitive and reliable of the three methods; the method is being statistically evaluated.

MATERIALS TESTING LABORATORY

L. J. Brady

The Materials Testing Laboratory reported the results of 22,140 analyses. Of this total, approximately 75% were for the Chemical Technology Division, 15% for the Reactor Chemistry Division, and 5% each for the Reactor and Metallurgy Divisions.

The analysis of fused fluoride salts for major components and for trace impurities was continued. The determination of oxygen in these salts is still of great interest, and two sets of equipment have been operated on a daily schedule for making these analyses.

Samples of granite from deep core drillings are being analyzed for thorium content.

Recently, a parallel-column adapter was installed on the model 154 Vapor Fractometer. As a result of this alteration, it is now possible to analyze for carbon dioxide together with the other components that have been reported on previous gas samples.

RADIOISOTOPES-RADIOCHEMISTRY LABORATORY

E. I. Wyatt

The work load of the Radioisotopes-Radiochemistry Laboratory increased about 50% over that of the last year. This increase is due primarily to an increase in fission-product analyses from fuel meltdown experiments and to a transfer of neutron activation work from the Nuclear Analyses Group.

Major items purchased during the year include a liquid scintillation counter and a low-background proportional counter that has an automatic sample changer for low-level radiochemical analyses. All the new equipment for the Analytical Cells for Radioisotopes in Building 3038 has been installed. This installation makes possible the analysis of radioisotope products that are much "hotter" than those which could formerly be analyzed.

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[6] G. Goldstein, D. L. Manning, and H. E. Zittel, "Iron II as an Indicator Ion for Amperometric Titration with (Ethylenedinitrilo)-tetraacetic Acid," *Anal. Chem.* 34, 358 (1962).

The use of computers was extended to include all flux-monitor work and burnup analyses.

Experiments were conducted to determine thermal-neutron fission yields for Am^{241}. These data will be given in an ORNL report.

A comparison of analytical results on standard solutions received by the Radioisotopes-Radiochemistry Laboratory during the year is given in Table 19.1.

A paper[7] on the determination of radioyttrium and radiopromethium was published. An analytical method for radiocesium is being submitted to *Analytical Chemistry*; the method was presented orally.[8] Anthracene crystals were compared with lithium-drifted silicon diodes as beta detectors for routine analytical work. Although the diode detector gives much better resolution of the energies of conversion

Table 19.1. Results Obtained on Standard Solutions of Radioisotopes

Isotope	Radioactivity	
	Reputed	Found
	From Nuclear-Chicago Corporation	
	dis sec^{-1} ml^{-1}	
	$\times 10^5$	$\times 10^5$
P^{32}	2.87	2.88
K^{42}	17.4	18.0
I^{131}	4.20	4.21
Au^{198}	2.82	2.66
	From International Atomic Energy Agency	
	$\mu c/g$	
Fe^{59}	(19.9)[a]	(19.5)[a]
Co^{60}	10.06	10.07
Sr^{89}	10.02	9.84
Sr^{90}	10.1	10.4
I^{131}	25.0	25.7
Ce^{144}	10.07	9.87
Au^{198}	24.8	24.0

[a] Total microcuries.

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[7] M. E. Pruitt, R. R. Rickard, and E. I. Wyatt, "Radiochemical Determination of Yttrium and Promethium," *Anal. Chem.* **34**, 283 (1962).

[8] C. F. Goeking, Jr., C. L. Ghann, and E. I. Wyatt, *A Chlorostannate Method for the Determination of Radiocesium,* presented at the 14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962.

electrons, it requires a much more highly radioactive source or a much longer time to collect the information required for identification of the beta emitter. A paper that described this work was presented.[9]

Methods were developed for the following special applications:

1. The determination of Pa^{231} in U^{232}. A solvent-extraction technique coupled with isotope dilution, in which Pa^{233} is used, allows for a greater range of sample size than do neutron activation techniques; hence lower concentrations of Pa^{231} can be determined.

2. The determination of Tc^{99} by neutron activation. The Tc^{99m} formed by neutron activation of Tc^{99} is measured vs a standard. Cationic species, which comprise the bulk of the induced activity, are removed by means of a cation-exchange resin, and the 140-kev photon of Tc^{99m} is measured with an NaI crystal and an analyzer.

3. The rapid determinations of specific activities. By use of an NaI crystal and a single-channel gamma analyzer in conjunction with the flame photometer, the feasibility of determining Na and Na^{24} in the same test portion was demonstrated. The technique was also applied to K and K^{42} and to La and La^{140}.

4. Measurement of neutron-moderating effects by paraffin in the ORNL Graphite Reactor. The neutron-moderating effects produced by $\frac{3}{4}$ in. of paraffin on pile neutrons in Hole 71 of the ORNL Graphite Reactor were investigated. The reactions $S^{32}(n,p)P^{32}$ and $Ni^{58}(n,p)Co^{58}$ were suppressed 40 and 20%, respectively; the reaction $Mn^{55}(n,\gamma)Mn^{56}$ was increased 30%. These results reflect only the neutron-spectrum effect at the position studied in Hole 71 with the particular fuel loading at that time and do not necessarily present a general picture of neutron-moderating effects.

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

L. G. Farrar

Containment in the cells of the High-Radiation-Level Analytical Facility (HRLAF) was improved. Further improvement in containment of the cell bank would involve major revisions of the individual cells. Total booting for all manipulators and the installation of a new fan have decreased the pressure inside the cell bank to −1.2 in. of water at full flow of exhaust air.

Several types of booting materials were tested to determine which material permits optimum operating conditions for hot-cell analytical work. The boots for the model 8 manipulator that are now in use at the HRLAF are thinner than those in use at other laboratory sites. The thinner boots permit more freedom of manipulator movement for analytical work. Urethane-rubber wrist gauntlets are now being used to extend the life of the manipulators in the presence of acid vapors and heat.

The procedures for operating the facility were revised completely to establish more administrative control, to remove minor operational difficulties, and to ensure the safe disposal of solid radioactive wastes to the burial ground.

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[9] J. E. Morton *et al.*, *The Use of Lithium Drifted P^{+}-I-N^{+} Junction Silicon Diode as a Detector for Beta Spectrometry and Its Comparison to an Anthracene Crystal*, presented at the 14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962.

Flame photometric work in the HRLAF was discontinued because of gross contamination of a work cell that resulted from inadequate containment of the flame during analyses of radioactive solutions. A new containment cubicle for the flame is being prepared.

