ORNL-3243
UC-4-Chemistry
TID-4500 (17th ed.)

ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
FOR PERIOD ENDING DECEMBER 31, 1961

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

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C. D. Susano, Associate Director

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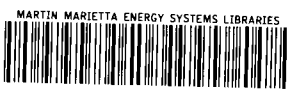

Summary

PART I. ANALYTICAL RESEARCH

1. Analytical Instrumentation

Instrumentation that measures the density, pulse amplitude, and pulse frequency of the continuous phase at a selected point in a pulsed solvent-extraction column was designed and fabricated and was tested on a test loop. The calibration curve for the densimeter is linear in the range from 1.000 to 1200 g/ml; the maximum error of the density measurement is ±0.2%.

A centrifugal-type impactor for air-borne alpha-containing particles had an efficiency of 36.8% by comparison with a vacuum collection system, and it produced a satisfactory small-area sample for alpha counting.

Modifications were made to extend the usefulness of some equipment needed in the High-Radiation-Level Analytical Facility (HRLAF). Apparatus was provided for the remotely controlled use of micropipets. It makes convenient the use of a separate pipet for each sample in order to prevent trace cross contamination in the preparation of dilute solutions of samples for radiochemical analysis. The design of the motorized Lab-Jack, which is used for remotely controlled vertical positioning, was improved. A 3-ml corrosion-resistant pipet was designed and tested. It fits interchangeably with the other pipets used in the ORNL servo-controlled pipetter for the remotely controlled pipetting of radioactive solutions. Satisfactory performance was obtained; the relative standard deviation of 14 deliveries of 300-μl volumes was 0.27%.

New direct-readout circuits were devised for the ORNL model Q-2005, automatic, electronic, controlled-potential coulometric titrator. This modification will simplify the calculation of results.

A standard-addition chronopotentiometric procedure for the determination of an ion in the presence of various concentrations of a more easily reduced species is being investigated. Preliminary results at low concentrations and at transition times in the range from 0.5 to 5 sec show fair agreement between the experimentally determined concentrations and those known to be present. Means are being sought to evaluate and to compensate for errors that are caused by charging current.

A recording conductometric titrator is being designed and tested; its output is linear with conductivity. The instrument is designed to give titration curves essentially free of distortion caused by faradaic processes and by changes in electrode capacitance.

A high-sensitivity, scanning, recording, flame spectrophotometer was designed, fabricated, and tested. It can be used at wavelengths up to 852 mμ. A chopped-light-beam system provides a stable zero with infrared-sensitive multiplier phototubes and makes possible the use of the instrument for either emission or

atomic absorption spectrophotometry. While the instantaneous output is being recorded, a 45-sec integration of the signal can be accumulated and automatically read out in the recorder. Integration is particularly useful at highest sensitivity when considerable noise accompanies the signal.

Development work on an ac controlled-potential polarograph was continued. The design of the circuit in the polarizing section is being improved in order to obtain a more accurate and undistorted cell-current signal. It is planned to compare the methods of second-harmonic current measurement and phase discrimination. The ORNL model Q-1988A controlled-potential and derivative polarograph was built and tested, electrical and mechanical drawings were prepared, and a check-out and test procedure was written. This instrument is now available commercially. The ORNL model Q-1988-ES controlled-potential and derivative polarograph was used in a study of quantitative dc derivative polarography. Methods of measurement and interpretation of dc derivative polarograms were developed. For reversible diffusion-controlled processes, the forms of the experimental derivative polarograms were compared by several methods with that predicted by theory; very close agreement was obtained. Conditions necessary to obtain dc derivative polarograms of theoretical form were delineated. The resolutions possible with regular and derivative polarography were compared by use of simple simultaneous equations to resolve mathematically the overlapped regular and overlapped derivative polarograms of solutions that contained both Tl^{+} and Pb^{2+}. The standard-addition method rather than the slopes of calibration curves was used to evaluate the proportionality constants. The derivative polarograms have superior qualitative resolution, and the measured increments of chart distance resulting from standard additions are greater. Both these characteristics are advantageous in quantitative work. Magnitudes of peak heights are as reproducible as those of wave heights. The relationship of peak height to concentration (with unvarying D.M.E. characteristics) has been observed for a number of ionic reductions over the concentration range from 10^{-6} to 10^{-3} M. Strict linearity is not obtained for some systems; however, peak height is directly proportional to wave height. With the ORNL models Q-1988-ES and Q-1988A polarographs, dc derivative polarograms can be obtained whose form is not influenced by instrument characteristics.

2. Dissolver-Solution Analyses

In the development of methods for the analysis of dissolver solutions, the major effort has been the application of controlled-potential coulometric titrimetry to the determination of plutonium and uranium in various reactor-fuel dissolver solutions. Several methods of separating plutonium from dissolver solutions prior to its titration were studied. A procedure for the determination of Pu^{3+}, Pu^{4+}, and Pu^{6+} individually and in mixtures by controlled-potential coulometric titration was developed.

A method for the determination of polymerized Pu was studied. The work in secondary controlled-potential coulometric titrimetry was continued, and a method for the determination of uranium by this technique was developed. The use of two different working electrodes in the same electrolysis cell was investigated for the titration of uranium in the presence of iron. The use of tri-*n*-octylphosphine oxide for the separation of uranium from dissolver solutions prior to its titration is being investigated.

The method for the determination of neptunium by controlled-potential coulometric titration was investigated. Two controlled-potential coulometric titration procedures for the determination of antimony

were developed. Exploratory studies of boron carbide electrodes for use in polarography and in controlled-potential coulometric titrimetry were made. A new method for the controlled-potential coulometric titration of uranium in the presence of molybdenum was developed.

The apparatus, described previously, for the automatic simultaneous measurement of m, t, w, and drop count (c) of a D.M.E. was built and evaluated and was used satisfactorily for obtaining constants for both glass capillaries and Teflon capillary tips. Teflon tips for use as a D.M.E. for polarographic studies in HF media were evaluated, and polarograms of 26 reducible ions in HF media were made.

3. Special Research Problems

An absorption spectrophotometric study was made of plutonium in solutions of $UO_2(NO_3)_2$, $Al(NO_3)_3$, and HNO_3 at elevated temperatures to determine the extent of hydrolysis and polymerization of Pu^{4+} in such systems. The rates of oxidation and disproportionation were also studied for application to methods of processing Pu-Al reactor fuel. Rates of formation of Pu^{4+} polymer and methods for its degradation are being studied.

The design was finished for a high-temperature high-pressure spectrophotometric system operable with aqueous solutions in specially designed absorption cells up to near the critical point of water (372°C) and with pressures up to 10,000 psi. The system, which has many unique features, was designed and is being constructed by the Applied Physics Corporation. A method was developed for measuring the densities of aqueous solutions at temperatures and pressures up to the critical point of water. A miniature loop circulating system, designed for use with an unmodified Cary model 14PM spectrophotometer, was constructed for operation at temperatures up to 150°C and pressures up to 200 psi.

Work on the mathematical resolution of spectral fine structure and overlapping absorption spectra by means of high-speed digital computing was continued; it is related to the program of spectrophotometry at high temperature and high pressure. Work is in progress on programs for the IBM 7090 machine for the manipulation and analysis of various types of spectral data.

An automatic, digital, data-output system wds designed and constructed and was installed on a Cary model 14PM automatic recording spectrophotometer. Its special features include magnetic core and printed circuitry, with all-decimal data output on IBM punched cards. Wavelength-absorbancy data are punched in pairs; other miscellaneous data are also punched out. Spectral data can be obtained at wavelength intervals as small as 1 A. The system will also punch out digital absorbancy-time data for reaction kinetic studies and, unattended, can be operated by the Cary automatic programmer to punch out spectra at preselected time intervals over multiples of a 24-hr period.

The effect of Cerenkov radiation on absorption spectrophotometric measurements has been calculated because of the potentially serious interference with spectrophotometric measurements of solutions so radioactive that they emit significant amounts of Cerenkov radiation. A method has been developed and reported for quantitatively calculating the intensity of the Cerenkov radiation from specified beta- or gamma-emitting (or both) sources, or mixtures of such sources, over a considerable portion of the visible and ultraviolet regions of the spectrum.

Spectrophotometric studies of molten-salt systems, particularly molten-fluoride-salt systems, were continued. Several modifications were made to improve the equipment. The graphite resistance heater was installed and operated satisfactorily; interesting phenomena are associated with its use. Study of the spectra of the 3*d* transition-element fluorides in molten alkali-metal fluorides was continued; the spectra of Co^{2+} in molten RbF and in molten CsF were obtained. The spectrum of U^{4+} was observed in several molten-fluoride media. Also, the spectra of Pr^{3+} and of Nd^{3+} in molten NaF were observed at 1100°C. Pertinent molar absorbancy indexes were determined. The spectrophotometric study of molten-salt systems is being continued.

Association constants of silver bromide species in molten $NaNO_3$ and their temperature dependence were determined from measurements of the emf of a concentration-type cell. The results were in agreement with predictions based on theory.

The radiolytic studies of simulated Purex waste solutions sorbed on NaCl were continued. The results indicate that there is little possibility of the practical disposal of radioactive liquids in natural deposits of NaCl.

In connection with a program on the use of radioisotopes in chemical analysis, which is supported by the AEC Division of Isotopes Development, a chemical method for the determination of thorium in granite was re-evaluated by means of Th^{234} tracer. Sources of possible error in the method were thereby located. The extent of the use of isotopes in analysis is being reviewed and will be described in a publication.

4. Reactor Projects Analyses

A rapid and precise method was developed for the indirect amperometric titrations with ethylenediaminetetraacetic acid in which VO^{2+} is used as back-titrant. The method was used to determine Zr^{4+} and Al^{3+} in HF-HNO_3 mixtures, Zr^{4+} in fluoride salts, and Zr^{4+} plus Th^{4+} in Molten-Salt Reactor Experiment fuel.

The off-gases from the dissolution of uranium monocarbide in water were identified and determined by means of gas chromatography. The work is of interest in the Gas-Cooled Reactor Experiment.

Relative to the Homogeneous Reactor Test, the sorption of the ions of uranium and also of copper and nickel on hydrous oxide was studied to provide data for use in interpreting the corrosion rates of zirconium and Zircaloy-2 in solutions of UO_2SO_4. An amperometric method for the titration of thorium was adapted to the determination of Cu^{2+} and certain rare-earth elements in HRT fuel and blanket solutions. A conductometric method for the indirect titration of sulfate was developed; a nonaqueous medium is used, but the presence of small amounts of water is advantageous rather than detrimental as it is in the similar potentiometric method. A program to evaluate methods for determining oxygen in K, Rb, and Cs is in progress. Apparatus was constructed, and limited tests were made with K. The program is related to the study of high-temperature materials.

5. X-Ray and Spectrochemical Analyses

Procedures were developed for dissolving the alloys Th-Ti, Th-Nb, Th-Sn, and Th-Zr. A stable standard solution of Sb was prepared from the pure metal. Volatile organic solutions were rendered safe for porous-cup analysis by adding mineral oil and evaporating the volatile solvent. Boron evaporated only very slightly from most acid solutions (except HCl) until dryness was approached. The use of a hollow aluminum "axicon" (conical light-guide) increased the effective speed of the spectrograph used in the HRLAF. A rapid technique was devised for determining traces of Be in air-borne dust and in smears. The x-ray absorption-edge technique is indifferent to matrix composition when Zr is determined in matrices with atomic numbers from 13 (Al) to 79 (Au). A device was designed and fabricated to direct the 50-μ-diam x-ray beam at a specific spot on a polished section. Use of a monochromator having a dispersion of 16 A/mm gave improved limits of detection in flame photometry. The flame emission spectrum of Ba was studied. Techniques were developed for determining traces of Sr in calcareous materials and for extracting and flame-photometrically determining Co (to 0.01 μg/ml), Ag (to 0.002 μg/ml), and Tl (to 0.0005 μg/ml). The addition of glycerol to sample solutions eliminated many solid-phase interference effects. The limits of detection of trace elements in human-tissue ash were lowered by installing 0.0015-in. slits on the Quantometer. The average relative standard deviation for trace-element determinations is 4.8%.

6. Mass Spectrometry

Improvements were made in the production of thermal ions from Pb and W by fusing the sample with B_2O_3.

7. Optical and Electron Microscopy

A procedure for preparing radioactive particulate material for electron microscopy was developed and evaluated. A modified filament was fabricated that gives marked improvement in the resolution of the electron microscope because it has a point source of electrons. A method was devised for replicating the surfaces of particles that range in size from 0.1 to 1.0 μ. Existing instrumentation was modified and improved. Research assistance was given to other divisions of the Laboratory.

8. Radiochemical Analyses

Eight tentative radiochemical methods were developed and tested for the Transuranium (TRU) Program. A survey of liquid-liquid extractions of metallic cations by means of O,O'-dialkylphosphorodithioic acids was continued. The investigation of neutron-deficient radionuclides is continuing. The water chemistry of the Oak Ridge Research Reactor loop is being studied in order to determine and control water-borne material. Assistance was given to the Isotopes Division on a number of problems, typical of which were the determination of the chemical species of P^{32} in phosphorus radioisotope products and the study of radionuclides present in tellurium radioisotope products. The program of preparation and study of large liquid

scintillators for detection of gamma rays has been enlarged to include work on α-methyl naphthalene with glass loading. Gamma-ray spectrometry has been applied to a large number and variety of samples; in addition, a high-level gamma-ray spectrometer system has been designed for use in a hot cell. A silicon surface-barrier alpha-particle spectrometer was assembled and tested for alpha energy analysis. The isotopes U^{238}, Th^{230}, and Ra^{226} were determined in animal lung tissue for the Health Physics Division. Lake silts were examined by gamma spectrometry. Disintegration rates of radioisotope standards were measured.

Effort has been expended in training noncitizen guests and in participating in national standardizing organizations.

9. Nuclear Analyses

Neutron-activation analysis has been used to determine many trace elements in Be, Nb, Zr, crystals of MgO and SiO_2, drugs, and radioactive materials. The technique was also used in biogeochemical studies and is being considered as a possible way to determine the origin of samples. Other activation analysis techniques, such as (α,n) reactions and delayed-neutron counting of U^{235}, have been used in certain analyses. Special projects have been carried out that were related to particle-size distribution analysis, neutron-flux monitoring, nondestructive methods of analysis, radiochemical separations, and measurements of radioactivity.

10. Inorganic Preparations

The preparation of nitrides and related compounds of the rare-earth metals is nearing completion, with only a few specific problems to be concluded. The fused-salts program for the Chemistry Division continues, and the preparations of some compounds of rhenium and technetium have solved some problems in the chemistry of these elements. A new program for the preparation of pure K_2O has been assumed for the Metallurgy Division.

Numerous miscellaneous preparations were completed for other divisions. The program for the preparation of high-purity MgO continues, with some problems still being studied.

11. Organic Preparations

Some special materials, most of which are not available commercially, were synthesized or purified. These materials were needed by staff members as reagents accessory to fundamental and applied research.

Several oximino ketones were prepared for use as complexing agents for Zr and Nb in studies of the tributyl phosphate (TBP) extraction process for the recovery of U from spent reactor fuels.

Two n-alkylbenzene compounds were prepared for use in studies of the degradation of these substances by HNO_3 when they are used as substitutes for the petroleum diluent in the TBP extraction process.

N-Methylacetamide was prepared for use as a solvent in a study of the exchange character of alkali metals in nonaqueous solvents on ion exchange resins; in this case a compound that has a high dielectric constant and that serves as a good ionizing medium is desired.

A number of alkali-metal salts of *p*-ethylbenzenesulfonic acid were prepared for use in studies of the relationship between free-energy differences and the selectivity of these substances in certain cation exchange separations.

PART II. ANALYTICAL DEVELOPMENT

12. Ionic Analyses

The analytical development work included many types of ionic analyses. Radiolytic decomposition products of Dowex 50 were identified by spot tests and titrated with $KMnO_4$. Chloride in K metal was determined by a special dissolution procedure and iodometric permanganate titration. The acid and Br^- contents of HBr-KBr were determined with a specified precision. Titrimetry with ethylenediaminetetraacetic acid was used to determine Al in an HF solution that contained Zr. An iodometric titration was used to determine PO_3^{3-} in H_3PO_4-HNO_3 mixtures. Thallium in CsI was determined by an ion exchange–polarographic method. Optimum temperature for boron-curcumin color development was established. A procedure for establishing CO_2 removal rate during Molten-Salt Reactor Experiment pump operations was developed. Accelerators used for the determination of carbon in stainless steel were studied. Magnesium was removed from LiF by an extraction procedure.

13. Infrared Spectral Studies

Spectrophotometric studies included the obtaining of infrared spectra to identify functional groups; to study the state of purity; and to detect changes in structure due to reaction, chelation, or radiation of various materials. Spectrophotometric studies concerned with various molten-salt systems were continued.

14. Anodization of Sector Coils for the Analog II Cyclotron

Special projects to assist other divisions included the anodization of sector coils for the Analog II cyclotron.

PART III. SERVICE ANALYSES

15. Quality Control

Many of the Statistical Quality Control (SQC) programs were partially or completely curtailed as a result of the relocation of the service laboratories and personnel. Revised SQC programs are now in effect. The quality of the work of the service laboratories and of the Division was about the same as that attained in 1960.

16. Ionic Analyses

Ionic service analyses were of the same types as in the past.

17. Low-Level Radiochemical Laboratory

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

18. Mass Spectrometric Analyses

The Analytical Mass Spectrometry Laboratory reported 31,520 determinations from 3845 samples. The number of stable isotope determinations increased 63%.

19. Spectrochemical Analyses Laboratory

The Spectrochemical Analyses Laboratory analyzed more than 2500 samples, most of them from the Isotopes Division. The stable isotopes of some 35 elements were determined. New standards for impurities in matrices of NiO and Mn_2O_3 were prepared and used.

20. Process Analyses

The twelve service laboratories at Y-12 and X-10 were consolidated into five laboratories. A great savings in manpower and a reduction in the duplication of equipment have resulted. The number of analyses performed this year increased by 2.0%, and the number of personnel was reduced 11.5%. A brief statement of new developments in each laboratory follows.

The High-Level Alpha Radiation Laboratory has put into service a new area for low-level alpha work. Several transuranium elements were determined by gross counting and alpha-pulse-height analysis. A Frisch-grid chamber and a solid-state detector were compared for pulse-height analysis.

The General Analyses Laboratory has extended its services to include several new types of density measurements and a vibratory compaction test. Determinations are also made of nitrogen in sol-gel ThO_2, Tc, gases evolved for mass assay, and valence states of uranium in UO_2 and in UO_2-ThO_2.

The General Hot Analyses Laboratory adapted the following methods and techniques to remotely controlled operations: conductometric titration of free acid and sulfate in HRT samples, removal and crushing of fluoride salt samples from copper sample ladles from the Volatility Process, dissolution of sections of irradiated fuel element, and measurement of oxygen-to-uranium ratio in irradiated UO_2 pellets.

The Materials Testing Laboratory is analyzing metal oxides and fused fluoride salts for oxygen content by the $KBrF_4$ method and is using a Perkin-Elmer vapor fractometer in the chromatographic analysis of gas mixtures.

The Radioisotopes-Radiochemistry Laboratory has been expanded to include sections for neutron-activation analysis and for low-level work. Two multichannel analyzers are in operation for assay of alpha-, beta-, and gamma-emitting samples. The half-lives of several radionuclides were determined, and the data were published.

As a part of the quality control program, several new synthetics were prepared, and a complete set of Bureau of Standards standard samples was secured.

The design work on the new High-Level Analytical Facility is completed; construction will be started in July 1962 and should be completed in September 1964. Construction of "hot" cells in the Radioisotopes-Radiochemistry Laboratory has started and should be completed by May 1962.

The High-Radiation-Level Analytical Facility has developed a booting procedure to maintain containment during repairs and replacement of manipulators. The main object of the work of this group has been to comply with containment specifications and to increase the versatility of work done in the hot cells.

21. Radiochemical Analyses

Special or unusual samples were analyzed by the Radiochemical Analyses Group. Most of the radiochemical service work is now being done in the Radioisotopes-Radiochemistry Laboratory.

22. Thermal Breeder Reactor Projects Analytical Chemistry Laboratory

The Thermal Breeder Reactor Projects Analytical Chemistry Laboratory analyzed some 4200 samples for the Reactor Chemistry, Health Physics, and Reactor Divisions. The types of samples and the methods used varied considerably.

PART IV. ORNL MASTER ANALYTICAL MANUAL

23. ORNL Master Analytical Manual

The third supplement to the reprinted form of the *ORNL Master Analytical Manual* was made available for public sale. Twenty-three new methods and nine revised methods were issued. The subsection 9 08, "Homogeneous Reactor Project (HRP) Methods," was recalled. The Table of Contents for the entire *Manual* was revised.

Contents

PART II. ANALYTICAL DEVELOPMENT

PART III. SERVICE ANALYSES

Part I. Analytical Research

Research in a variety of fields of analytical chemistry has been conducted during the past year for the Production, Physical Research, and Isotopes Development Divisions of the Atomic Energy Commission. Research has also been 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

INSTRUMENTATION FOR CONTINUOUS MEASUREMENT OF DENSITY, PULSE AMPLITUDE, AND PULSE FREQUENCY IN A PULSED SOLVENT-EXTRACTION COLUMN

R. W. Stelzner

A stainless steel float densimeter that measures the density of the continuous phase at a selected point in a pulsed solvent-extraction column was designed and fabricated and was tested on a test loop in Building 3019. The principle of operation is that the buoyant force exerted by the liquid on the float is balanced by an adjustable spring-tension force at a selected density. Any deviation from this density causes the float to move either up or down; the difference in position of the soft-iron armature fixed inside the float is sensed by a differential transformer located outside the stainless steel shell of the float compartment.

An electrical output signal is obtained from the differential transformer. The primary of the differential transformer is fed from the 6.3-v winding of a Sola constant-voltage transformer; the secondary of the differential transformer is resonated at 60 cps by a 0.33-μf capacitor. The 60-cps signal from the secondary of the differential transformer is rectified by a 1N 1084 silicon rectifier; 2% of the output of the rectifier becomes the input signal for a 10-mv Brown recorder.

The instrumentation has two programmed outputs: during a period of 15 sec, the pulse amplitude and frequency in the solvent-extraction column are presented on the recorder chart; during the next 45 sec, the density of the solution is measured. The latter measurement is achieved by connecting a 500-μf

capacitor from the rectifier output to circuit ground. A 1-rpm synchronous motor that operates cam-driven microswitches produces the cyclic program.

To test and calibrate the instrumentation, the densimeter was nulled at a density of 0.997 g/ml, and then $Al(NO_3)_3$ solutions of known densities were pumped through the test loop. A Lapp Pulsafeeder produced 2-in. pulses in the column at a frequency of 50 cpm. The calibration curve for the densimeter was linear in the range from 1.000 to 1.200 g/ml; in this range, a density measurement can be made with a maximum error of ±0.2%.[1]

Changes in pulse amplitude, pulse frequency, and density of the solution are readily observed on the recorder chart. The choice of materials of construction was such that the instrumentation can be operated satisfactorily in high-radiation fields. Further testing, in which the densimeter is being used to control the density of a flowing stream, is in progress.

This work was done jointly with T. S. Mackey.[2]

TEST OF A COLLECTOR FOR AIR-BORNE ALPHA-CONTAINING PARTICLES

R. W. Stelzner

A centrifugal-type impactor for air-borne alpha-containing particles, designed by T. S. Mackey,[2] was tested for efficiency by comparison with a vacuum collection system. Samples were collected from equal volumes of the same air on sampling disks by means of the two methods. The alpha emissions from the samples were counted with a ZnS(Ag) phosphor, mounted on a multiplier phototube, and an appropriate amplifier-scaler system. The impactor showed a satisfactory collection efficiency of 36.8% in producing a small-area sample, which is a desirable sample in counting the alpha particles. This work was done jointly with T. S. Mackey.

APPARATUS FOR REMOTELY CONTROLLED MANIPULATION OF MICROPIPETS IN THE HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

M. T. Kelley H. C. Jones D. J. Fisher W. L. Belew

It has been customary in the preparation of dilute solutions of samples for radiochemical analysis to use a separate micropipet for each sample in order to prevent trace cross contamination. Because of equipment limitations, it has been inconvenient to follow this precaution when making dilutions in the High-Radiation-Level Analytical Facility (HRLAF). Apparatus has now been provided for the remotely controlled use of micropipets. When the micropipets are used with air as the displacement medium, care must be taken to avoid errors arising from hydrostatic effects; also, the meniscus must be observed from outside a cell window with a monocular and adjusted to the calibration mark.

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[1] T. S. Mackey, *Inline Densimeter for Pulsed Column Liquid Density, Pulse Amplitude and Pulse Frequency Measurements*, ORNL-3129 (July 5, 1961).

[2] Chemical Technology Division.

An adapter was fabricated that makes possible the use of the ORNL servo-controlled 1-ml pipetter[3,4] as a control to fill a micropipet or a plain pipet tip by suction created by movement of the pipetter plunger. If a secondary displacement fluid is used with this pipetter, which is readily possible because of the design of the side arm, it is not necessary to use a calibrated micropipet or to adjust the meniscus to a calibration mark. Positive delivery action is attained as dictated by the calibrated servo-control dial; therefore separate uncalibrated pipet tips having good orifices (instead of micropipets) may be used for each sample. The use of a secondary displacement fluid is advantageous when only a small amount of sample is available or when it is desirable to deliver several volumes of sample from a single filling of the tip.

The "remote pipetter," developed at the Argonne National Laboratory to remotely control a calibrated micropipet with air as the displacement medium and available from Research Equipment Company, Wheaton, Illinois, has also been modified and used in the HRLAF for this purpose. An electrical limit switch was added to the remote pipetter to prevent overtravel of the motor drive, which would destroy the "syringe vacuum pump." A photograph (ORNL photograph No. P 55017) and a sketch of this modification have been made.

MODIFIED MOTORIZING ASSEMBLY FOR LAB-JACK

W. L. Maddox

The motorizing assembly for the Cenco-Lerner No. 19089 Lab-Jack, used for remotely controlled vertical positioning, was modified to eliminate the "sliding coupling unit" and to make the motorizing assembly more compact. The modified assembly is described in an unpublished memorandum.

CORROSION-RESISTANT 3-ml PIPET FOR REMOTELY SERVO-CONTROLLED PIPETTING OF RADIOACTIVE SOLUTIONS

D. J. Fisher W. L. Belew

The capacity of the corrosion-resistant pipet used in the pipetter for remotely controlled pipetting of radioactive solutions is 1 ml.[4] A 3-ml pipet has been designed, which is a modification of the 1-ml pipet. The outside dimensions of the 3-ml pipet are the same as those of the 1-ml pipet; therefore it fits interchangeably with the other pipets used in the standard position-servo drive unit. The outside diameter of the plunger and the inside diameter of the liner were increased, and an adapter, designed by B. Cook,[5] was added to fasten the 3-ml plunger to the lead screw. The seal quality and precision of delivery of the 3-ml pipet are satisfactory; the relative standard deviation of 14 deliveries of 300-μl volumes was 0.27%.

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[3]M. T. Kelley, H. L. Hemphill, and D. J. Fisher, "Servo-Controlled Pipetter for Precise Delivery of Microliter Drops," *Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology, Instrumentation, Remote Control Techniques, and Nucleonics,* TID-7568 (Pt. 2), pp 98–106 (April 1959).

[4]D. J. Fisher, M. T. Kelley, and W. L. Belew, "A Corrosion-Resistant Pipetter for Remote Measurement of Radioactive Samples," *Proceedings, Fourth Conference, Analytical Chemistry in Nuclear Reactor Technology,* TID-7606, pp 311–29 (January 1961).

[5]Chemistry Division Shop, Engineering and Mechanical Division.

The mechanical drawing for the pipet[4] has been revised so that it can be used for the fabrication of either 1- or 3-ml corrosion-resistant pipets. The annular groove has been omitted from the 1- and 3-ml liners because it was decided that the groove was an unnecessary refinement. At the time of assembly of the pipets with the new liners, the plungers are aligned angularly.

DIRECT-READOUT MODIFICATION TO THE ORNL MODEL Q-2005 COULOMETRIC TITRATOR

R. W. Stelzner

Voltage-divider networks that make possible the direct potentiometric readout of a multiple of the amount of uranium, copper, or nickel titrated (each 100 mv ≙ 1 mg) have been designed for use with the ORNL model Q-2005, automatic, electronic, controlled-potential, coulometric titrator.[6] This modification will simplify the calculation of results by the analyst and should reduce the time required for a single analysis. The General Analyses Laboratory has tested the modified system in routine chemical analyses and prefers it to the original readout system.

CHRONOPOTENTIOMETRY

W. L. Maddox D. J. Fisher

A chronopotentiometric procedure is being investigated for the determination of an ion (B) in the presence of a more easily reduced species (A), the concentration of which may vary from sample to sample. The presence of A enhances the transition time due to B (τ_B). For a particular applied current, the enhancement of τ_B is a linear function[7] of the concentration of A (C_A), but the concentration of B (C_B) can be determined only if τ_A is known. The variables are related by the equation[8]

$$(\tau_A + \tau_B)^{1/2} - \tau_A^{1/2} = kC_B ,$$

where the term $\tau_A^{1/2}$ contains implicitly a knowledge of C_A. The precision chronopotentiometer is designed to read out directly either τ_A or $(\tau_A + \tau_B)$. If a standard addition of B only is made and if a second readout of $(\tau_A + \tau_B)$ is taken, C_B can be calculated. Preliminary tests made with Pb^{2+} and Cd^{2+} have confirmed this.

The standard-addition method offers experimental simplicity. It requires neither the construction of a calibration curve nor the precise control from one sample to the next of electrode area, current, temperature, and matrix composition.

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

[7] C. N. Reilley, G. W. Everett, and R. H. Johns, "Voltammetry at Constant Current. Experimental Evaluation," *Anal. Chem.* 27, 483 (1955).

[8] P. Delahoy and G. Mamantov, "Voltammetry at Constant Current. Review of Theoretical Principles," *Anal. Chem.* 27, 478 (1955).

At low concentrations and at the relatively short transition times (0.5 to 5 sec) used to date, an appreciable loss of accuracy can be ascribed to a blank (nonfaradaic) time that is included in each measurement of transition time. Timing the interval from the inception of electrolysis until a chosen potential is attained by the working electrode, which is the principle of the timing circuit now in use, is an adequate way of determining concentration by means of a calibration curve (one reducible species present). In the presence of charging current, the calibration curve has an intercept; therefore a means of correcting for the intercept must be found if the standard-addition method is to be used. Ways to correct for or to minimize the effect of the charging current are being sought.

AUTOMATIC, RECORDING CONDUCTOMETRIC TITRATOR

T. R. Mueller R. W. Stelzner

An automatic, recording conductometric titrator is being designed and tested. Present design criteria require the application of an electronically controlled, small-amplitude (10-mv peak-to-peak), 1000-cps, sinusoidal voltage to the electrodes of a conventional dip-type conductivity cell. The ac current that flows through the cell is measured by a resistor in the feedback loop of a GAP/R K2-XA operational amplifier, is synchronously rectified, and is presented for recording on a 10-mv strip-chart recorder. Results of preliminary tests show that the output voltage is linear with conductivity to 2×10^5 micromhos. Limits for high-resistance solutions have not been established. The instrument should give titration curves essentially free of distortion caused by faradaic processes and by changes in electrode capacitance. In addition, the speed of analysis and accuracy attainable with it should make the instrument attractive from a practical standpoint.

HIGH-RESOLUTION, HIGH-SENSITIVITY, SCANNING, RECORDING FLAME SPECTROPHOTOMETER

H. C. Jones D. J. Fisher M. T. Kelley

Development progress on a new high-resolution, high-sensitivity, scanning, recording flame spectrophotometer was discussed previously.[9] The circuit design and fabrication have been completed. The instrument has been checked out for flame emission work at wavelengths up to 852 mμ and has been briefly evaluated for use in atomic-absorption flame spectrophotometry.

The performance of the chopped-light-beam ac system was compared with that of an unchopped dc system. The ac system was chosen because of the relatively stable zero obtained with that system, especially when infrared-sensitive multiplier phototubes are used, and because of the adaptability of the system for atomic-absorption flame spectrophotometry. The high, variable, and temperature-dependent dark current present in infrared tubes is not modulated by the beam chopper and is therefore not amplified by the ac system.

[9] D. J. Fisher, H. C. Jones, and M. T. Kelley, "High-Resolution, High-Sensitivity, Scanning, Recording, Flame Spectrophotometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 6–7.

A transistor used as a synchronous rectifier was chosen over a diode rectifier because the transistor operates at lower signal levels and has a linear response over a wide range of signal levels.

The folded optical path now in use was selected because of its compactness. C. Feldman made major contributions to the optical design. A straight-line optical path in which fewer optical elements are used should prove more satisfactory, especially at shorter wavelengths, if space limitations are not a factor to be considered.

The output of the rectifier, which is proportional to the instantaneous output of the flame source, can be either recorded as such or integrated over a fixed time. Two GAP/R USA-3 chopper-stabilized operational amplifiers follow the rectifier system. One is connected as an inverting dc amplifier, the other as a time integrator. The output from the inverting dc amplifier is fed through a zero-set circuit to a standard 10-mv Brown recorder. The input signal for the integrating amplifier is obtained from the synchronous rectifier through a switch operated by a timer. After a 45-sec integration period, the input switch is opened, and another switch that is operated by the same timer connects the recorder to the integrator output for a period of about 5 sec. The recorder input is then returned to the output of the dc amplifier. The precision of measurements made repeatedly by use of the integrated output is comparable with that obtained by use of the normal dc-amplifier output. At high sensitivity, the single value of the recorded integral is not liable to subjective interpretation as is the noise-containing dc-amplifier output. The signal being integrated is simultaneously recorded; therefore it is known whether any abnormal behavior occurs – for example, variation in flame source output or in feed rate of sample. If abnormal behavior does occur, the corresponding integral value must be rejected.

This instrument has been evaluated briefly for atomic-absorption flame spectrophotometry. In this use of the instrument, it is necessary to relocate the beam chopper.

The instrument is relatively stable. With repeated emission measurements made at a spectral band pass of 0.8 A on an aqueous solution of 1 ppm Li, a relative standard deviation of less than 0.5% was obtained. A paper that describes this instrument and its performance has been written.[10]

AC CONTROLLED-POTENTIAL POLAROGRAPHY

R. W. Stelzner

Development work on a system of ac controlled-potential polarography[11] has continued, with emphasis on improvement of circuit design so that adequate charging currents are produced at the electrode surface. Experimental data show that some harmonic distortion of the wave form occurs because the operational amplifiers cannot furnish the currents required. This distortion is in addition to that which can be ascribed to faradaic rectification at the electrode surface.

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[10] H. C. Jones, D. J. Fisher, and M. T. Kelley, *High-Resolution, High-Sensitivity, Scanning, Recording, Flame Spectrophotometer*, presented at the Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961.

[11] R. W. Stelzner, "AC Polarography," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 8–9.

A power transistor stage (Delco DTS-5) has been added to the control amplifier circuit in order to increase the current output. Current available from the transistor can be switched from 0.01 μamp to 0.01 amp with a maximum deviation in control potential of $\pm 0.5\%$.

Investigation of the anodic response of the three-electrode cell has shown that a platinized-platinum counter electrode is superior to a smooth platinum wire. The platinized-platinum electrode permits operation of the cell with a lower voltage applied between anode and cathode, thus reducing the error voltage at the summing point. In addition, the transient response of the electrode system is improved. These modifications will lessen the danger of harmonic generation by the instrumentation itself.

A harmonic analyzer that uses a parallel-T network (tuned to 159.2 cps) in the feedback path of a Philbrick P2 amplifier has been designed for second-harmonic analysis of the D.M.E. current. In this system, the ac polarograph is operated at a frequency of 79.6 cps, and only the second-harmonic current component is measured. A comparison of this method with that of phase discrimination now incorporated in the instrumentation is planned. The sensitivity of the phase-discrimination circuit remains at $\sim 5 \times 10^{-6}$ M Cd^{2+} in 0.1 M KCl.

The transistorized phase discriminator based on a 2N270 PNP transistor operates well at signal levels of 100 mv but fails at about 10 mv. It is hoped to extend the operation to the region from 1 to 10 mv in order to decrease the demand for open-loop gain in the operational amplifiers.

ORNL MODEL Q-1988A CONTROLLED-POTENTIAL AND DERIVATIVE POLAROGRAPH

M. T. Kelley D. J. Fisher H. C. Jones

The first model of the ORNL controlled-potential and derivative polarograph (i.e., model Q-1988) has been described.[12] The results of work done by others with a polarograph of this design have been published.[13] A complete set of mechanical and electrical drawings (Q-1988 series) and a check-out and test procedure (ORNL Test Specification No. ST-175) were prepared for this polarograph. This model has an electromechanical scanning unit.

Subsequently, an all-electronic polarizing section was designed.[14] The continuous output of the electronic scan circuit of the polarizing section has less noise than has the electromechanical circuit, a particular advantage in high-sensitivity derivative polarography. The second model of the polarograph, Q-1988-ES, consists of the new electronic polarizing section[14] and of current-amplifier and computing sections of the same design as those used in the first model.[12] The results of some work done with the

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

[13] J. H. Rowan, *The Determination of Trace Quantities of Zinc in Lithium Chloride by Derivative Polarography*, Y-1320 (Oct. 5, 1960).

[14] 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).

Q-1988-ES polarograph have been published.[15,16] An investigation of quantitative derivative polarography made with it has been completed (see "Quantitative Derivative Polarography," this report).