The cell-access area of the facility was air-conditioned to improve containment, conditions for working in contamination clothing, and control of in-cell temperatures.

Individual work cells were fitted with instrument connections to allow changeover of analytical instruments from cell to cell, and thus to give uninterrupted service during decontamination.

Routine work in the HRLAF has included 106 manipulator repair jobs and decontamination of 16 work cells.

20. Reactor Engineering Service Laboratory

C. D. Susano
C. K. Talbott

The Reactor Engineering Service Laboratory made over 14,000 analyses on some 4300 samples. Of these, about 55% were submitted by the Reactor Chemistry Division, 30% by the Reactor Division, and 10% by the Chemical Technology Division; the remainder were derived from 13 other sources. The samples consisted principally of water; dye solutions; high-alloy steel; solutions of HNO_3, HCl, and LiCl; mixtures of fluoride salts; and ThO_2 and slurries thereof. Analyses were made less frequently on a variety of materials such as graphite; solutions of HF, H_2SO_4, NaOH, and KOH; and corrosion scale samples. Over 100 cylinders of mixed gases were prepared during this period. Methods of analyses included volumetric analysis, gravimetry, spectrophotometric and potentiometric titrations, spectrophotometry, polarography, thermogravimetry, and gasometric analysis. Physical measurements were made on many of the samples; the measurements included pH, conductance, particle-size distribution, specific gravity, and turbidity.

21. Gas-Cooled Reactor Project

J. C. White
A. S. Meyer

The Gas-Cooled Reactor Project reported 3003 results. Approximately 95% of these were from gas chromatographic analyses or other types of gas analysis.

Part IV. ORNL Master Analytical Manual

22. ORNL Master Analytical Manual

M. T. Kelley
Helen P. Raaen
Authors of Methods

The fourth supplement was issued to the reprinted form of the *ORNL Master Analytical Manual.* It contains the new and revised methods issued in 1961. This supplement is available from the Office of Technical Services, Department of Commerce, Washington 25, D.C., for $3.75; it is designated TID-7015 (suppl 4).

Twenty-eight new methods were added to the *Manual* (see "Presentations of Research Results"); of these, one was for the purpose of record only. Fourteen revised methods were issued. The Table of Contents for the *Manual* was revised to bring it up to date.

A survey was made to determine from the authors of each existing method what revisions are needed; those needed are being made.

Presentation of Research Results

Several of the presentations listed below were made jointly with members of other divisions. In these cases the member of the Analytical Chemistry Division is indicated by a single asterisk.

PUBLICATIONS

Books, Theses, Monographs

AUTHOR(S)	TITLE	PUBLISHER
Cameron, A. E.	"Electromagnetic Separation," pp 119–31 in *Physical Methods in Chemical Analysis*, vol IV, ed. by W. G. Berl	Academic Press, New York, 1961
Cameron, A. E., E. Wichers[1]	"Report of the Commission on Atomic Weights (1961)," pp 281–327 in *Comptes Rendus de la* 21^{e} *Conference de l'Union Internationale de Chimie Pure et Appliquee*, ed. by R. Morf	Butterworths, London, 1961
Horton, C. A.	"Fluorine," pp 207–334 in *Treatise on Analytical Chemistry*, part II, vol 7, ed. by I. M. Kolthoff and P. J. Elving	Interscience, New York, 1961
Leddicotte, G. W.	*The Radiochemistry of Rubidium*, Nuclear Science Series Report NAS-NS-3053, February 1962	*National Academy of Sciences* – National Research Council, Washington, D.C.
Leddicotte, G. W.	*The Radiochemistry of Sulfur*, Nuclear Science Series Report NAS-NS-3054, February 1962	*Ibid.*
Mullins, W. T., G. W. Leddicotte[2]	*The Radiochemistry of Potassium*, Nuclear Science Series Report NAS-NS-3048, November 1961	*Ibid.*
Mullins, W. T., G. W. Leddicotte	*The Radiochemistry of Silicon*, Nuclear Science Series Report NAS-NS-3049, January 1962	*Ibid.*

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[1] National Bureau of Standards, Washington, D.C.

[2] Present address: Union Carbide Nuclear Company, Tuxedo, N.Y.

Mullins, W. T., G. W. Leddicotte	*The Radiochemistry of Sodium*, Nuclear Science Series Report NAS-NS-3055, March 1962	*Ibid.*
Mullins, W. T., G. W. Leddicotte	*The Radiochemistry of Phosphorus*, Nuclear Science Series Report NAS-NS-3056, March 1962	*Ibid.*
White, J. C.	"Recent Advances in Ultraviolet, Visible and Infrared Absorption Spectrometry," pp 257–312 in *Progress in Nuclear Energy*, series IX, vol 2, ed. by C. E. Crouthamel	Pergamon, New York, 1961

Articles

AUTHOR(S)	TITLE	PUBLICATION
Amiel, S., Y. Wellwart[33]	"Lithium and Lithium-6 Analysis by Counting Delayed Neutrons"	*Proceedings, Fifth Conference, Analytical Chemistry in Nuclear Technology,* TID-7629, p 258 (October 1962)
Biggers, R. E., D. A. Costanzo	"Glove Box Constructed for Model 14 Spectrophotometer Using Radioactive Samples"	*Carygraph* **2**(2), 10 (1962)
Burns, J. F.	"Experimental Detection of Auto-Ionizing Transitions in Krypton by Electron Impact"	*Nature* **192**, 651 (1961)
Costanzo, D. A., W. D. Shults	"Applications of Controlled-Coulometric Titrimetry to the Determination of Europium"	*Proceedings, Fifth Conference, Analytical Chemistry in Nuclear Technology,* TID-7629, p 313 (October 1962)
Dean, J. A.,[3] J. C. Burger,[3] T. C. Rains, H. E. Zittel	"Flame Spectrophotometric Study of Barium"	*Anal. Chem.* **33**, 1722 (1961)
Dunlap, Louise B., W. D. Shults[4]	"Controlled-Potential Coulometric Titration of Antimony"	*Anal. Chem.* **34**, 499 (1962)
Dunlap, Louise B., W. D. Shults	"Determination of Antimony by Controlled-Potential Coulometry"	*Proceedings, Fifth Conference, Analytical Chemistry in Nuclear Technology,* TID-7629, p 314 (October 1962)
Dunn, H. W.	"X-Ray Absorption Edge Analysis"	*Ibid.*, p 116
Eldridge, J. S.,* R. E. McDonald	"Use of a High-Level Gamma Spectrometer System for Non-Destructive Inspection"	*Trans. Am. Nucl. Soc.* **5**, 187 (1962)
Emery, J. F., W. T. Mullins, L. C. Bate, G. W. Leddicotte	"Trace-Element Determination in Niobium and Zirconium by Radioactivation Analysis"	*Proceedings, Fifth Conference, Analytical Chemistry in Nuclear Technology*, TID-7629, p 239 (October 1962)

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[3] University of Tennessee, Knoxville.