The third and latest model of the polarograph, the Q-1988A, has the design features of the Q-1988-ES instrument but has, in addition, an initial-current-compensation circuit. Three ranges of initial-current compensation (0 to 1, 0 to 10, and 0 to 100 μa) are available to suppress the diffusion current of prior waves. The model Q-1988A has been tested, electrical and mechanical drawings (Q-1988A series) have been prepared, and a check-out and test procedure (ORNL Test Specification No. ST-175A) has been written. This procedure includes a section on oscilloscopic tests of operation with a polarographic cell. For both the Q-1988-ES and Q-1988A polarographs, in each of which an unstabilized GAP/R K2-X or K2-XA operational amplifier and a voltage-reference diode are used, the maximum deviation of the electronically generated scan rate from the specified rate is about $\pm 0.5\%$. Improved stability, if required, can be attained by means of a more stable voltage-reference diode and a GAP/R USA-3 chopper-stabilized operational amplifier. The model Q-1988A polarograph is available commercially.

For each of the three models, the electrical calibration of the recorder scale is as follows. In regular polarography, wave height is measured in microamperes. The relationship between full-scale recorder deflection and cell current is indicated on the current-range switch; the current range in use, expressed in microamperes, corresponds to a deflection of 100% of full scale on the recorder. In derivative polarography, peak height, which is the maximum value of di/dt, is measured in microamperes per minute. In the derivative function, the value of a full-scale recorder deflection, measured in microamperes per minute, is numerically equal to $\frac{1}{5}$ the current-range value, measured in microamperes.

QUANTITATIVE DERIVATIVE POLAROGRAPHY

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

The work on dc derivative polarography with a D.M.E.[17,18] has been continued. The ORNL model Q-1988-ES, controlled-potential derivative polarograph was used.[12,14,15] For reversible, diffusion-controlled mass-transfer reactions, the forms of the experimental derivative polarograms have been compared with that predicted from theory. The resolutions possible with derivative and regular polarography have been compared. The reproducibilities of wave heights and peak heights and the relationships of peak height and wave height to concentration have been studied. This work is discussed briefly below.

Several methods were used in the comparison of the forms of experimental derivative polarograms with the form predicted from the theoretical equation for reversible, diffusion-controlled processes. It

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[15] 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.

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

[17] M. T. Kelley and D. J. Fisher, "Instrumental Methods of Derivative Polarography," *Anal. Chem.* 30, 929 (1958).

[18] D. J. Fisher, W. L. Belew, and M. T. Kelley, "Derivative Polarography," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 10–15.

was reported[18] that the maximum value attained (peak height) occurs at $E_{1/2}$ and that, for both a reversible and a nonreversible system, the experimental derivative polarogram is the sum of the derivative polarograms for all the constituents present in the solution. The theoretical equation predicts that

$$\text{peak height, } \mu\text{a/min} = -i_d \cdot \frac{n}{4} \cdot \frac{F}{RT} \cdot \frac{dE}{dt},$$

where i_d is the diffusion current of the regular wave in μamp, n is the number of faradays per mole, F/RT is 39.0 per volt at 25°C, E is the effective potential of the D.M.E. with respect to the reference electrode, and dE/dt is the scan rate in volts per minute. The theoretical equation also predicts that the peak should be symmetrical about a vertical axis that passes through $E_{1/2}$. The percent of the peak height at each value of E can be calculated; thus the equation predicts the extent of overlapping of adjacent peaks. The equation can also be used to calculate n from the values of peak width. Points from experimental derivative polarograms have been plotted on the theoretical peak. The $E_{1/2}$ values given in the literature were compared with the potentials at which the peak maxima occur. Determinations of n were made by measuring the widths of the peaks. Theoretical peak heights have been calculated from measured wave heights of average-current regular polarograms and compared with experimental peak heights. The results from each of these methods have shown that for reversible, diffusion-controlled processes the forms of the derivative polarograms obtained experimentally agree very closely with the form predicted from theory. In order to obtain experimentally derivative polarograms of form identical with that predicted from theory, it is necessary to do the following: (1) scan slowly to prevent damping circuits in the polarograph from affecting the shape of the derivative peak, (2) use a controlled-potential polarograph so that a constant and reproducible effective dE/dt is obtained throughout the peak, (3) have a diffusion-controlled reversible reaction uncomplicated by a varying degree of complex formation, (4) use a quadruple parallel-T filter made up of linear circuit elements in order to obtain the average value of cell current by linear damping before di/dt is computed, and (5) use an analog computer to obtain di/dt. The peak height must be measured relative to the derivative polarogram of the supporting electrolyte and at $E_{1/2}$ rather than by extrapolation. For optimum results, particularly at high sensitivity, the sparging of oxygen must be adequate, the scan voltage must be continuous and free of noise, and the current at the D.M.E. must be free of spurious noise pulses.

The resolutions obtained by regular and derivative polarography have been compared by means of simple simultaneous equations used to mathematically resolve the overlapped regular and overlapped derivative polarograms of solutions that contained Tl^+ and Pb^{2+}. The method of Frisque, Meloche, and Shain[19] was used to determine the potential at which current measurements from regular polarograms could be made most accurately. The heights of the derivative polarograms were measured at the $E_{1/2}$ values for each ion. The standard-addition method was used in both cases to evaluate the proportionality constants needed in the simultaneous equations to calculate the concentrations of the individual ions. The standard-addition method is preferred to the use of slopes of calibration curves. The results indicate

[19] A. Frisque, V. W. Meloche, and I. Shain, "Minimum Error Polarographic Analysis of Binary Mixtures," *Anal. Chem.* **26**, 471 (1954).

that both overlapping regular and overlapping derivative polarograms can be resolved mathematically, even in the absence of an intervening plateau in the case of regular polarograms. The derivative polarograms have better qualitative resolution, and the measured increments of chart distance resulting from standard additions are greater; both these characteristics are advantageous in quantitative work.

The reproducibility of peak heights of derivative polarograms was compared with the reproducibility of wave heights of the corresponding regular polarograms for a series of 15 solutions of Cd^{2+}. The long-term maximum deviation of the scan rate in the Q-1988-ES and Q-1988A polarographs is ±0.5%. A relative standard deviation of 0.6% was obtained for measurements of peak height and one of 0.5% for measurements of wave height.

The relationship of peak height to concentration (with unvarying D.M.E. characteristics) was determined for UO_2^{2+} in 0.1 *M* HNO_3 and for Tl^+, Cd^{2+}, Pb^{2+}, Zn^{2+}, and In^{3+} (each in 0.1 *M* KCl) over the concentration range from 5×10^{-6} to 1×10^{-3} *M*. The results show that the heights of the derivative peaks have the same relationship to concentration as do the corresponding wave heights. For Cd^{2+}, Zn^{2+}, and In^{3+}, neither wave nor peak heights were directly proportional to concentration over the entire concentration range studied. For Cd^{2+}, the deviation from linearity was affected by the nature and concentration of the supporting electrolyte and by the drop time but was not affected by the presence of gelatin. For Tl^+, Pb^{2+}, and UO_2^{2+}, the wave heights and peak heights were each directly proportional to concentration in the range from 5×10^{-6} to 1×10^{-3} *M*.

In conclusion, the results show that with the ORNL models Q-1988-ES and Q-1988A polarographs one can obtain dc derivative polarograms having a form controlled by the electrochemical reaction and not influenced by instrument characteristics. The data obtained also indicate that dc derivative polarograms, in comparison with regular polarograms, are less subject to interference from overlapping and can be corrected more easily for residual current. Also, they present the polarographic data in a form easily interpreted.

2. Dissolver-Solution Analyses

J. C. White
P. F. Thomason

CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF PLUTONIUM

W. D. Shults

The study of the controlled-potential coulometric titration of plutonium discussed earlier[1,2] has been continued.

[1] W. D. Shults, "Controlled-Potential Coulometric Titration of Plutonium," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 16–17.

[2] W. D. Shults, *Controlled Potential Coulometric Titration of Plutonium – Application to PRFR Samples*, ORNL-2921 (Apr. 11, 1960).

Separations. – The use of dilute HF and HF-HNO_3 solutions as eluents for submilligram and milligram quantities of Pu^{4+} (complexed as nitrate) from Dowex 1-X4 resin was studied. The optimum range of HF concentration is 0.01 to 0.03 *M*. Rapid and complete removal of Pu^{4+} from the resin column is obtained at room temperature by use of 0.01 *M* HF–0.1 *M* HNO_3 solution, but the eluate must be evaporated and fumed with $HClO_4$ before the Pu^{4+} is determined by controlled-potential coulometric titration. Fuming with $HClO_4$ is necessary to remove HF and to destroy any organic material introduced into the solution from the resin. The relative standard deviation of the complete procedure (adsorption, elution, fuming, and titration) for determining about 1 mg of Pu^{4+} is 0.6%.

Exploratory work was done on the separation of plutonium by anion exchange from sulfate medium. The distribution coefficient is approximately 400 when Pu^{4+} in 0.05 *M* H_2SO_4 is equilibrated with Dowex 1-X4 resin but decreases abruptly with an increase in acidity. The distribution coefficient is only 10 to 15 in 0.1 *M* H_2SO_4 or $(NH_4)_2SO_4$ medium. Consequently, this separation does not have promise for use in the analysis of dissolver solutions.

Work was begun on the separation of plutonium by extraction into 0.1 *M* tri-*n*-octylphosphine oxide (TOPO) in cyclohexane. Plutonium(IV) is quantitatively extracted from moderately strong HNO_3 solutions (3 to 6 *M*), and the extraction frees Pu^{4+} from many of the ions commonly present in dissolver solutions. Conditions for the quantitative stripping of Pu^{4+} from the organic phase are yet to be established.

Al-Pu Alloys. – Optimum conditions were established for the titration of plutonium in dissolver solutions of Al-Pu alloy fuels. These solutions are approximately 1.5 *M* in Al^{3+} and in HNO_3; they contain approximately 1 mg of Pu per milliliter and traces of F^-, Hg^{2+}, and Fe^{3+}. The best supporting electrolyte found for this type of sample was 0.2 *M* $AlCl_3$–0.2 *M* HCl, in which F^- is complexed by Al^{3+}, and Hg^{2+} is complexed by Cl^-. The E^0_{Pu} is +0.71 v vs the S.C.E. To minimize the interference of Fe^{3+}, reduction of Pu^{4+} to Pu^{3+} is made at +0.59 v (i.e., $E^0 = -0.12$ v rather than −0.18 v); Pu^{3+} is oxidized to Pu^{4+} at +0.89 v. The results of analyses of standard synthetic samples of this type by this procedure agreed within ±1% with results obtained by the thenoyltrifluoroacetone (TTA) extraction–counting technique.

Mixtures of Pu^{3+}, Pu^{4+}, and Pu^{6+}. – A procedure was developed for the determination of Pu^{3+}, Pu^{4+}, and Pu^{6+} individually and in mixtures by controlled-potential coulometric titration. Titrations are made on a single test portion in 1 *M* $HClO_4$ that contains a known amount of Fe^{3+}. Plutonium(III) is first determined by oxidation to Pu^{4+} at +0.88 v vs the S.C.E. Plutonium(VI) is then determined by the difference between the current consumed when all the Pu^{4+} and Pu^{6+} in the solution is reduced to Pu^{3+} at +0.30 v and the current consumed when the Pu^{3+} is then reoxidized to Pu^{4+} at +0.88 v. Total plutonium is determined simultaneously by this reoxidation titration; its determination thereby makes possible the calculation of the Pu^{4+} content of the test portion by difference between the total plutonium and the sum of Pu^{3+} and Pu^{6+}. The relative standard deviation of each titration is approximately 0.4%, and the errors in determining 5 mg of plutonium in each of the three valence states are each less than 1%. The difficulty of preparing stable standard solutions of plutonium in each of the three valence states prevents the measurement of the errors of this procedure more precisely than 1%.

Determination of Polymeric Plutonium. – Polymeric plutonium can be determined indirectly from the results of two controlled-potential coulometric titrations. In one test portion of a sample, monomeric

plutonium is determined in the presence of polymeric plutonium in the usual way;[3] polymeric plutonium does not interfere because it is electrolytically inactive. Total plutonium (monomeric plus polymeric) is determined in another test portion by treating the test portion with a trace of HF to destroy the polymer and then fuming off the HF with H_2SO_4. The E^0_{Pu} in 0.5 *M* H_2SO_4 is +0.50 v vs the S.C.E.; therefore reduction is made at +0.32 v, and oxidation is made at +0.68 v. Oxygen must be excluded. Polymeric plutonium is then calculated from the difference between the results of the two titrations.

SECONDARY CONTROLLED-POTENTIAL COULOMETRIC TITRIMETRY

W. D. Shults

Secondary controlled-potential coulometric titrimetry – that is, the coulometric generation and back-titration of intermediate reagents at controlled potential rather than with controlled current – has been discussed.[1,4] Additional work was done on the plutonium procedure already given;[4] also, the technique has been applied to the determination of uranium.

Plutonium. – Studies were made of the use of Ag^{2+} (as AgO) as oxidant prior to the titration of Pu^{6+} by secondary controlled-potential coulometric titration. It was found that the Ag^+ introducted into the electrolyte solution by the oxidation treatment can itself serve as the intermediate reagent; therefore addition of iron is unnecessary. Thus the titration involves electrolytic reduction of Ag^+ to obtain Ag^0 in excess, which reduces Pu^{6+}. The excess Ag^0 is then oxidized coulometrically back to Ag^+, and Pu^{6+} is measured by the difference between the currents used in the reduction and oxidation electrolyses. The relative standard deviation of this method is 0.4% at the 5-mg level and 1% at the 0.5-mg level. Consequently, oxidation with AgO gives results comparable with, but no better than, those obtained when $HClO_4$ is used as the oxidizing agent.

Uranium. – Uranium can also be determined by secondary controlled-potential coulometric titrimetry; iron is used as the intermediate reagent. The procedure consists in reduction of uranium to U^{4+} and of iron to Fe^{2+} by addition of Cr^{2+} (as $CrSO_4$) in excess, destruction of the excess Cr^{2+} by electrolytic oxidation at +0.2 v, generation of excess Fe^{3+} by coulometric oxidation at +0.6 v, and back-titration by coulometric reduction at +0.2 v of the Fe^{3+} remaining after reaction with U^{4+}. These electrolyses are made in 0.5 *M* H_2SO_4 at a platinum gauze electrode and must be carried out in an oxygen-free atmosphere. Uranium is measured by the difference in the current consumed in the generation (oxidation) and back-titration (reduction) electrolyses.

This procedure is analogous to the potentiometric titration of uranium with a standard solution of $Fe_2(SO_4)_3$ but has the following advantages: titrations are made at room temperature, smaller amounts of uranium are titrated, no standard solutions are required, and adaptability of the procedure to remotely

[3] W. D. Shults, "Plutonium, Automatic Controlled-Potential Coulometric Titration Method," Method Nos. 1 216220 and 9 00716220 (9-22-60), *ORNL Master Analytical Manual;* TID-7015, suppl 3.

[4] W. D. Shults, "Coulometric Generation and Back-Titration of Intermediate Reagents at Controlled Potential. Application to the Determination of Plutonium," *Anal. Chem.* 33, 15 (1961).

controlled operations is greater. Uranium can be determined by this technique with relative standard deviations of 0.4 and 0.2% (or better) when 2.5 and 10 mg or more, respectively, of uranium are titrated.

Iron, nickel, chromium, Cl^-, and small amounts of NO_3^- do not interfere, but molybdenum does interfere. Consequently, the procedure can be used for the direct determination of uranium in stainless steel type dissolver solutions without prior separation if molybdenum is absent.

COULOMETRIC TITRATION OF U^{6+} IN THE PRESENCE OF IRON

W. D. Shults Louise B. Dunlap

Some work has been done to develop a coulometric titration method for the determination of U^{6+} in the presence of iron. Iron is prereduced at a platinum electrode at a potential of +0.05 v vs the S.C.E.; U^{6+} is then reduced at a mercury cathode at a potential of −0.30 v vs the S.C.E. The results shown in Table 2.1 indicate the precision and accuracy of the titration in the presence of various amounts of iron. In future work, the maximum amount of iron that can be tolerated and the effects of possible interferences will be studied.

Table 2.1. Precision and Accuracy of Coulometric Titration of U^{6+} in the Presence of Iron

Iron Added (mg)	U^{6+} (mg)		*N*, Number of Titrations	*S*, Relative Standard Deviation (%)
	Taken	Found		
None	5.92	5.92	9	0.3
5 to 12	5.92	5.92	8	0.3
18 to 50	5.92	5.95	15	0.8

DETERMINATION OF URANIUM BY TRI-*n*-OCTYLPHOSPHINE OXIDE EXTRACTION AND COULOMETRIC TITRATION

W. D. Shults

Work was begun on the separation and determination of uranium by extracting the uranium into 0.1 *M* tri-*n*-octylphosphine oxide (TOPO) in cyclohexane, stripping it back into an aqueous supporting electrolyte, and titrating it coulometrically. The extraction from 5 *M* HCl or 1 *M* HNO_3 is quantitative and does not introduce an interfering amount of organic material into the supporting electrolyte. A number of solutions were investigated as possible stripping agents, the best of which are 0.1 *M* Na_2CO_3 and 0.5 *M* Na_3PO_4–0.5 *M* H_3PO_4. The relative standard deviation of the complete procedure is 0.5%, and the results have a bias of −0.8%; therefore more work is indicated. The method has considerable promise for the determination of uranium in several types of dissolver solutions, particularly those that contain components of stainless steel.

CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF NEPTUNIUM

W. D. Shults

The Hanford procedure[5,6] for the determination of either total neptunium or Np^{4+}, Np^{5+}, and Np^{6+} by controlled-potential coulometric titration was verified and was put into use in the High-Level Alpha Radiation Laboratory.

CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF ANTIMONY

Louise B. Dunlap W. D. Shults

Two procedures were developed for the controlled-potential coulometric titration of antimony. In the first, the following reaction occurs at a mercury cathode controlled at −0.28 v vs the S.C.E.:

$$Sb^{3+} + 3e + Hg \rightarrow Sb(Hg) .$$

The supporting electrolyte is 0.4 *M* tartaric acid–1 *M* HCl. The amalgam thus formed can then be oxidized at −0.08 v vs the S.C.E. to free the antimony as Sb^{3+} if this is desired. If Sb^{5+} is to be determined by this procedure, it must first be reduced to Sb^{3+}; hydrazine hydrate is a suitable chemical reductant. The data in Table 2.2 were obtained by analysis of standard solutions of antimonous chloride and antimonic chloride and are considered to indicate the precision and accuracy of the procedure.

Table 2.2. Precision and Accuracy of Controlled-Potential Coulometric Titration of Antimony

One-Step Electrolytic Reduction

Species	Amount of Species (mg)			*N*	*S* (%)	
	Taken	Found				
		By Oxidation	By Reduction		Oxidation	Reduction
Sb^{3+}	2.59	2.57	2.59	12	0.5	0.4
	5.17	5.14	5.17	13	0.4	0.3
Sb^{5+}	4.76	4.72	4.76	15	0.2	0.2

In the second procedure, Sb^{5+} is made to undergo a two-step electrolytic reduction by increasing the concentration of HCl in the supporting medium to 6 *M* while maintaining the tartrate concentration constant at 0.4 *M*. The Sb^{5+} is reduced to Sb^{3+} at a mercury cathode controlled at −0.21 v vs the S.C.E.; total antimony is then determined by reducing the Sb^{3+} to Sb^0 at −0.35 v. The reactions are

$$Sb^{5+} + 2e \rightarrow Sb^{3+} ,$$

$$Sb^{3+} + 3e + Hg \rightarrow Sb(Hg) .$$

[5] R. W. Stromatt, *Analysis for Neptunium by Controlled Potential Coulometry*, HW-59447 (Feb. 2, 1959).

[6] R. W. Stromatt, "Determination of the Valence States of Neptunium Ions in Solution by Controlled Potential Coulometry," *Anal. Chem.* 32, 134 (1960).

The Sb^{3+} content is determined by difference. The precision and accuracy attainable with the procedure, as determined by the analysis of standard solutions of antimonic chloride and mixtures of standard solutions of antimonic chloride and antimonous chloride, are indicated in Table 2.3. The effects of possible interferences will be studied next.

Table 2.3. Precision and Accuracy of Controlled-Potential Coulometric Titration of Antimony

Two-Step Electrolytic Reduction

N	Sb^{5+} (mg)		Sb^{3+} (mg)		Total Sb (mg)	
	Taken	Found	Taken	Found	Taken	Found
6	2.38	2.38	None		2.38	2.39
6	4.76	4.75	None		4.76	4.76
4	2.38	2.39	2.07	2.08	4.45	4.47
4	4.76	4.76	2.07	2.08	6.83	6.84
5	2.38	2.39	5.17	5.18	7.55	7.57
5	None		5.17	5.19	5.17	5.19
Estimated *S*, %		0.4		0.7		0.3

This work was discussed in a paper presented at The Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology.

POLAROGRAPHY WITH BORON CARBIDE ELECTRODES

W. R. Mountcastle, Jr.[7] P. F. Thomason W. D. Shults

Exploratory studies were made of the polarographic and coulometric behavior of boron carbide, B_4C, electrodes. Well-defined polarographic waves were obtained for the reduction of Co^{2+}, Cu^{2+}, Fe^{3+}, Sb^{3+}, Sb^{5+}, and U^{6+}. Coulometric titrations of Fe^{2+} and Fe^{3+} proceeded with approximately 98% current efficiency but required long times because of insufficient electrode surface area. The working range of this electrode was found to be approximately -0.8 to $+1.0$ v.

POLAROGRAPHIC DETERMINATION OF U^{4+}

H. E. Zittel Louise B. Dunlap

A method has been reported by which U^{6+} is titrated coulometrically in the presence of molybdenum; a solution of sodium tripolyphosphate–sodium sulfate of pH 7.5 to 9 is used as supporting electrolyte.[8]

[7] Research participant from Birmingham-Southern College, Birmingham, Ala.

[8] H. E. Zittel, L. B. Dunlap, and P. F. Thomason, "Determination of Uranium in the Presence of Molybdenum by Controlled-Potential Coulometric Titration," *Anal. Chem.* 33, 1491 (1961).

A supporting electrolyte that contained the same constituents and of pH approximately 9 was used in a polarographic method developed for the direct determination of U^{4+} in the presence of U^{6+} and other ions. The relationship of diffusion current to concentration of U^{4+} is linear in the range of U^{4+} concentration from 50 to 200 μg/ml. The effects of pH and of possible interfering ions have been studied, and a procedure for the dissolution and subsequent handling of test samples to prevent air oxidation of the U^{4+} present has been delineated. The feasibility of the direct polarographic determination of both U^{4+} and U^{6+} (e.g., in U_3O_8) in the same medium will be studied. The possibility of developing a controlled-potential coulometric titration method for U^{4+} comparable with the polarographic method in which the sodium tripolyphosphate–sodium sulfate medium is used will also be studied.

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

Helen P. Raaen

The apparatus, described previously,[9,10] for the automatic simultaneous measurement of m, t, w, and drop count of a dropping-mercury electrode (D.M.E.) was built, evaluated, and used satisfactorily for obtaining constants for both a reference glass capillary and Teflon capillary tips.

The precision of the measurement of t_{total} (ref 10) (i.e., the time required for the mercury level to fall between the two fixed points of the mercury-level-detecting unit) was determined for the highest and lowest positions of the mercury-level-detecting unit. The precision was measured by means of a throttling capillary through which the mercury flowed freely and was thus independent of the formation and fall of mercury drops. A summary of the data follows ($\bar{h} = h$ at the midpoint of the mercury-level-detecting unit):

$\bar{h}$ (cm)	N	t_{total} (sec)	S (%)
115	10	780	0.22
48	11	2000	0.16

The standtube constant, k, was determined from seven measurements made at three values of $\bar{h}$ in nitrogen-deaerated 0.1 M KCl. The relative standard deviation of the measurements was 0.11%; the value of k is 3.592 g.

The performance of the apparatus was demonstrated to be satisfactory by obtaining with it capillary data and an electrocapillary curve for a Sargent S-29419 "2-to-5" sec glass capillary in 0.1 M KCl. The data and the curve are typical.

[9] H. C. Jones, H. P. Raaen, and D. J. Fisher, "Drop-Counting and Timing Devices for a Polarographic Dropping Mercury Electrode," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 9.

[10] H. P. Raaen, "Apparatus for the Automatic Simultaneous Measurement of m, t, w, and Drop Count of a Dropping Mercury Electrode," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 21–23.

The apparatus was used to evaluate the behavior of a 78-μ-diam Teflon capillary tip (see "Dropping-Mercury Electrode for Polarographic Studies in Hydrofluoric Acid Media," this report). It is being used currently to obtain similar data for other Teflon capillary tips. A paper that describes the apparatus is being prepared for publication in the open literature.

DROPPING-MERCURY ELECTRODE FOR POLAROGRAPHIC STUDIES IN HYDROFLUORIC ACID MEDIA

Helen P. Raaen

Teflon capillary tips for polarography in hydrofluoric acid media, as well as in any other media that attack glass, have been discussed previously.[11] A satisfactory method of fabricating such tips has been developed with the help of Fox[12] and Walker.[13] A set of tips of orifice diameter in the range from 15 to 110 μ were made. Photomicrographic inspection showed that the orifices are round and smooth-walled and that the faces on the tips about the orifices are flat and smooth; these are the geometric and surface properties that were sought. The maximum deviation between the specified orifice diameter and that achieved in the fabrication was 8 μ.

The performance of a Teflon capillary tip of 78-μ orifice diameter in both air- and nitrogen-saturated water and in 0.1 M KCl was evaluated by means of the apparatus described in "Apparatus for the Automatic Simultaneous Measurement of m, t, w, and Drop Count of a Dropping-Mercury Electrode," this report. For these media, plots of h versus the following values were made: t, m, w, and $m^{2/3}t^{1/6}$. For the purpose of reference, similar data were taken for a Sargent S-29419 "2-to-5" sec glass capillary. No anomalous behavior of the Teflon capillary tip was observed. Also, electrocapillary curves were taken for both the reference glass capillary and the Teflon capillary tip. The data were normalized to the same $m^{2/3}t^{1/6}$ value at zero applied potential. A region of erratic behavior was observed for the Teflon capillary tip. The erratic behavior was related to cold flow that had occurred at the upper end of the tip and to the technique for assemblying the capillary.

A paper that describes the method of fabricating the Teflon capillary tips is being prepared for publication in the open literature.

POLAROGRAPHY IN HYDROFLUORIC ACID MEDIA

Helen P. Raaen

Qualitative polarographic studies have been made of 26 reducible ions in 0.1, 1, and/or 14 M (49%) HF. The studies were a cursory check for the existence of polarographic waves in aqueous HF media in

[11] H. P. Raaen, "Dropping Mercury Electrode for Polarographic Studies in Hydrofluoric Acid Media," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 20–21.

[12] Instrumentation and Controls Division.

[13] Fabrication Shops, Research and Development Group.

the range of applied potential from 0 to −2 v vs a mercury-pool anode. The concentration of the reducible ion studied was usually millimolar. The polarograms were taken by means of a 47-μ-diam Teflon capillary tip. The results are summarized in Table 2.4. The polarograms of cadmium and of sulfite, which are of excellent form, are shown in Figs. 2.1 and 2.2, respectively. The polarographic waves that are indicated to be difficult to interpret are of the types that may have maxima, may be catalytic waves, or may coalesce with the hydrogen wave. Similar qualitative studies will be made on other reducible ions.

Table 2.4. Summary of Cursory Check for Existence of Polarographic Reduction Waves in Aqueous Hydrofluoric Acid Media

Element	Form of Element	HF Supporting Electrolyte (M)	Polarographic Wave			
			Present			Absent
			Excellent Form	Good Form	Difficult to Interpret	
Arsenic	As_2O_5	0.1				X
Beryllium	Be metal	0.1				X
Cadmium	$CdCl_2$	0.1	X			
		1	X			
Chromium	K_2CrO_4	0.1			X	
Cobalt C	$CoCl_2$	0.1			X	
Germanium	GeO_2	1			X	
Indium	In metal	0.1			X	
Iron	$FeCl_3$	0.1			X	
Lead	$Pb(C_2H_3O_2)_2$	0.1	X			
Lithium	LiCl	0.1			X	
Nickel	$Ni(NO_3)_2$	0.1		X		
Niobium	Nb_2O_5	0.1			X	
		1			X	
Osmium	"Osmic" solution	1			X	
Rhenium	$KReO_4$	0.1				X
Silicon	SiO_2	1				X
Sulfur (Sulfite)	H_2SO_3	0.1	X			
		14	X			
	Na_2SO_3	0.1	X			
Tantalum	TaO(?)	1			X	
Tellurium	Te metal	0.1			X	
Thallium	$TlNO_3$	0.1	X			
Thorium	ThO_2	0.1				X
Tin	Sn metal	1			X	
Titanium	TiO_2	1				X
Tungsten	WO_3	1			X	
Uranium	$UO_2(NO_3)_2$	0.1		X		
Zinc	Zn metal	0.1			X	
	$ZnCl_2$	0.1	X			
		1	X			
Zirconium	$ZrOCl_2$				X	

The results of the studies made to date invite more exhaustive studies, especially of quantitative polarography in aqueous HF media and of the use of polarography in the elucidation of reaction mechanisms in these media. Work in these areas is planned.

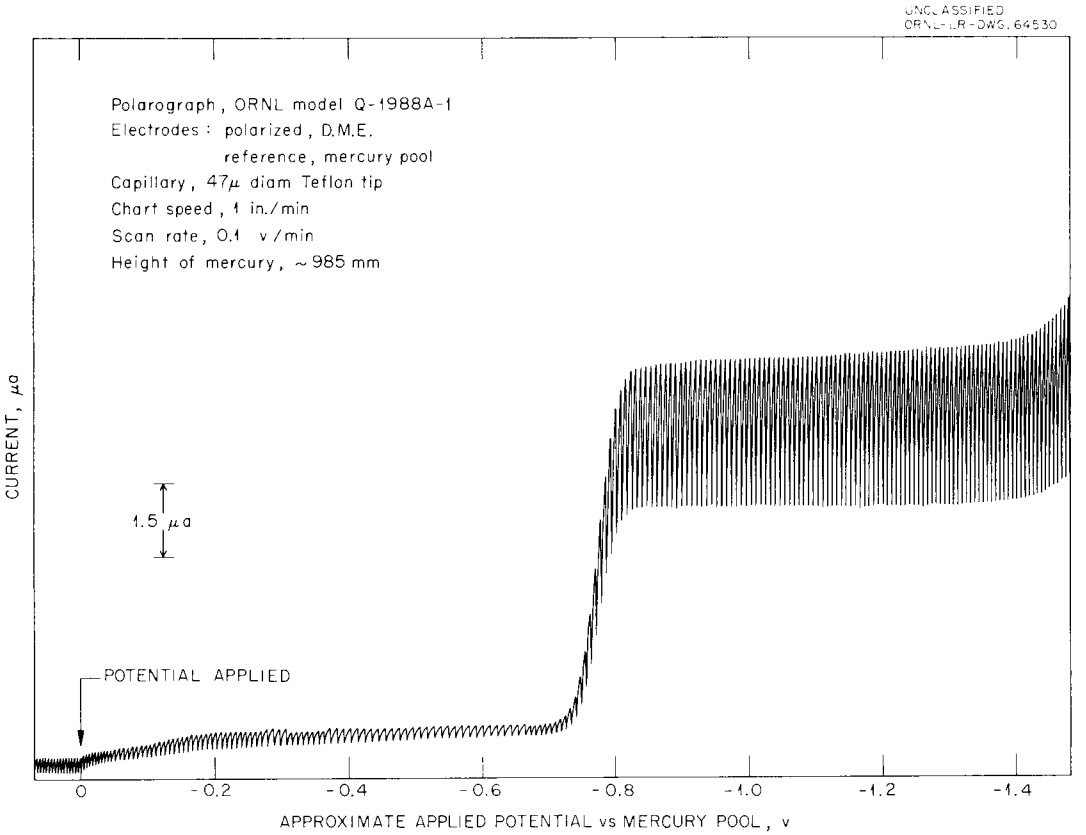

Fig. 2.1. Polarogram of 1×10^{-3} *M* $CdCl_2$ in 0.1 *M* HF.

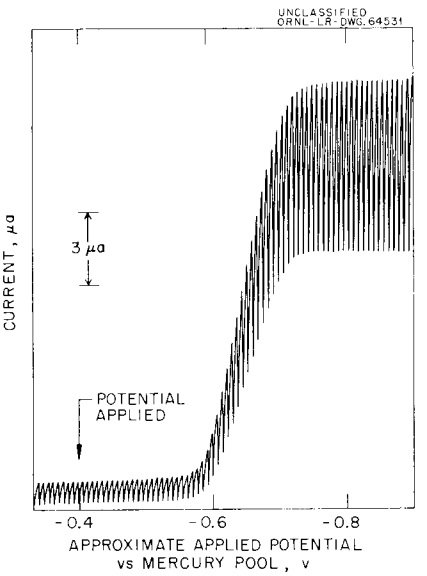

Fig. 2.2. Polarogram of $\sim 1 \times 10^{-2}$ *M* Na_2SO_3 in 0.1 *M* HF. (Conditions same as indicated for Fig. 2.1.)

3. Special Research Problems

J. C. White
P. F. Thomason

ABSORPTION SPECTROPHOTOMETRIC STUDIES OF PLUTONIUM IN SOLUTIONS OF $UO_2(NO_3)_2$, $Al(NO_3)_3$, AND HNO_3 AT ELEVATED TEMPERATURES

D. A. Costanzo R. E. Biggers

During the processing by anion exchange of Pu-Al fuel rods and of solutions that contain plutonium, the disproportionation, oxidation, hydrolysis, and polymerization of Pu^{4+} can cause considerable difficulty because the Pu^{3+}, Pu^{6+}, and polymeric Pu^{4+} that may be formed do not sorb on the anion exchange resin. Additional, and sometimes drastic, chemical treatment and processing of the plutonium solutions may therefore be required.

An absorption spectrophotometric study of these problems is being made in order to determine the rate and extent of the oxidation, disproportionation, hydrolysis, and polymerization of Pu^{4+} in solutions of $Al(NO_3)_3$ and HNO_3 at elevated temperatures. This work is being done in conjunction with the more basic program of study, described previously,[1] of the hydrolysis and polymerization of Pu^{4+} in solutions of $UO_2(NO_3)_2$ and HNO_3.

In order to apply the spectrophotometric method of analysis to solutions that contain Pu^{3+}, Pu^{4+}, Pu^{6+}, and polymeric Pu^{4+}, absorption spectral data of the required accuracy have been taken for plutonium in each of its oxidation states. The data were taken under conditions of acidity, temperature, and anion concentration that correspond to equilibrium conditions encountered in the processing and purification operations of interest. Absorption spectra for either Pu^{3+} or Pu^{6+} in 0.05 to 7.5 *M* solutions of HNO_3 do not change appreciably with changes in HNO_3 concentration; however, at higher HNO_3 concentrations, differences do occur with changes in HNO_3 concentration. The absorbancy decreases markedly with an increase in temperature (25 to 95°C). The molar absorbancy indexes for Pu^{3+}, Pu^{4+}, and Pu^{6+} have been determined as a function of temperature and NO_3^- concentration. Measurements have also been made on solutions that contained Pu^{4+} in the polymeric state only. High-speed digital-computing techniques, developed at ORNL,[2,3] will be used to resolve mathematically the absorption spectra of solutions that con-

[1] 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.

[2] R. E. Biggers, "Mathematical Resolution of Complex Overlapping Absorption Spectra by Digital Computation," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 29–31.

[3] R. E. Biggers, *Mathematical Resolution of Complex Overlapping Spectra and Spectral Fine Structure by Means of High-Speed Digital Computing*, presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, August 6–12, 1961 (to be published).

tain Pu^{3+}, Pu^{4+}, Pu^{6+}, and polymeric Pu^{4+}; to establish the valence-state distributions; and to make other types of analyses of the data.

Solutions that contain only polymeric Pu^{4+} were prepared for polymer-degradation and aging studies, and the spectra of the solutions have been obtained. Centrifugation of some of the solutions at 35,000*g* has shown an apparently small degree of fractionation of the polymer at this speed; the fractionation is indicated by changes in the absorption spectrum of the solution.

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

R. E. Biggers

The program for absorption spectrophotometric study of solutions at high temperatures and pressures has been discussed previously.[4] The design and the installation of the spectrophotometric system planned and now under construction for this program have been discussed recently.[5] The work at ORNL is being done jointly with R. G. Wymer.[6]

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 3000 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 design and detailed drawings for the entire system have been completed. The major parts of the system are: Cary model 14PM spectrophotometer redesigned to provide a 20-cm optical path length and larger optical and cell components, optical bench, chopper and beam-alternator system and compartment, phototube and source compartment, high-pressure high-temperature cell compartment, cell assemblies, heating system, high-vacuum system, main spectrophotometer cart, and control console.

The cell design, chosen from five possible designs, was proved satisfactory by the fabrication of a complete cell assembly and the extensive testing of it at 350°C and 5000 psi. The cell was designed to withstand a pressure of 10,000 psi at 350°C. It has a variable 1- to 20-cm optical path length and is of a pressurized annulus (cell-within-a-cell) type.

The system has many unique features, among them being an automatic digital data-readout system that reads out on either IBM cards or magnetic tape; a viewing port and mirror arrangement to permit visual

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[4] R. E. Biggers, "Program for Spectrophotometric Study of Solutions at Elevated Temperatures and Pressures; Subcontract between ORNL and Applied Physics Corporation for the Construction of a High-Temperature High-Pressure Spectrophotometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 27–28.

[5] R. E. Biggers and R. G. Wymer, *Design and Development of a High-Temperature High-Pressure Spectrophotometer System: Status Report*, ORNL CF-60-11-96 (Nov. 12, 1960).