[4] Present address: Graduate School, Department of Chemistry, Indiana University, Bloomington.

Gaitanis, M. J., C. E. Lamb, L. T. Corbin	"A Pulverizer-Mixer for Solidified Molten Salt Reactor Fuel Samples"	*Proceedings of the 10th Conference on Hot Laboratories and Equipment*, p 333, Washington, D.C., November 1962
Goldberg, G.	"Determination of Oxides and Nitrides in Salts and Metals by High-Temperature Fluorination with Potassium Bromotetrafluoride"	*Ibid.*, p 295
Goldberg, G.	"Determination of Oxides and Nitrides in Lithium Metal by High-Temperature Fluorination with Potassium Bromotetrafluoride"	*Anal. Chem.* **34**, 1343 (1962)
Goldstein, G., D. L. Manning, H. E. Zittel	"Conductometric Determination of Sulfate by the Nonaqueous Barium Acetate Method"	*Ibid.*, p 1169
Goldstein, G., D. L. Manning, H. E. Zittel	"Iron(II) as an Indicator Ion for Amperometric Titrations with (Ethylenedinitrilo)-tetraacetic Acid"	*Ibid.*, p 358
Handley, T. H., J. A. Dean	"O,O'-Dialkyl Phosphorodithioic Acids as Extractants for Metals"	*Ibid.*, p 1312
Harmatz, B., T. H. Handley,* J. W. Mihelich	"Properties of Nuclear Levels in a Number of Odd-A Nuclei ($151 \leq A \leq 191$)"	*Phys. Rev.* **128**, 1186 (1962)
Horton, A. D.	"Gas Chromatography as Applied to Nuclear Technology – I"	*Nucl. Sci. Eng.* **13**, 103 (1962)
Jones, H. C., D. J. Fisher, M. T. Kelley	"High-Resolution, High-Sensitivity, Scanning, Recording, Flame Spectrophotometer"	*Proceedings, Fifth Conference, Analytical Chemistry in Nuclear Technology*, TID-7629, p 31 (June 1962)
Leddicotte, G. W.	"Nucleonics"	*Anal. Chem.*, Review Issue **34**, 143R (1962)
Leddicotte, G. W.	"Radioactivation Analysis – Specific for Trace Element Determinations"	*Am. Soc. Testing Mater. Spec. Tech. Publ.* No. 308, 21–43 (1962)
Lyon, W. S., J. S. Eldridge, L. C. Bate	"A New Isomer of Yttrium (3.1-hr Y^{90m})"	*Proceedings, Fifth Conference, Analytical Chemistry in Nuclear Technology*, TID-7629, p 219 (October 1962)
Lyon, W. S.,* R. L. Macklin, G. DeSaussure, J. D. Kington	"Manganese Bath Measurements of η of Pu^{239}"	*Trans. Am. Nucl. Soc.* **5**, 88 (1962)
Lyon, W. S., S. A. Reynolds, J. S. Eldridge	"Radiochemistry Can Help Analyze Nuclear Accidents"	*Nucleonics* **20**(5), 92 (1962)
McConnell, K. P.,[5] H. G. Mautner,[6] G. W. Leddicotte	"Radioactivation as a Method for Preparing Se^{75}-Labelled Selenium Compounds"	*Biochim. Biophys. Acta* **59**, 217 (1962)
Maddox, W. L.	"Remote Decapper"	*Proceedings of the 10th Conference on Hot Laboratories and Equipment*, p 335, Washington, D.C., November 1963

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[5] Veterans Administration Hospital, Louisville, Ky.

[6] Yale University School of Medicine, New Haven, Conn.

Maddox, W. L., M. T. Kelley, J. A. Dean	"Determination of Chloride Ion in Dilute Solutions by Cathodic Stripping Voltammetry"	*J. Electroanal. Chem.* **4**, 96 (1962)
Manning, D. L.,* M. Blander	"Association Constants of Silver(I) and Cyanide Ions in Molten Equimolar Sodium Nitrate—Potassium Nitrate Mixtures"	*Inorg. Chem.* **1**, 594 (1962)
Manning, D. L.,* J. Braunstein,[7] M. Blander[5]	"Association Constants of Silver(I) and Chloride Ions in Molten Potassium Nitrate"	*J. Phys. Chem.* **66**, 2069 (1962)
Manning, D. L.,* R. C. Bansal,[8] J. Braunstein,[7] M. Blander	"Association Constants in the System $AgNO_3$-NaBr-$NaNO_3$ and Their Comparison with the Quasi-Lattice Theory"	*J. Am. Chem. Soc.* **84**, 2028 (1962)
Manning, D. L., O. Menis[6]	"Spectrophotometric Determination of Ruthenium with 2-Nitroso-1-naphthol"	*Anal. Chem.* **34**, 94 (1962)
Mautner, H. G., B. Donnelly,[6] C. M. Lee,[6] G. W. Leddicotte	"Neutron Activation as a Method for Labelling the Phosphorus of Nucleotides"	*J. Am. Chem. Soc.* **84**, 2021 (1962)
Menis, O.,[9] R. H. Powell[10]	"Pyrolytic Separation of Ruthenium"	*Anal. Chem.* **34**, 166 (1962)
Mullins, W. T., J. F. Emery, L. C. Bate, G. W. Leddicotte	"The Determination of Minor Elements in Ultrapure Beryllium and Its Compounds by Neutron Radioactivation Analysis"	*Proceedings, Fifth Conference, Analytical Chemistry in Nuclear Technology*, TID-7629, p 245 (October 1962)
Pruitt, M. E., R. R. Rickard, E. I. Wyatt	"Radiochemical Determination of Yttrium and Promethium. A Precipitation Technique"	*Ibid.*, p 283
Raaen, Helen P., H. C. Jones	"Instrumentation for the Automatic Simultaneous Measurement of *m, t, w,* and Drop Count of a Dropping Electrode"	*Ibid.*, p 1594
Raaen, Helen P.	"Teflon Dropping-Mercury Electrode for Polarography in Hydrofluoric Acid and Other Glass-Corroding Media"	*Ibid.*, p 1714
Rains, T. C., H. E. Zittel, N. M. Ferguson	"Flame Spectrophotometric Determination of Micro Concentrations of Strontium in Calcareous Material"	*Ibid.*, p 778
Reynolds, S. A.	"Methods and Standards in Radioanalysis of Water"	*Health Phys.* **8**, 391 (1962)
Reynolds, S. A.	"Progress in Radioreagent Techniques"	*Trans. Am. Nucl. Soc.* **5**, 202 (1962)
Reynolds, S. A.	"Radioactive Sources: Radioactive Chemicals"	*Intern. J. Appl. Radiation Isotopes* **10**, 217 (1961)
Zittel, H. E., Louise B. Dunlap, P. F. Thomason	"Determination of Uranium in the Presence of Molybdenum by Controlled-Potential Coulometric Titration"	*Anal. Chem.* **33**, 1491 (1961)