[6] Chemical Technology Division.

observation of the test solution at all operating temperatures and pressures; and a variable, vertical, auxiliary slit system to permit spectral measurements on individual phases of a two-phase system. The absorption cells can be rocked while the system is operated at the maximum conditions of temperature and pressure in order to mix the solutions (or separate phases), to equilibrate the gas and liquid phases in the absorption cell, and to facilitate the removal of bubbles that form on the windows.

Detailed subcontract specifications for the fabrication, testing, and installation of the system at ORNL have been completed,[7] and construction has been started. Installation is planned for mid-1962.

Miniature Circulating-Loop System for a Cary Model 14PM Spectrophotometer

A miniature loop system, discussed previously,[8] was designed for use with an unmodified Cary model 14PM spectrophotometer and for operation at moderate pressures (200 psi) and at temperatures up to about

[7] "Specification No. CTD-4 for the 'Fabrication, Testing, and Installation of a High-Temperature, High-Pressure Recording Spectrophotometer System,'" September 27, 1961. Previous revisions: CTD-3 (Apr. 27, 1961), CTD-2 (Dec. 16, 1959), and CTD-1 (Jan. 19, 1959). Copies are retained by R. E. Biggers, R. G. Wymer, W. O. Greever, H. B. Graham, and B. E. Black (UCNC).

[8] R. E. Biggers, "Program for Spectrophotometric Study of Solutions at Elevated Temperatures and Pressures; Miniature Circulating Loop System," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 28–29.

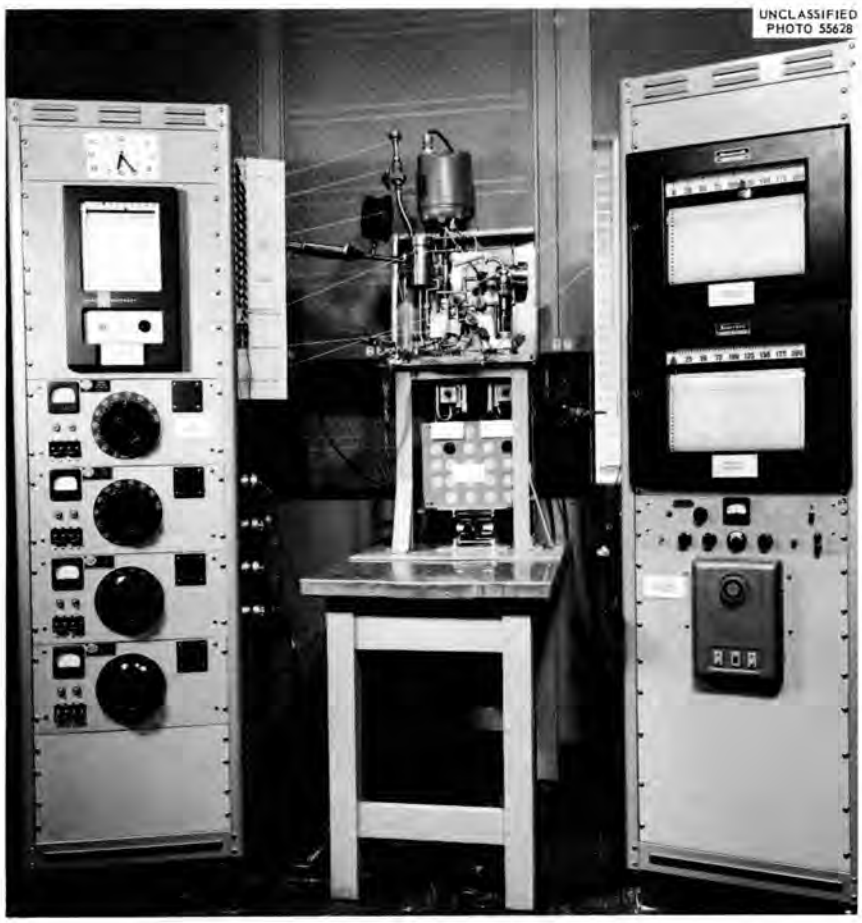

Fig. 3.1. Circulating Loop System for the Cary Model 14PM Spectrophotometer with Related Control Instrumentation. (Loop is removed from the spectrophotometer system.)

150°C (Figs. 3.1 and 3.2). The system and the related instrumentation were constructed, and experimentation with it was begun. The experience gained will facilitate the eventual extension of the high-temperature high-pressure spectrophotometric technique to loop and flowing-stream operations.

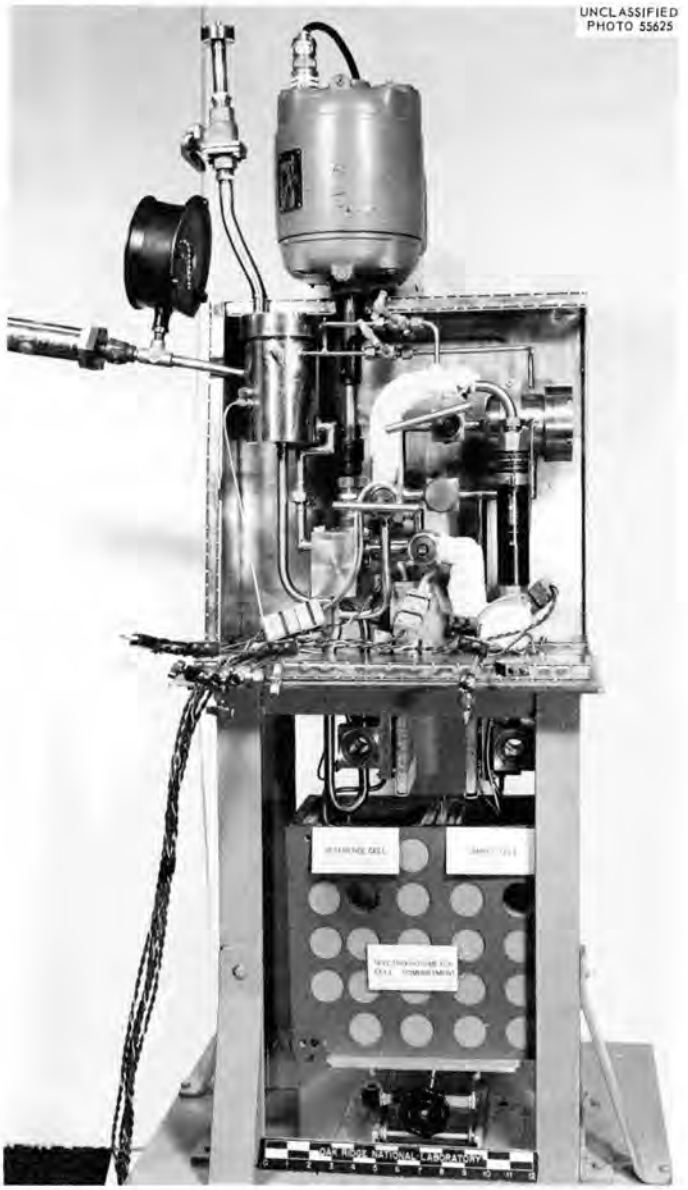

Fig. 3.2. Closeup View of the Circulating Loop System of the Cary Model 14PM Spectrophotometer, Together with Its Companion Spectrophotometer Cell Compartment.

The system has several unusual features. The volume of the loop is ~500 ml, and the liquid is circulated by a miniature Teflon-gear pump at a continuously variable rate up to about 3 liters/min. The windows of the sample and reference cells are $\frac{3}{8}$-in.-thick single-crystal sapphires and are adequate for the maximum temperatures and pressures expected. Provisions are made for using gas overpressures in

conjunction with a unique surge reservoir. The inlet system of the reservoir is designed to decrease the velocity of the liquid entering the reservoir in order to facilitate the removal of bubbles from the flowing stream. A screen system is included for further removal of bubbles. The loop contains an in-line variable-porosity filter system and a sample-container system that makes possible the exposure to the circulating liquid of corrosion test specimens or particulate matter of various particle sizes (e.g., ion exchange resins, metal oxides, and other solid materials).

Other features of the system are not unusual. The flow of liquid in the loop is measured by the pump-speed controller or with an in-line flowmeter. The pressure of the gas phase within the loop is monitored by a gage and a Baldwin-cell type of pressure transducer and recorder. The temperature of the cell is controlled and recorded by an L & N temperature controller. The loop is electrically heated and is divided so that individual sections can have different heat inputs. The valves included in the loop are adequate for different modes of bypass for various components of the loop. The loop is constructed entirely of type 347 stainless steel and is designed so that material can be added to the surge reservoir while the loop is operating.

Measurement of Liquid Densities at High Temperatures and High Pressures

As an important adjunct to the program of spectrophotometry at high temperatures and pressures, a method was devised for measuring the densities of aqueous solutions at temperatures and pressures up to the solution critical points. The liquid volume of a weighed solution of known composition is determined in an autoclave, constructed of suitable material, by obtaining an x-ray photograph 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. The feasibility of the method was established by the close agreement between experimentally determined densities of a solution of UO_2SO_4 and those reported for a very similar solution over the temperature range from 20 to 300°C. The error of the density measurement is about ±0.1%.

MATHEMATICAL RESOLUTION OF SPECTRAL FINE STRUCTURE AND OVERLAPPING ABSORPTION SPECTRA BY MEANS OF HIGH-SPEED DIGITAL COMPUTING

R. E. Biggers

Work has been continued on the mathematical resolution of spectral fine structure and overlapping absorption spectra.[2,3] The work is related to the program of spectrophotometry at high temperatures and high pressures. The necessary computer programs for the IBM 7090 machine are being written. Also, the codes for the Oracle and IBM 704 are being converted for operation on the IBM 7090 machine. The conversion includes the writing of curve-plotting programs for plotting 7090 output on the curve-plotting facility of the Oracle; the IBM 7090 does not have a curve-plotting facility. Use of the recently installed automatic, digital, data-output (on IBM cards) system (see the following section, "Automatic, Digital, Data-Output Systems for the Cary Model 14PM Spectrophotometer," this report) will greatly implement the spectrophotometry program. The related computer work is therefore expected to increase considerably.

The program will be continued as originally planned,[2,3] the emphasis being on problems basic to the chemistry of the transition metals, the lanthanides, and the actinides; aqueous solutions of these elements will be studied at normal and elevated temperatures and pressures.

AUTOMATIC, DIGITAL, DATA-OUTPUT SYSTEMS FOR THE CARY MODEL 14PM SPECTROPHOTOMETER

R. E. Biggers

An automatic, digital, all-decimal, data-output system (IBM punched-card type)[9-11] for the Cary model 14PM spectrophotometer has been constructed and installed (Figs. 3.3 and 3.4). A magnetic-tape data-output system is being considered. This work is being done in collaboration with D. Hampel[12] and B. J. Moore,[13] the primary designer and builder, respectively, of the system.

IBM Punched-Card Data-Output System

Modifications to the Cary Model 14PM Spectrophotometer. – The Cary model 14PM spectrophotometer has been modified in several ways in order to adapt it for use with the IBM punched-card data-output system. It now has a photoelectric pulse generator that will transmit pulses to the control system at 1-A intervals over its entire wavelength range of 1850 to 26,500 A. A single-pen folded-scale recorder, having a slidewire with absorbancy-unit ranges of 0 to 1 and 1 to 2, has been installed instead of the standard two-pen recorder; a 0- to 2.4-absorbancy-unit slidewire can also be used. The circuitry of the instrument has been modified to prevent output of the digital data during the time the recorder is changing between the absorbancy-unit ranges 0 to 1 and 1 to 2. When range change occurs, the wavelength scanning and the chart drive stop long enough (1.5 sec) for the pen servo system to equilibrate on the next scale. When the wavelength drive mechanism stops, the output from the photoelectric pulse generator that is attached to the wavelength drive mechanism also stops. A transmitting potentiometer has been added to the recorder system to indicate externally the absorbancy. The automatic programmer and instrument circuitry have also been modified to permit operation of the programmer in the reverse way (i.e., to scan from a short to a long wavelength limit and then to return to the short wavelength limit).

Output of Decimal Wavelength Data. – Decimal wavelength data in angstroms is obtained from the spectrophotometer by the control system in the following manner. Pulses from the photoelectric pulse generator are fed into the control system, which is constructed insofar as possible of ferrite-magnetic-core and

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[9]R. E. Biggers, "Automatic Digital, Data-Output System for the Cary Spectrophotometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 31–32.

[10]R. E. Biggers and J. M. Chilton, *Spectrophotometric Studies of Solutions at Elevated Temperatures and Pressures: Status and Program for FY-1961 and Part of FY-1962*, ORNL CF-60-7-51 (July 19, 1960).

[11]D. Hampel, *A Spectrophotometer Digital Output System*, unpublished report.

[12]Loan employee from Radio Corporation of America to the Computer Development and Engineering Group, Instrumentation and Controls Division, ORNL, May 1960–May 1961; present address: RCA Service Company, Government Services, 206-2, Cherry-Hill, Camden, N. J.

[13]Computer Development and Engineering Group, Instrumentation and Controls Division.

other solid-state components. The initial wavelength is set manually into the magnetic core counter (five-decimal-digit capacity), which is monitored by Trixie readout tubes, and can thereby be observed visually. The contents of this high-speed counter is then incremented by the 1-A pulses from the spectrophotometer. The wavelength-absorbancy data pairs can be punched out at any of the following wavelength-output intervals: 1, 2, 5, 10, 20, 50, 100, 200, 500, and 1000 A.

Output of Decimal Absorbancy Data. – The absorbancy data are obtained from the spectrophotometer by applying a standard voltage to a precision transmitting potentiometer that is attached to the slidewire system of the recorder. The standard voltage is adjusted in such a way that the numerical value of the

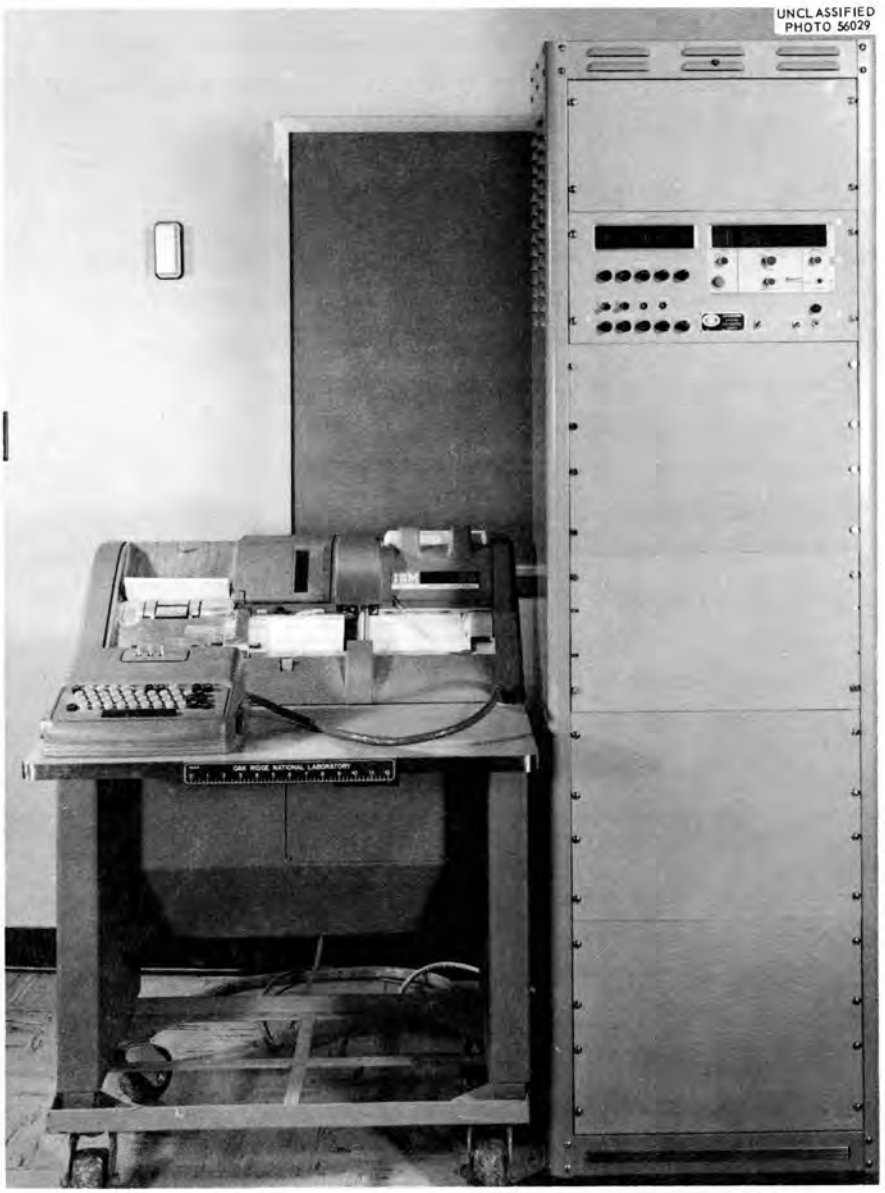

Fig. 3.3. View of the Automatic, Digital, Data-Output System for the Cary Model 14PM Spectrophotometer, Together with the IBM Type 026 Printing Card Punch Machine. (Spectrophotometer system not shown.)

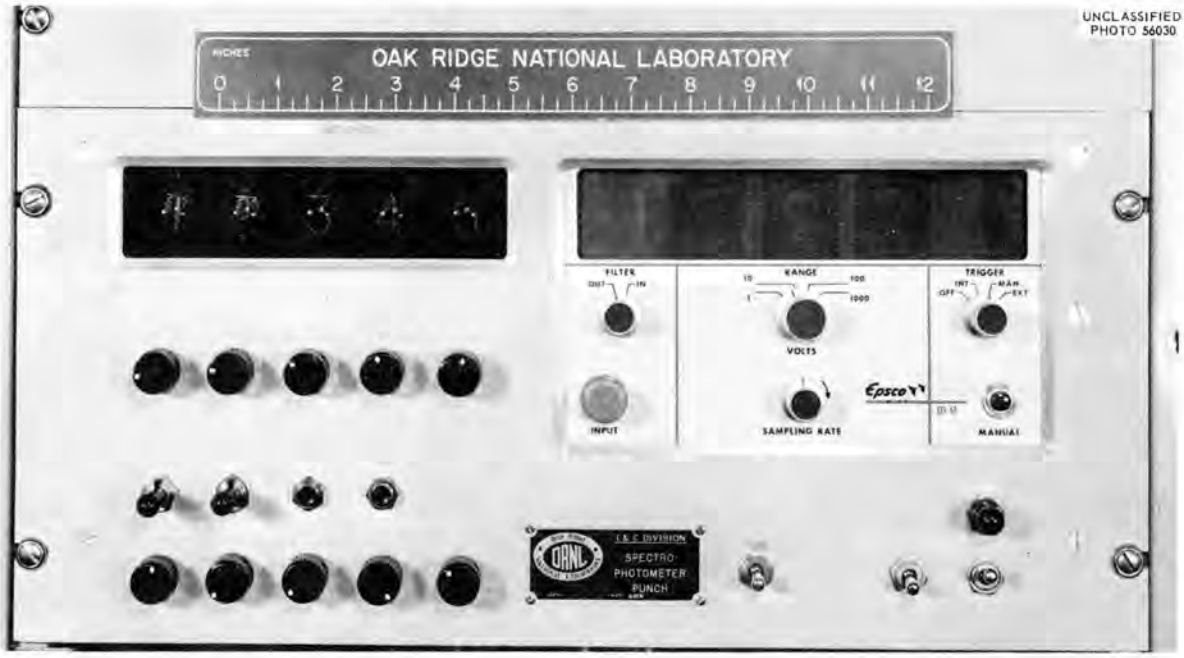

Fig. 3.4. Closeup View of the Main Control Panel of the Automatic, Digital, Data-Output System for the Cary Model 14PM Spectrophotometer.

voltage output from the potentiometer, expressed in volts, is equal to the numerical value of the absorbancy. This output voltage is then read by a high-speed, externally triggered digital voltmeter (all-solid-state circuitry). The moment of triggering is determined from the wavelength counter system and the wavelength-output interval chosen.

Output of Recorder Scale Information. – In the use of a folded-scale system, it is necessary to know at all times on which range the recorder pen is operating. This information is indicated as follows. The digital voltmeter is a three-digit meter having a fourth (ten-thousands digit) overflow digit that can be set externally. A relay is used within the spectrophotometer to indicate the range on which the pen is operating (i.e., for the 0- to 1-absorbancy-unit range, a 0 is caused to appear in the overflow digit of the digital voltmeter; for the 1- to 2-unit range, this digit is made a 1). Thus, regardless of the range, the output from the potentiometer is 0 to 0.999 v (or absorbancy). When up-scale range change occurs, the number registered on the digital voltmeter is made 1.999. Data-output suppression occurs at this instant; the pen then immediately returns to 0.000 absorbancy, and the digital voltmeter then reads 1.000. After the delay period is over, the digital voltmeter then can continue to read up-scale to the limit of 1.999 v (or absorbancy). The reverse changes occur on down-scale travel of the recorder pen system.

Sequence of Data Output on IBM Punched Cards. – The various decimal digital data are punched out on cards in the following sequence. When a pulse from the pulse generator is to cause output at a particular wavelength interval, determined by the initial wavelength and the wavelength-output interval chosen, the contents of the wavelength register are punched out on cards by an IBM type 026 printing card punch. Then the number that identifies the attenuator in use is punched out automatically (zero represents no attenuation). This number is a number in the range 0 through 9 and represents any of nine different

reference-beam conical-screen attenuators, or combinations thereof, that can be used to measure very high absorbancies. The attenuator number is dialed in on the control panel. Then the *initiation* of the punching of the wavelength causes the digital voltmeter to interrogate the position of the transmitting potentiometer. This interrogation occurs at the beginning of the punch cycle since pulses at every angstrom are continuing to be transmitted to the control system. The voltage (i.e., the absorbancy) read by the digital voltmeter from the transmitting potentiometer is then punched as four digits, the thousands digit having been set by the scale-indicator relay within the spectrophotometer. The card punch machine is programmed to then skip a space on the card and start punching the next cycle of data. A bookkeeping run number is then punched at the end of each card of a particular spectrum. This number, three digits of 0 through 9, is dialed in on the control panel. The system will punch out one wavelength-absorbancy point-pair per second and will record seven such point-pairs per card.

Relative Accuracy of Single-Range vs Folded-Scale Operation. – When the 0- to 2.4-absorbancy-unit single-range slidewire is used, the output to the digital system is attenuated by a factor of 3; therefore at 2.4 absorbancy units the output on cards is 0.800 v or absorbancy unit. In this way, use of the ten-thousands digit in the digital voltmeter is avoided since this digit can be inserted only by range change. The folded-scale operation is therefore much more accurate than the single-range; 1 mv on folded-scale operation represents 0.001 absorbancy unit, whereas the single 0- to 2.4-absorbancy-unit slidewire system requires 1.0 mv to represent 0.003 absorbancy unit.

Output of Absorbancy-Time Data for Reaction Kinetic Studies. – The system is so designed that it is possible to punch out spectrophotometric kinetic data in digital form on the IBM cards by following absorbancy changes at a fixed wavelength as a function of time. In this case, the spectrophotometer does not scan; therefore no wavelength pulses are obtained from the photoelectric pulse generator in the spectrophotometer. Pulses are required to initiate data readout. A digital time pulse at intervals of seconds is obtained from a line-frequency-controlled time-pulse generator and is transmitted to the magnetic-core counter. This counter reads in seconds from 0 to 99,999 or about 27.8 hr. Kinetic data can be obtained at intervals of 1, 2, 5, 10, 20, 50, 100, 200, 500, and 1000 sec. If experiments are to be made that require data to be taken at intervals longer than 1000 sec, the system can be changed to the minute-interval output mode. The time is punched in the same positions on the IBM cards as were used for the wavelength output in the other mode of operation.

Other Features. – The system has been so designed that many spectra can be punched out successively by the digital system when the unattended spectrophotometer is being operated by the Cary automatic programmer system. The spectrophotometer has eight wavelength scanning rates and seven chart speeds that can be coupled to yield 56 different modes of spectral display on the recorder chart. For the digital data-output system, not all these modes of output are obtainable or, for that matter, desirable. With the data-output system, there are certain maximum wavelength-scanning speeds that can be used for each of the wavelength-output intervals. Other combinations of scanning speed and output interval are prohibited by the maximum speed of the IBM card punch. Spectra recorded by the recorder pen on a strip chart can be obtained while digital output is in process.

Magnetic-Tape Data-Output System

An automatic, digital, data-output system is also planned for the high-temperature high-pressure spectrophotometer that is being constructed. Digital output from it may be "written" directly on magnetic tape in computer input format, the wavelength-absorbancy point-pair information being obtained on a frequency-controlled rather than a wavelength-pulse basis. The use of magnetic-tape output has both advantages and disadvantages compared with the use of card output, but for some important purposes the former far outweigh the latter.

CALCULATED EFFECT OF CERENKOV RADIATION ON ABSORPTION SPECTROPHOTOMETRIC MEASUREMENTS ON INTENSELY RADIOACTIVE SOLUTIONS

R. E. Biggers

Extraneous light from Cerenkov radiation is a potential source of interference in absorption spectrophotometric and other light-dependent measurements made on radioactive solutions. The extent of the interference can be evaluated if the intensity of the Cerenkov radiation is known. A method is therefore needed for calculating quantitatively the intensity of Cerenkov radiation from specified beta- or gamma-emitting (or both) sources or from mixtures of such sources over the visible and near-ultraviolet spectral regions. The problems attendant upon making absorption spectrophotometric measurements on solutions so radioactive that they emit Cerenkov radiation have been considered with regard to both static and flowing-stream operations.[14] For the analysis of such solutions, absorption spectrophotometry is frequently ideal, since it is widely applicable, gives much basic information, is quantitative and can therefore serve for analytical purposes, and is adaptable to remotely controlled operations.

The calculation of Cerenkov radiation intensity for Sr^{90} and Co^{60} in water are described in a recently issued report.[15] The Cerenkov radiation intensity is calculated from initial electron-energy distributions. To illustrate the use of the method for a pure beta-particle emitter, the intensity of the Cerenkov radiation from 1 curie of Sr^{90} in secular equilibrium with Y^{90} in water was calculated[15] from the beta-particle energy spectrum. For a pure gamma-ray emitter, the intensity of the Cerenkov radiation from 1 curie of Co^{60} in water was calculated from the Compton electron-energy spectrum. The steps necessary to obtain the Compton electron-energy spectrum from a gamma-ray emitter are indicated therein.

The memorandum listed previously[14] as "to be published" has been revised extensively and will be issued soon as an ORNL topical report.[16] Many parameters concerned with spectrophotometric measurements and the operation of the spectrophotometer are considered therein.

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[14] R. E. Biggers, "Calculated Effect of Cerenkov Radiation on Spectrophotometric Measurements," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 17.

[15] R. G. Wymer and R. E. Biggers, *Cerenkov Radiation Intensity Calculations for Sr^{90} and Co^{60} in Water*, ORNL-3180 (Sept. 5, 1961).

[16] R. E. Biggers and R. G. Wymer, *Calculation of the Effect of Cerenkov Radiation from Intensely Radioactive Solutions on Spectrophotometric Measurements*, ORNL topical report to be published.

This work was done jointly with R. G. Wymer[17] in connection with the high-temperature, high-pressure, aqueous-systems spectrophotometry program being carried out as a cooperative effort between the Analytical Chemistry Division and the Chemical Technology Division.

ABSORPTION SPECTROPHOTOMETRIC STUDIES OF MOLTEN-SALT SYSTEMS

J. P. Young

Absorption spectrophotometric studies of various molten-salt systems were continued. Molten-fluoride-salt systems have been of primary interest. The technique of confining the salt as a pendent drop in a platinum tube has been used in essentially all the work.

Equipment Modifications

Several new or modified components have been designed and fabricated for use with the high-temperature cell assembly and related apparatus. The graphite resistance heater[18] was installed in the cell assembly; it operates very satisfactorily from room temperature up to about 1300°C. Some of the insulating material in the cell assembly decomposes at this temperature and thus limits the maximum temperature. A detailed description of this heater will be published. Some of the interesting chemical phenomena that are associated with its use are discussed in the following subsection, "Spectral Studies."

The top plate and the lid of the high-temperature cell assembly have been modified slightly to increase the efficiency of the apparatus. The modifications also make the cell assembly reasonably gastight; it can be evacuated to pressures of about 20 μ at room temperature and then refilled with an inert gas. Detailed drawings of all components of the cell assembly have been prepared.

In addition, a compartmented lid for the cell assembly has been designed and fabricated so that a hygroscopic tamped[18] sample of a salt can be transferred from a dry box to the high-temperature cell assembly without exposure of the sample to the atmosphere. Use of this lid has made possible spectral studies of transition-element fluorides in molten RbF and in molten CsF.

Spectral Studies

The study of spectra of the 3*d* transition-element fluorides in pure alkali-metal fluorides is being continued.[18] The spectra of Co^{2+} (as CoF_2) in molten RbF and in molten CsF have been obtained. The spectrum of Co^{2+} shifts to longer wavelengths as the size of the alkali-metal ion of the molten salt increases. A plausible explanation of this shift is that the configuration of Co^{2+} becomes more tetrahedral as the size of the molten-salt cation increases. If this explanation is correct, a pronounced spectral shift

[17] Chemical Technology Division.

[18] J. P. Young, "Spectrophotometric Studies of Molten Salts," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 67–70.

should be observed for Ni^{2+} in the same fluoride salts. Attempts to obtain the spectrum of Ni^{2+} (as NiF_2) in these salts have been unsuccessful to date, however.

The spectrum of U^{4+} (as UF_4) has been observed in LiF-BeF_2-ThF_4 (66-30-4 mole %), to which it was added, and in nonradioactive synthetic Molten-Salt Reactor Experiment fuel, which is LiF-BeF_2-ZrF_4-ThF_4-UF_4 (70-23-5-1-1 mole %). The absorbancy maxima are given in Table 3.1 and are compared with those of U^{4+} in LiF-NaF-KF (46-12-42 mole %).[19] The absorbancy maxima of U^{4+} in these three molten-fluoride solvents are similar but not identical. The UF_4 was slowly hydrolyzed in LiF-BeF_2-ThF_4; therefore no reliable calculation of the molar absorbancy index could be made. The hydrolysis and subsequent precipitation of UO_2 may account for the apparent lack of spectral resolution in the region from 400 to 500 mμ.

The use of the graphite resistance heater in the high-temperature cell assembly has made possible spectral studies at temperatures above 1000°C. The spectra of Pr^{3+} (as PrF_3) and of Nd^{3+} (as NdF_3) in molten NaF have been observed at 1100°C. The wavelengths of the absorbancy peaks for these rare-earth-metal ions in NaF are very similar to their wavelengths of maximum absorbancy in lower-melting salts and

[19] J. P. Young and J. C. White, "Absorption Spectra of Molten Fluoride Salts. Solutions of Several Metal Ions in Molten Lithium Fluoride–Sodium Fluoride–Potassium Fluoride," *Anal. Chem.* **32**, 799 (1960).

Table 3.1. Absorbancy Maxima of U^{4+} (as UF_4) in Molten Fluoride Salts

Molten Fluoride Salts	Temperature (°C)	Absorbancy Maxima (mμ)	Estimated Molar Absorbancy Index
LiF-NaF-KF	570	1100	15
		658	
		615[a]	
		530	
		470	
		428	
LiF-BeF_2-ThF_4	525	1090	
		642	
		610[a]	
		520[a]	
		442[b]	
LiF-BeF_2-ThF_4-ZrF_4	525	1010	10
		880[a]	
		640	
		610[a]	
		516	
		469	
		452	

[a] Shoulder.
[b] Broad peak.

in aqueous solution. These results are perhaps not too surprising, but they do emphasize the strong shielding effect of the *f* electrons in these rare-earth-metal ions. However, the composition of the molten-salt solvent appears to affect the transition probability of absorption in the case of some of the rare-earth-metal ions. This study is being continued. Some of the pertinent molar absorbancy indexes are presented in Table 3.2. It should be remembered that the molar absorbancy indexes reported for molten-fluoride-salt

Table 3.2. Molar Absorbancy Indexes of Solutions of Several Rare-Earth-Metal Ions

Ion	Wavelength (mμ)[a]	Molar Absorbancy Index				
		NaF, 1100°C	LiF, 900°C	LiF-NaF-KF, 550°C	LiCl-KCl,[b] 400°C	0.1 *M* $HClO_4$, 25°C
Pr^{3+}	444	*c*	1.2	1.4	1.47	9.80
	479	*c*	1.1	1.3	1.30	3.85
Nd^{3+}	582	1.8	2.1	2.3	11.90	5.97
Sm^{3+}	399		0.63		2.65	2.98

[a] Wavelengths correspond to peaks found in molten LiF.

[b] C. V. Bonks, 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).

[c] Spectrum observed, but molar absorbancy index values could not be calculated.

systems are reliable to only ±10% because of the nature of the pendent-drop technique. The molar absorbancy index of the 582-mμ peak of Nd^{3+} in molten LiF, determined earlier[20] to be 1.7, was redetermined and found to be 2.1. The small correction is probably due to various improvements in the experimental technique. The work of Banks *et al.*[21] provides an excellent means for comparison of quantitative data obtained by the use of square-cross-section type of spectrophotometric cells with those obtained by means of the pendent-drop technique; the molar absorbancy index for Pr^{3+} in LiCl-KCl is nearly identical with that for Pr^{3+} in LiF-NaF-KF. Such agreement is not observed for Nd^{3+} and Sm^{3+}. The similarity of the Pr^{3+} data in the two molten-salt systems could be fortuitous. A comparison of the molar absorbancy indexes for Pr^{3+}, Nd^{3+}, and Sm^{3+} in the three fluoride media with those obtained in LiCl-KCl indicates that this similarity is not fortuitous and that Nd^{3+} and Sm^{3+} possibly exhibit behavior different from that of Pr^{3+}. This difference in behavior is also indicated by comparison of the data taken in LiCl-KCl with that taken in water.

An interesting effect of the use of the graphite resistance heater is the appearance of the resonant absorption lines of alkali-metal vapor when alkali-metal fluorides are melted in the high-temperature cell assembly. The two strongest lines each for sodium, potassium, and rubidium were observed. The resonant

[20] J. P. Young and J. C. White, "Absorption Spectra of Molten Fluoride Salts. Solutions of Praseodymium, Neodymium, and Samarium Fluoride in Molten Lithium Fluoride," *Anal. Chem.* 32, 1658 (1960).

[21] 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).

absorption lines for lithium were not observed even though LiF was heated to 1000°C or higher. In preliminary experiments with the molten eutectic of LiF-NaF-KF, the potassium lines began to be observable at approximately 650°C as sharp absorption peaks. The sodium peaks appeared at approximately 800°C. The appearance of these absorption peaks indicates that alkali-metal vapor is present in small concentration in the gas phase within the cell assembly. The metal (e.g., Na) is probably formed as follows:

$$4NaF + C \longrightarrow 4Na + CF_4 .$$

It has not been possible to obtain a solution of CoF_2 in the molten alkali-metal fluorides by melting the mixtures by means of the graphite heater. Futhermore, when the cooled sample was dissolved in an aqueous medium and the resulting solution was analyzed colorimetrically, no cobalt was found. Cobalt was found on the inside surface of the platinum tube that had contained the molten-fluoride salts; the cobalt was identified by means of electron diffraction.[22] There is no direct physical contact of the molten salt with the graphite heater. On the basis of these facts, it has been postulated that the alkali-metal vapor, which is known to be present in the cell assembly, migrates to the molten sample and reduces CoF_2 according to the following reactions, written for Na as an example:

$$4NaF + C \longrightarrow 4Na + CF_4 ,$$

$$2Na + CoF_2 \longrightarrow Co + 2NaF ,$$

$$Co + Pt \xrightarrow[\Delta]{} Co\text{-}Pt \text{ alloy} .$$

Work is being continued to prove or disprove this hypothesis.

DETERMINATION OF ASSOCIATION CONSTANTS OF SILVER BROMIDE SPECIES IN MOLTEN $NaNO_3$ FROM ELECTROMOTIVE FORCE MEASUREMENTS

D. L. Manning

The general method used to determine association constants from emf data is described elsewhere.[23] It is based on the calculation of activity coefficients (log γ) from measurements of the emf of a concentration-type cell. The specific cell used in this work was as follows:

$$\mathrm{Ag} \left| \begin{array}{c|c} AgNO_3 & AgNO_3 \\ & NaBr \\ NaNO_3 & NaNO_3 \end{array} \right| \mathrm{Ag}$$

[22] From T. E. Willmarth to J. P. Young, private communication (May 12, 1961).

[23] J. Braunstein, M. Blander, and R. Lindgren, "Association Constants in Molten Salt Solutions," to be published in *Journal of the American Chemical Society*.

The association constants were calculated by means of the equation

$$\Delta E = \left(\frac{2.303RT}{F}\right) \log \gamma_{AgNO_3},$$

where ΔE is the change in emf on addition of NaBr to one of the electrode compartments at fixed concentrations of $AgNO_3$ in the molten $NaNO_3$. Conditions were maintained so that the concentrations of Ag^+ and Br^- were too low to cause precipitation of AgBr. The association constants K_1, $K_{1,2}$, and K_2 (which correspond to the groupings AgBr, Ag_2Br^+, and $AgBr_2^-$, respectively) are given in Table 3.3. The temperature dependence of the association constants, within the experimental error, is in agreement with predictions based on theory.[24]

Table 3.3. Association Constants of Silver Bromide Species in Molten $NaNO_3$

Temperature (°C)	Association Constants (moles per mole of solvent)		
	AgBr (K_1)	Ag_2Br^+ ($K_{1,2}$)	$AgBr_2^-$ (K_2)
402	633	280	246
438	500	200	180
460	430	167	151
500	325	120	103

This work, which is part of a general study of thermodynamic properties of fused-salt systems, was performed in cooperation with the Reactor Chemistry Division.