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[7] University of Maine, Orona.

[8] Research participant in Reactor Chemistry Division from Atomics International, Canoga Park, Calif.

[9] Present address: Nuclear Materials and Equipment Corporation, Apollo, Pa.

[10] Present address: Nevada Mining Analytical Laboratory, University of Nevada, Reno.

Zittel, H. E., Louise B. Dunlap	"Polarographic Determination of Uranium(IV) in Sodium Tripolyphosphate Supporting Electrolyte"	*Anal. Chem.* **34**, 1757 (1962)

Reports

AUTHOR(S)	TITLE	REPORT NO.
Bate, L. C., *et al.*	*A Rapid Chemical Separation for Radiomanganese*	ORNL TM-438 (Dec. 6, 1962)
Bate, L. C., W. J. Hampton,[11] G. W. Leddicotte	*Non-Destructive Analysis of Uranium in Graphite Fuel Elements by Neutron Activation*	ORNL TM-64 (Nov. 28, 1961)
Bate, L. C., G. W. Leddicotte	*A Production Control Method for Determining the Particle Size Distributions of Thorium Oxide and Thorium Oxalate*	ORNL TM-255 (June 15, 1962)
Bate, L. C., M. J. Pro,[12] G. W. Leddicotte	*Identification and Comparison of Physical Evidence for Law Enforcement Purposes by Neutron Activation Analysis*	ORNL TM-363 (Sept. 11, 1962)
Corbin, L. T., E. I. Wyatt	*Report on Foreign Travel*	Aug. 6, 1962 (unpublished report)
Costanzo, D. A., R. E. Biggers	*Preliminary Spectrophotometric Study of Plutonium(IV) in Solutions of Aluminum Nitrate—Nitric Acid at Elevated Temperatures*	Nov. 27, 1961 (unpublished report)
Dyer, F. F., J. F. Emery, G. W. Leddicotte	*A Comprehensive Study of the Neutron Activation Analysis of Uranium by Delayed-Neutron Counting*	ORNL-3342 (July 27, 1962)
Gaitanis, M. J., C. E. Lamb, L. T. Corbin	*Homogenization of Molten-Salt Reactor Project Fuel Samples*	ORNL TM-291 (July 5, 1962)
Holsopple, H. L.	*Synthesis of* n-*Hexyl- and* n-*Heptylbenzene*	ORNL TM-254 (June 14, 1962)
Kelley, M. T.	*ORNL Analytical Chemistry Division Research and Development Quarterly Progress Report for Period Ending Sept. 15, 1962*	Sept. 27, 1962 (unpublished report)
Kelley, M. T.	*Report on Foreign Travel, Analytical Chemistry Panel of Nuclear Materials, IAEA, Vienna, Sept. 17 to 21, 1962*	Nov. 9, 1962 (unpublished report)
Kelley, M. T.	*Statistical Quality Control Report, Analytical Chemistry Division, January Through September 1962*	Nov. 14, 1962 (unpublished report)

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[11] Present address: Union Carbide Nuclear Company, Tuxedo, N.Y.

[12] Alcohol and Tobacco Tax Laboratory, Internal Revenue Service, Treasury Department, Washington, D.C.

Leddicotte, G. W., J. F. Emery, L. C. Bate	*The Assay, Characteristics, Composition, and Origin of Opium. I. The Preliminary Study of the Use of Activation Analysis in the Determination of the Origin of Opium*	Feb. 26, 1962 (unpublished report)
Leddicotte, G. W., D. W. Moeller[13]	*Determination of Trace Elements in Water by Neutron Radioactivation Analysis*	May 29, 1961 (unpublished report)
McDonald, R. E., A. C. Winther,[14] H. W. Wright*	*A Discussion on the Feasibility of Providing an Electron Microscope Facility for the High Radiation Level Examination Laboratory*	Feb. 28, 1962 (unpublished report)
Moore, F. L.	*Report of Foreign Travel*	May 28, 1962 (unpublished report)
Moore, F. L.	*Separation of Americium from Other Elements. Application to the Purification and Radiochemical Determination of Americium*	Sept. 25, 1962 (unpublished report)
Quincy, R. B., Jr.	*Preparation of High-Purity Magnesium Oxide*	ORNL TM-302 (Aug. 15, 1962)
Raaen, Helen P.,* R. J. Fox, V. E. Walker	*Fabrication and Assembly of a Teflon Dropping-Mercury Electrode*	ORNL-3344 (Nov. 31, 1962)
Raaen, Helen P., ed., and authors of methods	*ORNL Master Analytical Manual*	TID-7015, suppl 4 (June 1962)
Shults, W. D.	*Controlled-Potential Coulometric Titration of Uranium(VI) in the Presence of Nitrate*	ORNL TM-113 (Jan. 17, 1962)
Shults, W. D.	*ORNL Procedures for Controlled-Potential Coulometric Titration of Plutonium*	ORNL TM-366 (Sept. 14, 1962)
Strain, J. E., W. J. Hampton, G. W. Leddicotte	*The ORNL Analytical Chemistry Division's 150-KV Cockcroft-Walton Generator*	ORNL TM-362 (Sept. 10, 1962)
Strain, J. E., G. W. Leddicotte	*The Preparation, Properties, and Uses of Americium-241, Alpha-, Gamma-, and Neutron Sources*	ORNL-3335 (Aug. 23, 1962)
Susano, C. D., H. P. House	*Analytical Chemistry in Nuclear Reactor Technology*	TID-7629 (June 1962)
Susano, C. D., H. P. House, R. F. Apple	*Potentiometric Titration of Aluminum with Ethylenediaminetetraacetic Acid*	Feb. 8, 1962 (unpublished report)
Ward, J. C.	"Radioactivity of Nuclear Reactor Cooling Fluids"	ORNL-3152 (Sept. 20, 1961)
White, J. C.	*Analytical Chemistry Research and Development Quarterly Progress Report for Period Ending March 15, 1962*	Apr. 4, 1962 (unpublished report)
White, J. C.	*Analytical Chemistry Research and Development Quarterly Progress Report for Period Ending June 15, 1962*	July 12, 1962 (unpublished report)
White, J. C., H. L. Holsopple	*Synthesis of* N-*Methylacetamide*	Mar. 23, 1962 (unpublished report)

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[13] Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

[14] Research participant in Metals and Ceramics Division from AEK, Risø, Roskilde, Denmark.