CHEMICAL AND RADIOLYTIC STUDIES OF SIMULATED PUREX WASTE SOLUTION–NaCl SYSTEM

H. Kubota

The results of the continued studies of the radiolysis of the simulated Purex waste solution–NaCl system indicated that there is very little possibility of reducing the steady-state pressure of a confined system to a level low enough to allow the practical disposal of radioactive liquids directly in natural deposits of NaCl. On the other hand, when simulated Purex waste solution is adsorbed on solid particles of NaCl, a decrease in the pressure of the system results. This phase of the study is being continued, and studies are planned in which fission products, instead of external Co^{60}, will be used as a source of radiation.

Field studies of the storage of simulated Purex waste solutions in salt (NaCl) mines showed that considerable deformation of the shape of the storage cavity occurred during the course of the experiments

[24] D. G. Hill, J. Braunstein, and M. Blander, "Electromotive Force Measurements in the System $AgNO_3$-NaCl-$NaNO_3$ and Their Comparison with the Quosi-Lattice Theory," *J. Phys. Chem.* 64, 1038 (1960).

(about nine months). Laboratory studies have indicated that this deformation is caused by the alternate oversaturation and undersaturation of the solution that are associated with the vaporization and condensation, respectively, of solvent. The details of this work are reported elsewhere.[25,26]

APPLICATION OF RADIOISOTOPES IN ANALYTICAL CHEMISTRY

S. A. Reynolds

The AEC Division of Isotopes Development is supporting a program on the uses of radioisotopes in chemical analysis. Applications such as the testing of new methods, isotope-dilution techniques, and the like will be studied.

Determination of Thorium in Granite

S. A. Reynolds J. M. Peele

The chemical method for determining thorium in granite, devised by Ross,[27] gave satisfactory results on a number of samples. However, for some samples discrepancies were noted between results from the chemical method and those from gamma spectrometry.[28] By means of Th^{234} tracer, which was added to several granite samples before they were dissolved, losses of thorium were found to occur in the tri-*n*-octylphosphine oxide (TOPO) extraction step and in the stripping of thorium from TOPO. Typical data are shown in Table 3.4. When simple radiometric correction of the yield of thorium, based on spectrophotometric measurement, was made, the results were high; thus the possibility of a positive interference was indicated. The total thorium was therefore repurified by means of a procedure different from that included in the chemical method. Thorium was then redetermined spectrophotometrically. The results obtained after the repurification are also shown in Table 3.4. Subsequent investigation has shown that the losses during the stripping can be greatly reduced by diluting the TOPO solution to approximately 0.015 *M* with cyclohexane and stripping with 1 *M* H_2SO_4. Studies of the extraction step are contemplated.

In connection with the work described above, a brief study was made of the effect of thorium concentration in the extraction of thorium from solutions of various ionic strength into thenoyltrifluoroacetone (TTA)-xylene. The data of Table 3.5 indicate that the extraction is very rapid and nearly complete at reasonable thorium concentrations provided the ionic strength is not too low.

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[25] H. Kubota, R. E. Blanco, and E. G. Struxness, *Salt Cavity Alterations*, ORNL CF-61-7-3 (Aug. 1, 1961).

[26] W. J. Boegly, Jr., *et al.* (including H. Kubota), "'Cavity Alteration Studies.' Disposal in Salt Formations," *Health Physics Div. Ann. Progr. Rept. July 31, 1961*, ORNL-3189, pp 62–67.

[27] W. J. Ross, "Determination of Uranium and Thorium in Granite," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 73.

[28] S. A. Reynolds, *Determination of Thorium in Rock Samples by Gamma Spectrometry*, ORNL CF-60-6-37 (June 7, 1960).

Table 3.4. Results of Determination of Thorium Content of Granite in the Presence of Tracer Th^{234}

Sample	Loss (%)		Thorium Content (ppm)			
			Chemical Method			Gamma Spectrometry
	In Extraction	In Stripping	Uncorrected	Corrected		
				No Repurification[a]	Repurification[b]	
1	2 to 18	11 to 44	$\leq$74	93	75	76
				94	76	
				94	78	
2	4 to 28	2 to 27	24	29	24	25
				32	27	
				35	27	
3	10 to 25	1 to 13	23	35	27	30
					30	
					31	

[a] Thorium-234 content of solution used for the spectrophotometric measurement was measured, and a yield correction was applied.

[b] Total thorium in solution used for the spectrophotometric measurement was repurified and then measured, and a yield correction was applied.

Table 3.5. Extraction of Thorium into TTA-Xylene

$NaNO_3 + HNO_3$ Concentration (M)	Calculated Thorium Concentration (M)	Contact Time (min)	Thorium Extracted (%)[a]	Material Balance (%)
0.2	2.4×10^{-10}	10	89[b]	96[b]
0.2	2.9×10^{-10}	10	50[b]	76[b]
0.2	3.9×10^{-10}	10	72[b]	92[b]
0.2	1.1×10^{-9}	10	76[b]	93[b]
0.4	7.7×10^{-10}	10	65[b]	70[b]
0.4	5.9×10^{-6}	15	99.5	100
0.4	5.9×10^{-6}	15	99.6	98
0.4	5.9×10^{-6}	15	99.5	105(?)
0.54	1.7×10^{-8}	10[c]	98.5	
0.54	1.7×10^{-8}	20[c]	99.6	99
0.54	1.7×10^{-8}	6	95.8	
0.54	1.7×10^{-8}	10	99.3	100
0.54	1.7×10^{-7}	1[c]	99.5	
0.54	1.7×10^{-7}	2[c]	99.9	100
0.54	2.6×10^{-7}	2	99.5	
0.54	2.6×10^{-7}	4	99.5	100
0.54	2.6×10^{-6}	1	97.1	
0.54	2.6×10^{-6}	2	99.7	101
0.54	2.6×10^{-5}	1	99.0	
0.54	2.6×10^{-5}	2	99.8	100
2.0	9.7×10^{-10}	10	97.3	97
[1 M $Al(NO_3)_3$]	1.7×10^{-6}	10	99.9	

[a] Based on aqueous phase, except those in note *b*.

[b] Possible reagent impurity or hydrolytic behavior; percent extracted determined by direct measurement.

[c] 0.25 M TTA; all others 0.5 M.

Review Article on Isotopes in Analysis

S. A. Reynolds

A review of the field of the use of isotopes in analysis is in progress. When the review is finished, an article on applications of radioisotopes in analysis will be written.

4. Reactor Projects Analyses

J. C. White
A. S. Meyer

MOLTEN-SALT REACTOR EXPERIMENT

Vanadyl Ion as a Back-Titrant for Indirect Amperometric Titrations with Ethylenediaminetetraacetic Acid

G. Goldstein D. L. Manning H. E. Zittel

A rapid and precise method was developed for indirect amperometric titrations with ethylenediaminetetraacetic acid (EDTA) in which VO^{2+} is the back-titrant. EDTA is added in excess to the test solution; the excess is then back-titrated in an acetate-buffered solution of pH 4. The equivalence point is detected with a platinum-foil electrode at a potential of +0.6 v vs the S.C.E. At this potential the VO^{2+}-EDTA complex is not oxidized, but VO^{2+} is. The presence of an excess of titrant is therefore indicated by a linear increase in current. Cations that form EDTA chelates having a stability constant (K) of 10^{16} or greater can be determined; typical titration results are shown in Table 4.1. Some selective titrations can be performed if masking agents are used. The relative standard deviation of replicate titrations is about 1%.

Table 4.1. Results of Titrations of Various Cations

Cation	Log K	Quantity of Cation (mg)		Recovery (%)
		Taken	Found	
Fe^{3+}	25.1	1.86	1.82	98
Th^{4+}	23.2	4.98	4.91	99
Sc^{3+}	23.1	1.00	0.96	96
Hg^{2+}	21.8	4.00	4.09	102
Zr^{4+}	19.9	2.17	2.13	98
Lu^{3+}	19.8	3.37	3.32	99
Yb^{3+}	19.5	3.48	3.55	102

Table 4.1 (continued)

Cation	Log K	Quantity of Cation (mg)		Recovery (%)
		Taken	Found	
Ti^{4+}	19.4	1.04	1.09	105
Bi^{3+}		3.85	3.85	100
Er^{3+}	18.9	3.67	3.66	100
Cu^{2+}	18.8	1.48	1.43	97
VO^{2+}	18.8	0.89	0.88	99
Ho^{3+}	18.7	4.97	4.80	97
Ni^{2+}	18.6	1.47	1.43	97
Dy^{3+}	18.3	3.71	3.57	96
Y^{3+}	18.1	2.00	1.99	100
Tb^{3+}	17.9	4.00	3.89	97
Gd^{3+}	17.4	3.75	3.64	97
Eu^{3+}	17.4	4.21	3.98	95
Sm^{3+}	17.1	4.00	3.79	95
Nd^{3+}	16.6	4.00	3.85	96
Zn^{2+}	16.5	1.63	1.66	102
Cd^{2+}	16.5	2.61	2.56	98
Pr^{3+}	16.4	4.00	3.79	94
Co^{2+}	16.3	1.47	1.44	98
Al^{3+}	16.1	0.90	0.87	97
Ce^{3+}	16.0	3.50	3.41	97
La^{3+}	15.5	3.00	2.76	92

The method was used to determine Zr^{4+} and Al^{3+} in HF-HNO_3 mixtures, Zr^{4+} in fluoride salts, and Zr^{4+} plus Th^{4+} in MSRE fuel.

This work is described in a paper that will be submitted for publication in *Analytical Chemistry*.

GAS-COOLED REACTOR EXPERIMENT

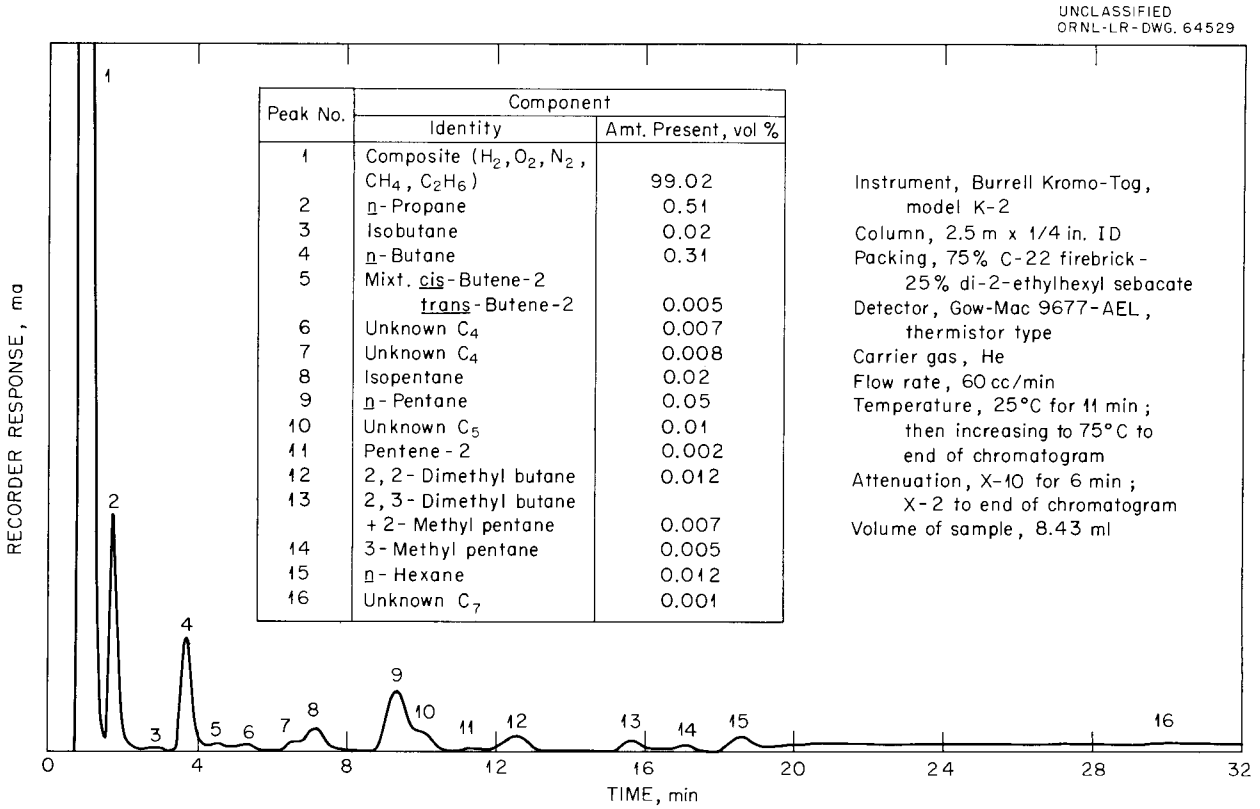
Gas Chromatographic Determination of Products of Dissolution of UC

A. D. Horton

The scope of the gas chromatographic method for the identification and determination of off-gases from the dissolution of uranium monocarbide (UC) in water[1] has been extended. Separation of the gases on a

[1]A. D. Horton, "Gas-Solid Chromatography," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 32–34.

2.5-m-long by 5-mm-ID chromatographic column packed with a mixture of 75 wt % C-22 firebrick and 25 wt % di-2-ethylhexyl sebacate has shown that they contain most of the paraffins of carbon chain lengths up to and including C_7 and some of the olefins of carbon chain lengths through C_5. Some of the components have not yet been identified. A typical chromatogram of the off-gases from the dissolution of UC in water at 80°C is shown in Fig. 4.1. The first peak on the chromatogram is the composite of peaks for H_2, O_2, N_2, CH_4, and C_2H_6. To resolve these gases, it is necessary to analyze a second test portion of the off-gases by use of a 2.5-m-long by 5-mm-ID column packed with 20- to 35-mesh Linde type 5-A molecular sieves.[1]



Peak No.	Component	
	Identity	Amt. Present, vol %
1	Composite (H_2, O_2, N_2, CH_4, C_2H_6)	99.02
2	n-Propane	0.51
3	Isobutane	0.02
4	n-Butane	0.31
5	Mixt. cis-Butene-2 trans-Butene-2	0.005
6	Unknown C_4	0.007
7	Unknown C_4	0.008
8	Isopentane	0.02
9	n-Pentane	0.05
10	Unknown C_5	0.01
11	Pentene-2	0.002
12	2,2-Dimethyl butane	0.012
13	2,3-Dimethyl butane + 2-Methyl pentane	0.007
14	3-Methyl pentane	0.005
15	n-Hexane	0.012
16	Unknown C_7	0.001

Fig. 4.1. Typical Chromatogram of the Off-Gases from the Dissolution of UC in Water at 80°C.

Phillips Petroleum Company standard gas mixtures Nos. 36, 40, and 42[2] and a special blend (i.e., 16-A) that contains *n*-hexane and all its isomers were used as calibration mixtures and also as references in the qualitative analysis of the samples.

[2] *Phillips 66 Hydrocarbons and Sulfur Chemicals*, Bulletin 518, 5th ed., p 119, Phillips Petroleum Co., Bartlesville, Okla.

HOMOGENEOUS REACTOR TEST

Sorption of Uranium on ZrO_2

G. Goldstein

The sorption of the ions of uranium and also of copper and nickel on hydrous ZrO_2 was investigated at temperatures in the range 25 to 250°C. The purpose of the work was to obtain data that are useful in interpreting the corrosion rates of zirconium and Zircaloy-2 in solutions of UO_2SO_4. The experiments were performed by equilibrating 5 ml of the test solution with 0.5 g of ZrO_2 in a titanium autoclave, which was heated by means of a rocking furnace. The sorption of uranium was affected by the characteristics of the ZrO_2, temperature of equilibration, and concentrations of uranium and free acid in the solutions of UO_2SO_4. Conclusions were drawn concerning the relationship between each of these factors and the sorption of uranium; the results have been reported.[3]

Amperometric Titration of Cu^{2+} and Certain Rare-Earth Elements

G. Goldstein D. L. Manning H. E. Zittel

An amperometric method for the titration of thorium, described previously,[4] has been adapted for the determination of Cu^{2+} and certain rare-earth elements in synthetic HRT fuel and blanket solutions. The titration with EDTA is carried out in a chloroacetate buffer solution at pH 2.5 for Cu^{2+} and 4.5 for the rare-earth elements; Fe^{2+} is used as the indicator ion. Those rare-earth elements that form EDTA chelates having stability constants of the order of 10^{17} or greater (i.e., Tb, Dy, Ho, Er, Tm, Yb, and Lu) can be titrated satisfactorily. For synthetic HRT samples that contain from 3 to 8 mg each of these elements and also for those that contain from 1 to 2 mg of Cu^{2+}, the recovery by amperometric titration is complete. Since this method can be adapted for remotely controlled operations, it is suitable for determining Cu^{2+} in radioactive samples.

Conductometric Titration of Sulfate by the Nonaqueous Barium Acetate Method

G. Goldstein D. L. Manning H. E. Zittel

A conductometric method was developed for the indirect titration of sulfate. The method is essentially the same as the potentiometric nonaqueous method already described,[5] except that the back-titration is performed conductometrically. The potentiometric method is affected adversely by small amounts of water

[3]G. Goldstein, *Sorption of Uranium on Zirconium Oxide*, ORNL-3177 (Aug. 28, 1961).

[4]G. Goldstein and D. L. Manning, "Amperometric Titration of Thorium," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 89.

[5]G. Goldstein, O. Menis, and D. L. Manning, "Indirect Determination of Sulfate by Nonaqueous Titrimetry," *Anal. Chem.* 33, 266 (1961).

present in the acetic acid medium, whereas the conductometric method is not; in fact, a small amount is advantageous. The interferences are the same for both methods. The conductometric procedure is described in detail in an unpublished memorandum.

HIGH-TEMPERATURE MATERIALS

Determination of Oxygen in Higher Alkali Metals

J. C. White A. S. Meyer G. Goldberg

A program to evaluate methods for the determination of O_2 in the higher alkali metals (K, Rb, and Cs) is in progress. A vacuum dry box has been fabricated to permit the necessary handling and sampling of alkali metals. In addition, an apparatus for the analysis of samples by the method of amalgamation[6] and an apparatus for the reaction of alkali metals with butyl bromide (C_4H_9Br) in a sealed apparatus under pressure or vacuum[7] have been built. A novel apparatus, described by Kirtchik,[8] for taking a test portion of K by extrusion from the ½-in.-OD tubing in which it was cast will also be constructed when the components are received.

It is proposed to evaluate the method for O_2 in K by comparing the results of analysis by the method of amalgamation with those obtained by the butyl bromide method. Also, modifications to the conditions of reaction with C_4H_9Br and to the titration of the unreacted K_2O in both aqueous and nonaqueous media will be studied. The flame photometric method will be tested for determining K in the K_2O that is separated from the metallic K in the amalgamation. If the results of these investigations indicate that it is desirable, an alternate halogenation procedure proposed by Kirtchik[8] in which amyl chloride is substituted for C_4H_9Br will be evaluated. Measured amounts of oxide (as K_2O) will be added to a potassium loop; the efficiency of recovery will be studied in cooperation with the Metallurgy Division.