White, J. C., H. L. Holsopple	*Synthesis of Some Alkali-Metal* p-*Ethylbenzenesulfonates*	ORNL TM-183 (Mar. 30, 1962)

New Methods Issued to *ORNL Master Analytical Manual*

AUTHOR(S)	TITLE	NUMBER(S)	DATE
Bate, L. C., G. W. Leddicotte	"Lanthanum, Neutron Activation Analysis (Direct Measurement) Method"	5 11431	5-14-62
Bate, L. C., G. W. Leddicotte	"Uranium, Neutron Activation Analysis (Direct Measurement of Neptunium-239) Method"	5 11921	5-15-62
Botts, J. L.	"Surface Area of Solids, Krypton Adsorption Method"	1 105 9 00605	12-28-61
Grimanis, A. P.,[15] G. W. Leddicotte	"Rhenium, Neutron Activation Analysis (Isotopic Carrier; Solvent Extraction Precipitation) Method"	5 117001	11-15-61
Horton, A. D.	"Paraffins, Permanent Gases, and Rare Gases, Gas Chromatographic Method"	1 221005 9 00721005	9-17-62
Leddicotte, G. W.	"Cesium, Neutron Activation Analysis (Ion Exchange) Method"	5 11192	5-17-62
Leddicotte, G. W.	"Chlorine, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11200	6-5-62
Leddicotte, G. W., W. T. Mullins	"Gold, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11330	6-4-62
Leddicotte, G. W.	"Potassium, Neutron Activation Analysis (Ion Exchange) Method"	5 11642	5-10-62
Leddicotte, G. W.	"Rhenium, Neutron Activation Analysis (Isotopic Carrier; Distillation-Precipitation) Method"	5 117000	5-1-62
Leddicotte, G. W., A. P. Grimanis	"Rhenium, Neutron Activation Analysis (Isotopic Carrier; Solvent Extraction-Precipitation) Method"	5 117001	5-8-62
Leddicotte, G. W.	"Rubidium, Neutron Activation Analysis (Ion Exchange) Method"	5 11722	5-21-62
Leddicotte, G. W.	"Ruthenium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11730	6-12-62
Leddicotte, G. W.	"Sodium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11790	6-15-62
Leddicotte, G. W.	"Sodium, Neutron Activation Analysis (Ion Exchange) Method"	5 11792	5-21-62
Leddicotte, G. W., W. T. Mullins	"Thorium, Neutron Activation Analysis (Solvent Extraction; Measurement of Protactinium-233) Method"	5 11874	6-8-62
Mullins, W. T., G. W. Leddicotte	"Chromium, Neutron Activation Analysis (Isotopic Carrier; Distillation) Method"	5 112101	5-28-62

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[15] Temporary employee from Nuclear Research Center, Greek Atomic Energy Commission, Athens.

Mullins, W. T., G. W. Leddicotte	"Manganese, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11480	5-25-62
Mullins, W. T., G. W. Leddicotte	"Phosphorus, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11600	5-28-62
Mullins, W. T., G. W. Leddicotte	"Potassium, Neutron Activation Analysis (Isotopic Carrier-Tetraphenylboron) Method"	5 1164002	8-28-62
Mullins, W. T., G. W. Leddicotte	"Scandium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11750	8-27-62
Mullins, W. T., G. W. Leddicotte	"Scandium, Neutron Activation Analysis (Direct Measurement) Method"	5 11751	5-7-62
Mullins, W. T., G. W. Leddicotte	"Uranium, Neutron Activation Analysis (Nonisotopic Carrier; Measurement of Neptunium-239) Method"	5 11923	6-14-62
Mullins, W. T., G. W. Leddicotte	"Zirconium, Neutron Activation Analysis (Direct Measurement) Method"	5 11981	5-15-62
Mullins, W. T., G. W. Leddicotte	"Zirconium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11980	6-1-62
Rubin, I. B.	"Helium in Beryllium Oxide, Gas Chromatographic Method"	1 213590	7-31-62
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Revised Methods Issued to *ORNL Master Analytical Manual*

AUTHOR(S)	TITLE	NUMBER(S)	DATE
Jones, H. C.	"Automatic Coulometric Titrator, ORNL Model Q-2005 Electronic Controlled-Potential"	1 003029 9 003029	R. 2-7-62
Leddicotte, G. W.	"Barium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11080	R. 5-10-62
Leddicotte, G. W.	"Calculation of Activation Analysis Data"	5 10123	R. 5-23-62
Raaen, Helen P.	"Authorization and Classification of Methods for the *ORNL Master Analytical Manual*"	02	R. 3-2-62
Raaen, Helen P.	"Maintenance of the *ORNL Master Analytical Manual*"	04	R. 3-2-62
Raaen, Helen P.	"Organization of the *ORNL Master Analytical Manual* and Numbering of the Methods"	00	R. 3-7-62
Raaen, Helen P.	"Typing and Printing of Methods for the *ORNL Master Analytical Manual*"	03	R. 3-2-62
Raaen, Helen P.	"Writing Methods for the *ORNL Master Analytical Manual*"	01	R. 3-2-62
White, J. C.	"Sulfur in Inorganic Compounds, Spectrophotometric Methylene Blue Method"	1 218110 9 00718110	R. 3-7-62
Wyatt, E. I.	"Antimony-125 CF, Product Analysis Guide"	9 0733042	R. 3-3-62
Wyatt, E. I.	"Arsenic-77, Product Analysis Guide"	9 0733064	R. 3-27-62
Wyatt, E. I.	"Barium-131, Product Analysis Guide"	9 0733085	R. 3-27-62
Wyatt, E. I.	"Iridium-192, Product Analysis Guide"	9 0733401	R. 3-27-62
Wyatt, E. I.	"Molybdenum-99, Product Analysis Guide"	9 0733501	R. 3-26-62

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AUTHOR	TITLE	NUMBERS	DATE
Manning, D. L.	"Uranium, Spectrophotometric 1-(2-Pyridylazo)-2-Naphthol (PAN) Method"	1 219214 9 00719214	8-9-61

ORAL PRESENTATIONS

The Analytical Chemistry Division sponsored a Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology at Gatlinburg, Tennessee, on October 9–11, 1962. The committee consisted of C. D. Susano (chairman), H. P. House, C. A. Horton, W. L. Maddox, J. A. Norris, J. E. Strain, and T. E. Willmarth. Fifty-three papers were presented.

This conference was held concurrently with the Third Conference on Nuclear Reactor Chemistry. There were 331 registrants: 160 from Oak Ridge, 53 from industrial organizations, 47 from other AEC installations, 32 from foreign countries, 13 from colleges and universities, 8 from governmental agencies other than the AEC, 16 from AEC, and 2 others.

The proceedings of this conference will be published, as were the proceedings of prior conferences in this series. The proceedings of the First Conference were published as TID-7555; those of the Second Conference as TID-7568 (Parts 1, 2, 3); those of the Third Conference as a special issue (by Pergamon Press) of *Talanta*, Vol 6, in September 1960; those of the Fourth Conference as TID-7606; and those of the Fifth Conference as TID-7629.

A Seventh Conference on Analytical Chemistry in Nuclear Reactor Technology has been tentatively scheduled to be held at Gatlinburg, Tennessee, on October 8–10, 1963.

At Meetings of Professional Societies

AUTHOR(S)	TITLE	PRESENTED AT
Baes, C. F., T. H. Handley*,[16]	"PWR Chemistry: Studies of the ORR In-Pile Loop"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Bate, L. C.,[16] G. W. Leddicotte	"Activation Analysis Studies of the Possible Effects of Microelements on the Properties of Soil and Vegetation"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
Bate, L. C., G. W. Leddicotte[16]	"Identification and Comparison of Physical Evidence for Enforcement Purposes by Neutron Activation Analysis"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlingburg, Tenn., Oct. 23–26, 1962
Biggers, R. E.,[16] R. Eno[17]	"The Design and Development of a Spectrophotometer System for Optical Measurements on Liquids at High Temperatures and High Pressures"	141st Meeting, American Chemical Society, Washington, D.C., Mar. 20–29, 1962

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[16] Speaker.

[17] Applied Physics Corporation, Monrovia, Calif.

Biggers, R. E.,[16] R. Eno	"The Design and Development of a Spectrophotometer System for Optical Measurements on Liquids at High Temperatures and High Pressures"	Symposium on Molecular Structure and Spectroscopy, Departments of Physics and Astronomy, The Ohio State University, Columbus, Ohio, June 11–15, 1962
Bradshaw, R. L.,[16] W. J. Boegly, Jr. F. M. Empson, H. Kubota,* F. L. Parker, J. J. Perona, E. G. Struxness	"Ultimate Storage of High-Level Radioactive Waste Solids and Liquids in Salt Formations"	Symposium on the Treatment and Storage of High-Level Radioactive Wastes, Vienna, Austria, Oct. 8–13, 1962
Burns, J. H.	"The Crystal Structures of Two New Alkali Fluorides: $LiRbF_2$ and $LiCsF_2$"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
Costanzo, D. A.,[16] R. E. Biggers	"Studies of the Polymerization of Quadrivalent Plutonium by Spectrophotometric Means"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Dyer, F. F.,[16] G. W. Leddicotte	"The Routine Analytical Application of Delayed-Neutron Counting to the Determination of U-235"	13th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Mar. 5–9, 1962
Eldridge, J. S.,[*,16] R. E. McDonald	"Use of a High-Level Gamma Spectrometer System for Non-Destructive Inspection"	8th Annual Meeting, American Nuclear Society, Boston, Mass., June 18–21, 1962
Emery, J. F.,[16] G. W. Leddicotte	"Determination of Phosphorus in Silicon at the PPB Impurity Level by Neutron Activation"	Spring Meeting, Semiconductor Analytical Group, New York, N.Y. Apr. 21, 1962
Emery, J. F.,[16] W. T. Mullins, L. C. Bate, G. W. Leddicotte	"Trace Element Determination in Niobium and Zirconium Metal by Radioactivation Analysis"	5th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961
Feldman, C.,[16] R. K. Dhumwad[18]	"An Atomic-Absorption Tube for Use with an Atomizer-Burner: Application to the Determination of Mercury"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Feldman, C., T. C. Rains[16]	"The Collection and Flame Photometric Determination of Cesium"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Feldman, C., T. C. Rains[19]	"The Collection and Flame Photometric Determination of Cesium"	13th Annual Mid-America Spectroscopy Symposium, Chicago, Ill., Apr. 30–May 3, 1962
Feldman, C.	"Emulsion Calibration"	Southeastern Seminar on Spectroscopy, University of Florida, Gainesville, Fla., Jan. 10–12, 1962
Feldman, C.	"Quantitative Spectrochemical Analysis"	Southeastern Seminar on Spectroscopy, University of Florida, Gainesville, Fla., Jan. 10–12, 1962

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[18] Temporary employee from Atomic Energy Establishment, Trombay, India.

[19] Paper read by J. Terraro, Argonne National Laboratory, Lamont, Ill.

Goeking, C. F., Jr.,[16] C. L. Ghann, E. I. Wyatt	"A Chlorostannate Method for the Determination of Radiocesium"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
Goldstein, G.	"Some Problems Involved in Utilizing Radioisotopic Tracers"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Goldstein, G., D. L. Manning,[16] H. E. Zittel	"Vanadyl Ion as a Back-Titrant for Indirect Amperometric Titrations with Ethylenediaminetetraacetic Acid"	141st Meeting, American Chemical Society, Washington, D.C., Mar. 20–29, 1962
Grimanis, A. P.,[16] G. W. Leddicotte	"Application of Radioisotope Methodology to the Determination of Arsenic in Copper Alloys and in Organic Materials"	Annual Meeting, American Nuclear Society, Boston, Mass., June 18–20, 1962
Grimanis, A. P., G. W. Leddicotte[20]	"Rapid Separation of Arsenic by Liquid-Liquid Extraction"	Third Panhellenic Chemical Conference, Athens, Greece, June 5–11, 1962
Grimanis, A. P.,[16] G. W. Leddicotte	"The Extraction of Rhenium with Tributylphosphate"	Southwest and Southeast Regional Meeting, American Chemical Society, New Orleans, La., Dec. 7–9, 1961
Handley, T. H.	"Di-*n*-Butyl Phosphorothioic Acid as an Extractant for Metal Ions"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
Handley, T. H.	"Organothiophosphates as Metal Extractants"	Solvent Extraction Chemical Symposium, Gatlinburg, Tenn., Oct. 23–26, 1962
Handley, T. H., J. A. Dean,[16] Raquel H. Zucal[21]	"Solvent Extraction Behavior of Metal Di-*n*-Butyl Phosphorodithioates"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
Kelley, M. T.	"Activation Analysis at Oak Ridge National Laboratory"	Seminar at Democritus Nuclear Center, Athens, Greece, Sept. 13–14, 1962
Kubota, H.	"Determination of Thallium in Cesium Iodide Scintillators"	141st Meeting, American Chemical Society, Washington, D.C., Mar. 20–29, 1962
Kubota, H.	"Direct Disposal of Radioactive Waste Solutions in Salt: Radiolytic Decomposition and Cavity Alteration"	National Research Council, Meeting of Committees on Waste Disposal, Earth Sciences Division, Savannah River Plant, Aiken, S.C., Dec. 8, 1961
Kubota, H.,[16] R. F. Apple	"Dissolution of Irradiated High-Fired, Refractory, Nuclear Materials"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Laing, W. R.	"Chemical Analysis of Uranium Dioxide"	Symposium on the Characterization of Uranium Dioxide, Oak Ridge, Tenn., Dec. 12–13, 1961
Leddicotte, G. W.	"Radioactivation Analysis: Present Status and Development Trends"	Eastern Analytical Symposium, New York, N.Y., Nov. 17, 1961

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[20] Paper read by P. Demotakis, Nuclear Research Center, Greek Atomic Energy Commission, Athens.

[21] Temporary employee from Comision Nacional de Energia Atomica, Buenos Aires, Argentina.

Leddicotte, G. W.	"The Use of a Nuclear Reactor for Neutron Activation Analysis"	8th Annual Meeting, American Nuclear Society, Boston, Mass., June 18–20, 1962
Lyon, W. S.	"The Application of Neutron Activation Analysis to Individual Identification"	Winter Meeting, American Nuclear Society, Washington, D.C., Nov. 26–28, 1962
Lyon, W. S.,[*,16] R. L. Macklin, J. D. Kington, G. deSaussure	"Manganese Bath Measurements of η of Pu^{239}"	8th Annual Meeting, American Nuclear Society, Boston, Mass., June 18–21, 1962
Lyon, W. S.	"Radioactive Isotopes as Industrial Tracers"	Mid-South Conference on Industrial Uses of Radioisotopes, University of Mississippi, Oxford, Miss., May 7, 1962
Lyon, W. S.	"The Use of Neutron Activation Analysis in Forensic Science Applications"	Winter Meeting, American Nuclear Society, Washington, D.C., Nov. 26–28, 1962
Miller, F. J.,[16] H. E. Zittel	"Spectrophotometric Determination of Technetium with 1,5-Diphenylcarbohydrazide"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Moore, F. L.	"High Molecular Weight Amines – Versatile Modern Extractants"	Feigl International Symposium on Analytical Chemistry, Birmingham, England, Apr. 9–13, 1962
Morton, J. E.,[16] R. R. Rickard, H. A. Parker, E. I. Wyatt	"The Use of Lithium Drifted P^+-I-N^+ Junction Silicon Diode as a Detector for Beta Spectrometry and Its Comparison to an Anthracene Crystal"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
Mueller, T. R.	"Voltammetric Applications of Non-Mercury Electrodes to Electroanalytical Chemistry"	Seminar, Analytical Chemistry Division, ORNL, July 11, 1962
Mullins, W. T., J. F. Emery, G. W. Leddicotte[16]	"Activation Analysis Applied to Oceanography"	1962 Meeting of American Geophysical Union, Washington, D.C., Apr. 25–28, 1962
Norris, J. A.	"Research and Development Using Photoelectric Spectrometric Equipment"	5th Annual Meeting, Rocky Mountain Spectroscopy Conference, Denver, Colo., Aug. 6–7, 1962
Pal, B. C.,[16,22] C. A. Horton[*]	"The Structure of 3-Methyladenine and Methylation of 6-Dimethylaminopurine"	142nd National Meeting, American Chemical Society, Atlantic City, N.J., Sept. 9–14, 1962
Reynolds, S. A.	"Basic Radiochemical Techniques"	R. A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Feb. 12–13, 1962
Reynolds, S. A.	"Radiochemical Techniques for Specific Radionuclides"	*Ibid.*
Reynolds, S. A.	"Radioisotopes in Chemical Analysis"	*Ibid.*

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[22] Research participant in the Biology Division from Chemistry Department, Tuskegee Institute, Tuskegee Institute, Ala.

Reynolds, S. A.	"Determination of Thorium and Alkaline-Earth Elements by Isotope Dilution"	6th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962
Reynolds, S. A.	"Progress in Radioreagent Techniques"	8th Annual Meeting, American Nuclear Society, Boston, Mass., June 18–20, 1962
Ross, W. J.,[16] W. T. Mullins, L. C. Bate, G. W. Leddicotte	"A Comprehensive Analysis of Beryllium by Neutron Activation"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
Stelzner, R. W.	"Some Direct-Readout and Linearization Circuits in Analytical Laboratory Instrumentation"	15th Annual Summer Symposium on Analytical Chemistry, American Chemical Society, University of Maryland, College Park, Md., June 13–15, 1962
Strain, J. E.,[16] G. W. Leddicotte	"Industrial Activation Analysis"	8th National Symposium on Instrumental Methods of Analysis, Instrument Society of America, Charleston, W. Va., Apr. 30–May 2, 1962
Strain, J. E.	"Neutron Sources"	Activation Analysis Symposium, Chicago, Ill., Oct. 17, 1962
Strain, J. E.,	"Sensitivities of Neutron Activation Analysis"	*Ibid.*
Weekley, R. E.,[16] J. A. Norris	"A Versatile Electronic Computer for Photoelectric Spectrochemical Analysis"	International Conference on Spectroscopy, University of Maryland, College Park, Md., June 18–22, 1962
Wellwart, Y.,[16,23] L. C. Bate, W. T. Mullins, J. R. Stokely,[24] G. W. Leddicotte	"Stable Isotope Tracer – Activation Analysis Methodology: Use in Water Flow Studies"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962
White, J. C.	"Alkali Metal Analytical Program at ORNL, Determination of Oxygen in Potassium"	Atomic Energy Commission – National Aeronautics and Space Agency, Liquid Metals Meeting, Brookhaven National Laboratory, Upton, Long Island, N.Y., Dec. 14–15, 1961
White, J. C.	"New Developments in Analytical Solvent Extraction"	Solvent Extraction Chemistry Symposium, Gatlinburg, Tenn., Oct. 23–26, 1962
White, J. C.	"Research in Analytical Chemistry at Oak Ridge National Laboratory"	Annual Meeting, Tennessee Academy of Science, George Peabody College, Nashville, Tenn., Nov. 23–24, 1962
Zittel, H. E.,[16] Louise B. Dunlap	"The Polarographic Determination of Uranium(IV) in Sodium Tripolyphosphate"	142nd National Meeting, American Chemical Society, Atlantic City, N.J., Sept. 9–14, 1962

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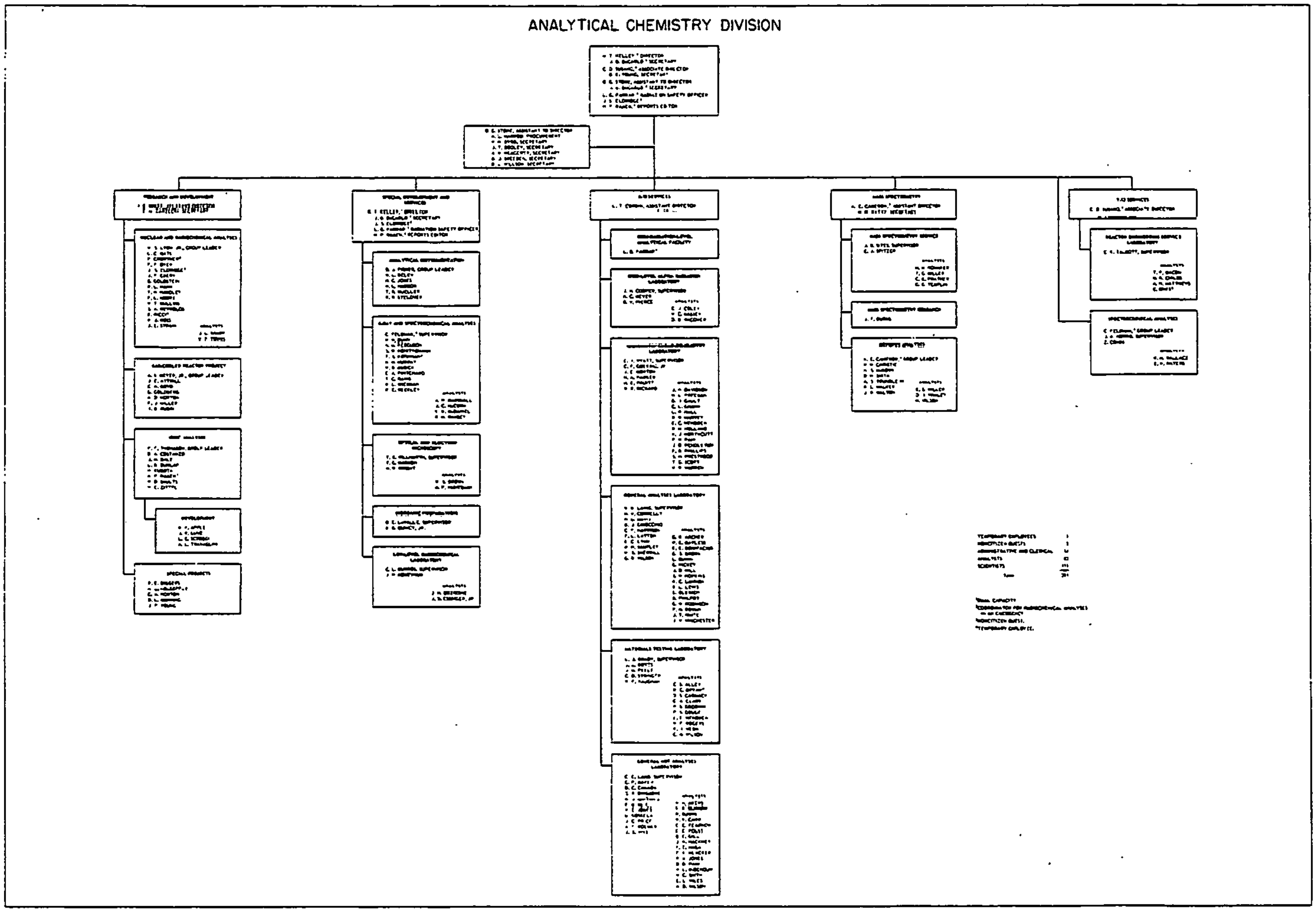
[23] Israel Atomic Energy Commission, Seroq Research Establishment, Rehovoth, Israel.

[24] Clemson College, Clemson, S.C.

Zucal, Raquel H.,[16] J. A. Dean, T. H. Handley	"Properties of Dialkyl Phosphorodithioic Acids in Extraction Systems"	14th Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tenn., Nov. 1–3, 1962

Under the ORNL Traveling Lecture Program

LECTURER	LECTURE TITLE	PRESENTED AT
Biggers, R. E.	"Absorption Spectrophotometric Study of Solutions at High Temperatures and High Pressures"	University of South Carolina, Columbia, S.C., Oct. 25, 1962
Cameron, A. E.	"Geological Age Determination by Isotopic Measurements"	Hood College, Frederick, Md., Oct. 3, 1962
Cameron, A. E.	*Ibid.*	Oklahoma State University, Stillwater, Okla., Apr. 12, 1962
Cameron, A. E.	*Ibid.*	University of Tulsa, Tulsa, Okla., Apr. 11, 1962
Cameron, A. E.	*Ibid.*	Tuskegee Institute, Tuskegee Institute, Ala., Dec. 14, 1961
White, J. C.	"New Reagents for Separation in Analytical Chemistry by Solvent Extraction"	Texas Woman's University, Denton, Tex., Dec. 10, 1962
White, J. C.	*Ibid.*	Stephen F. Austin State College, Nacogdoches, Tex., Dec. 12, 1962



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