On the basis of limited tests, it appears that these conventional analytical methods are applicable to the determination of O_2 in Rb; therefore it is planned to carry out for Rb a program similar to that proposed for the study of methods for O_2 in K. Substantial modification and perhaps some fundamental studies may be required for the application of these methods to Cs, since it is reported that Cs forms oxides of unusual stoichiometry and reacts with glassware at room temperature.[9]

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[6]L. P. Pepkowitz and W. C. Judd, "Determination of Sodium Monoxide in Sodium," *Anal. Chem.* **22**, 1283 (1950).

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

[8]H. Kirtchik and G. Riechmann, "Research on Analytical Methods for Oxygen in Liquid Alkali Metals," *Quarterly Progress Report No. 1, Dec. 15, 1960 to Mar. 31, 1961*, Applied Research Operation, Flight Propulsion Laboratory Department, General Electric Co., Cincinnati 15, Ohio.

[9]From Frederick Tepper, Mine Safety Appliance Research Corporation, Callery, Pa., to G. Goldberg, private communication (September 1961).

5. X-Ray and Spectrochemical Analyses

X-RAY AND SPECTROCHEMICAL ANALYSES (X-10)

M. T. Kelley
C. Feldman

Chemical Preparation of Samples

Dissolution of Th Alloys. – Procedures were devised for dissolving Th-Sn, Th-Ti, Th-Nb, and Th-Zr alloys for x-ray absorption and/or spectrochemical analysis. The Th-Sn alloys were dissolved in boiling concd H_3PO_4(1 vol)–concd $HClO_4$(3 vol). Any residue was then dissolved by adding one drop of 1 *M* HF to the boiling mixture. The use of H_3PO_4 prevented the volatilization of Sn. The Th-Ti alloys were dissolved in boiling concd $HClO_4$; any residue was dissolved as described above. The Th-Nb alloys were treated with 6 *M* HNO_3 that contained three drops of 1 *M* HF per 100 ml. The undissolved sludge (principally Nb^0) was isolated by centrifugation and dissolved in a minimum of 2 *M* HNO_3–5 *M* HF. If ThF_4 precipitated at this point, it was redissolved by adding excess $Al(NO_3)_3$. This solution and the supernatant liquid from the centrifugation were analyzed separately. The Th-Zr alloys dissolved completely in 6 *M* HNO_3 that contained three drops of 1 *M* HF per 100 ml.

Preparation of a Stable, 25-mg/ml Standard Solution of Sb. – High-purity, lump, metallic Sb was crushed to give particles smaller than 1 mm and was dissolved in 6 *M* HNO_3 that contained excess tartaric acid. When dissolution was complete, the solution was evaporated to dryness on a steam bath; the residue was dissolved in, and the resulting solution diluted with, 10% tartaric acid solution.

Preparation of Volatile Organic Solutions for Spark Spectrochemical Analysis. – A way was devised to prevent ignition of the solvent by the spark when volatile organic extracts are analyzed spectrographically for trace metallic constituents. The sample is treated with an equal volume of light mineral oil, the volatile constituent is vaporized on a hot plate, and the mineral-oil solution is exposed by the carbon porous-cup technique. Mixtures that contained hexane, gasoline, and benzene were analyzed successfully in this way.

Volatilization of B from Acid Solutions

Spicer and Strickland's[1] statement that little B is lost during the evaporation of acid solutions of B until they approach dryness was confirmed for HNO_3, H_2SO_4, and $HClO_4$ solutions, but was found not to

[1] G. S. Spicer and J. D. H. Strickland, "The Determination of Microgram and Submicrogram Amounts of Boron. II. The Separation of Boron by Distillation and the Evaporation of Distillates," *Anal. Chim. Acta* 18, 523 (1958).

hold true for HCl solutions. The latter had lost substantial amounts of B by the time evaporation was 90% complete.

Ultraviolet "Axicon" Optics

It was desired to increase the effective speed of the external optical system that illuminates the spectrograph in the High-Radiation-Level Analytical Facility (HRLAF). "Axicon" optics, first suggested by McLeod,[2] seemed applicable to this problem. Since ultraviolet light was to be transmitted, it was decided to use the hollow reflecting-cone modification. A hollow cone 18 in. long and having $\frac{1}{2}$- and $\frac{1}{8}$-in. openings at the ends was constructed of aluminum and was polished internally. The results of preliminary experiments indicate that this device, placed along the optic axis immediately in front of the slit, caused a threefold increase in the amount of light entering the spectrograph. Investigation of its use is continuing.

Determination of Be in Air-Borne Dust Samples and in Smears

C. Feldman W. R. Musick

A rapid technique has been developed for determining submicrogram quantities of Be on smears and on filter paper obtained from air samplers. A $\frac{1}{2}$-in.-diam circular piece is punched out of the paper and is cemented to a $\frac{1}{2}$-in.-diam graphite disk. This disk is mounted in a conventional spectrographic rotating disk-holder (axis vertical) and is excited by means of a high-voltage spark. Standards are prepared by pipetting appropriate amounts of an aqueous suspension of submicron BeO particles onto a filter paper that contains Be-free air-borne dust or onto a Be-free smear collected under field conditions. The accuracy of this calibration technique is being evaluated by comparing the result obtained for a sample disk by the above technique with the result obtained by dissolving a duplicate disk and analyzing the solution by the porous-cup technique.

X-Ray Analysis

H. W. Dunn

X-Ray Absorption-Edge Technique. – Analytical results obtained for Zr by the x-ray absorption-edge technique[3] have been found to be independent of matrix composition for elements of atomic number between 13 (Al) and 79 (Au). Optimum conditions and parameters have now been established for determining U, W, Th, and Sn in any soluble matrix, in addition to the elements already determined by this technique (Zr, Hf, Nb, Mo, and Y).

A demountable solution cell was designed in which all parts in contact with the solution are polystyrene, but structural strength and rigidity are provided by metal.

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[2] J. H. McLeod, "The Axicon: A Net Type of Optical Element," *J. Opt. Soc. Am.* 44, 592 (1954).

[3] H. W. Dunn, "X-Ray Absorption-Edge Analysis," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 83–84.

X-Ray Fluorescence. – A pinhole device was acquired to provide a collimated, white, 50-μ-diam x-ray beam for local microanalysis by x-ray fluorescence. A device was designed and built to aim the beam accurately at a specific point on a polished section.

Flame Photometry

Sensitivity of Jarrell-Ash Ebert Scanning Spectrometer (T. C. Rains, Marion Ferguson, H. E. Zittel). – A new high-resolution flame spectrophotometer (Jarrell-Ash Ebert scanning spectrometer) was received. This instrument has higher dispersion (16 A/mm) and resolving power than instruments used previously in flame photometry and gives correspondingly higher line-to-background ratios and lower limits of detection. The limits of detection of several elements attainable with the Jarrell-Ash Ebert and Beckman model DU flame spectrophotometers are shown in Table 5.1; the RCA 1P28 multiplier phototube was used with each instrument.

Table 5.1. Limits of Detection for Jarrell-Ash Ebert and Beckman Model DU Flame Spectrophotometers

Element	Wavelength (mμ)	Limit of Detection (μg/ml per 0.1 mv)	
		Jarrell-Ash Ebert	Beckman Madel DU
Ag	338.3	0.02	0.06
Ba	455.4	0.1	0.6
	553.6	0.01	0.09
Ca	422.7	0.0009	0.007
Fe	372.0	0.1	0.2
K	404.4	0.1	0.3
	766.5	0.008	0.03
Li	460.3	0.7	
	670.8	0.0003	0.0009
Mn	403.4	0.008	0.01
Ru	372.8	0.07	0.2
Sr	460.7	0.001	0.006

In an effort to increase the sensitivity of flame spectrophotometry for many elements, a sheath was built to fit the Beckman-type atomizer-burner. Additional oxygen flows in the sheath and around the flame and thus prevents nitrogen in the air from cooling the flame. The sheath is similar to that proposed by Gilbert[4] (Fig. 5.1). The enhancement resulting from use of the sheath in the analysis of

[4]P. T. Gilbert, Jr., "Chemiluminescent Flame Spectrophotometry," presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 27–Mar. 1, 1961.

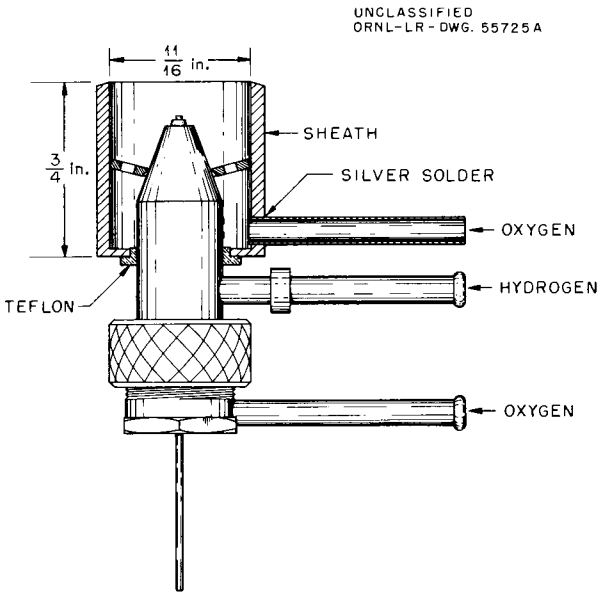

Fig. 5.1. Sheathed Atomizer-Burner.

Table 5.2. Enhancement Resulting from Use of Sheath on the Atomizer-Burner

Jarrell-Ash Ebert spectrometer
Multiplier phototube, 1P28
Voltage per dynode, 45 to 60 v
Slit width, 50 μ
Additional O_2 flow through sheath, 0.06 ft^3/min

Element	Wavelength (mμ)	Enhancement Factor	
		Aqueous Solution	50 vol % Methanol
Ag	338.3	4.5	8.0
Ba	455.4	8.7	11.8
	553.6	1.2	3.0
Ca	422.7	2.0	5.1
Fe	372.0	4.3	6.9
Mn	403.4	4.4	9.1
Sr	460.7	1.8	4.3

aqueous and organic solutions of several elements is shown in Table 5.2. Further work with the sheath will be done.

Flame Spectrophotometric Study of Ba (T. C. Rains, J. A. Dean,[5] H. E. Zittel). – The complex flame emission spectrum of Ba and the effects of experimental variables on the emission intensity of Ba were

[5]University of Tennessee, Knoxville.

studied. Both a prism type (Beckman model DU) and a high-resolution grating type (Jarrell-Ash Ebert) flame spectrophotometer were used. The flame emission characteristics of the Ba ionic doublet at 455.4 and 493.4 mμ, the atomic resonance line at 553.6 mμ, and the BaOH and BaO bands at 488 and 513 mμ were studied. A paper that describes this study has been published in *Analytical Chemistry*.[6]

Flame Spectrophotometric Determination of Micro Concentrations of Sr in the Presence of Macro Concentrations of Ca (T. C. Rains, Marion Ferguson, H. E. Zittel). – A method was developed for the determination of micro concentrations of Sr in natural water, clamshells, fish flesh, various types of bones, and other calcareous materials. A solution of the ash in HCl is diluted to contain 0.1 to 0.5 μg of Sr and 0.5 to 5 mg of Ca per milliliter. Since the intensity of the Sr line varies with Ca concentration below 0.5 mg/ml, Sr-free Ca, prepared by a method developed by Farmer[7] and reported by Mitchell,[8] is added if necessary. The Sr concentration is measured with the aid of the atomic Sr line at 460.7 mμ; the Ca concentration of the standards is maintained at 0.5 mg/ml. When SO_4^{2-} or PO_4^{3-} is present, the test solution must be made 10 vol % in glycerol and 0.1 *M* in $HClO_4$.

Effect of Anions on the Flame Emission Intensity of the Alkaline-Earth Elements (T. C. Rains, Marion Ferguson, H. E. Zittel). – The effects of various anions on the flame emission intensity of the alkaline-earth elements and the use of releasing agents to overcome the inhibition due to the anion[9] were studied further. Glycerol is the most effective of the releasing agents studied. Calcium at a concentration of 10 μg/ml in 1 *M* H_2SO_4–1 *M* H_3PO_4–10 vol % glycerol was determined without error. Glycerol is being used in the flame photometric determination of Ca in soils, plants, and aquatic organisms. It eliminates the interferences of Al and Fe in the determination of Ca, Sr, Ba, and Mg and the suppression of Li and K emission by SO_4^{2-}.

Extraction and Flame Photometric Determination of Co (T. C. Rains, Marion Ferguson). – Substitution of methyl isobutyl ketone (hexone) for chloroform as the solvent used for the extraction of Co with 1-(2-pyridylazo)-2-naphthol (PAN)[10] extends the original pH range 3 to 6 to the range 1 to 6. When the 354.2-mμ Co line (isolated by means of a Jarrell-Ash Ebert monochromator) is used, the limit of detection for Co is 0.3 μg/ml in aqueous solution and 0.01 μg/ml in hexone solution. Use of a hexone solution of PAN to extract Co can thus increase the sensitivity of the flame method for determining this element in natural waters, plants, and soils.

Determination of Ag in Be Metal (T. C. Rains, C. Feldman). – A method was developed for the spectrochemical determination of Ag in Be metal. The sample is dissolved in dilute HNO_3-H_2SO_4. An aliquot that contains 1 to 5 μg of Ag is adjusted to pH 2 and is shaken with a 0.1% solution of dithizone in

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[6] J. A. Dean *et al.*, "Flame Spectrophotometric Study of Barium," *Anal. Chem.* 33, 1722 (1961).

[7] V. C. Farmer, *Spectrographic Investigation on the Minor Element Content of Plants and Soils*, thesis, University of Aberdeen (unpublished), 1946.

[8] R. L. Mitchell, *The Spectrographic Analysis of Soils, Plants and Related Materials*, Commonwealth Bureau of Soil Science, Technical Communication No. 44, pp 129–30, Harpenden, England, 1948.

[9] T. C. Rains, "Effect of Anions on the Flame Radiant Intensity of Calcium," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 92.

[10] G. Goldstein, D. L. Manning, and O. Menis, "Spectrophotometric Determination of Cobalt with 1-(2-Pyridylazo)-2-naphthol. Separation from Interfering Ions," *Anal. Chem.* 31, 192 (1959).

chloroform. The chloroform extract is aspirated through an oxyhydrogen flame, and the intentisy of the 338.3-mμ line of Ag is measured. The limit of detection for Ag in the extract is 0.002 μg/ml when the Jarrell-Ash Ebert monochromator is used.

Determination of Tl in CsI Crystals (T. C. Rains). – A spectrochemical method for Tl in CsI crystals was developed. The crystal is dissolved, and the sample solution is made 1 *M* in HCl, treated with NaClO to oxidize Tl^0 to Tl^{3+}, and shaken with hexone. Tracer studies have shown that the extraction of Tl^{3+} is complete under these conditions. The hexone solution is burned in an oxyhydrogen aspirator-burner, and the intensity of the 377.6-mμ line of Tl is measured. Approximately 0.5 ng (nanogram) of Tl^{3+} per milliliter of hexone solution can be detected.

Tissue Analysis

S. R. Koirtyohann C. Feldman

Installation of 0.0015-in. slits has been completed on all trace-elements channels of the Quantometer. Samples of human-tissue ash are now analyzed both on this instrument and on a photographic spectrograph. Approximately one-third the analytical values obtained are below the Quantometer's limit of detection but are measurable photographically. Relevant sensitivity and precision values are given in Table 5.3. These figures were obtained by arcing a 1:1:1 mixture of ash, $K_2S_2O_7$ (or NaBr), and graphite

Table 5.3. Sensitivity and Precision of Spectrographic Determinations of Trace Elements

Element	Wavelength of Line (A)	Limit of Detection (μg per g of ash)		Relative Standard Deviation (%)[a]
		Quantometer	Photographic Spectrograph	
Ag	3382.9	1.5	0.5	6.0
Al	3082.2	14	3	1.5
Bo	4554.0	3.5		2.1
Be	3130.4		1	7.0
Bi	3067.7	9	5	4.4
Cd	2288.0	7	5	6.4
Co	3453.5	6	2	2.9
Cr	4254.3	6	1	5.3
Cu	3274.0	~2	<1	9.4
Mo	3132.6	5	2	4.0
Mn	4030.8	5	2	3.3
Nb	4058.9		20	6.3
Ni	3114.8	9	2	4.7
Pb	2833.1	26	5	6.1
Sn	2840.0	27	4	5.3
Sr	4077.7	1	0.2	4.7
Ti	3361.2	11	5	1.8
V	3102.3	7	4	3.4
Zn	3345.0	150	50	6.8
Zr	3392.0		5	4.8
			Av	4.8

[a]Element/Pd 3634.6; Quantometer; 9 exposures.

as described previously.[11] Ashing and analysis of a sample for 23 trace constituents requires approximately 2.0 hr (0.087 hr per constituent).

SPECTROCHEMICAL ANALYSES (Y-12)

C. D. Susano
J. A. Norris

Analog Computer for Direct-Reading Spectrometer

R. E. Weekley J. A. Norris

The analog computer described previously[12] has been in routine operation for several months. Exhaustive tests have been made, which demonstrate that the dynamic error band of this instrument is less than 0.5% on a long-term (8-month) basis. The computer has required only a minimum of maintenance and adjustment. Through its use, the time required for analyses has been reduced about 30%.

Additions to the computer include a system for unambiguous print-out of machine error and an automatic control to bypass unneeded sections of data print-out.

Spectrochemical Determination of Gases in Metals and Other Materials

R. E. Weekley

Better precision and greater speed have been attained in the spectrochemical determination of gases in metals and other materials through the use of an improved model of the analog computer, described previously,[13] for automatic reduction of spectral data. With the new model, stability is improved and the noise level is decreased; greater analytical precision is thus possible.

A further improvement was accomplished in the determination of O_2 through the use of Kr rather than Ar as an internal standard. On the basis of energy-level considerations, Kr appeared to be a better choice than Ar. Consequently, tests were made which showed that by use of 8% Kr in the Ar support gas and by measurement of the O_2/Kr intensity ratio, precision can be increased by a factor of 2 (see Fig. 5.2). In the figure, each point, which corresponds to the difference between the average intensity ratio of sample and of blank, represents one measurement on a single sample. The vertical line through each point indicates the maximum difference in intensity ratios assignable to each sample on the basis of the measurements of the real-time intensity ratio, which are recorded on the chart. For O_2 in steel, the minimal level of measurement is 100 ppm because of equipment limitations; above this concentration limit the relative standard deviation is 5%.

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[11] S. R. Koirtyohann and C. Feldman, "Tissue Analysis," *Proceedings, Fourth Conference, Analytical Chemistry in Nuclear Reactor Technology*, TID-7606, p 51 (January 1961).

[12] 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 85–86.

[13] R. E. Weekley, "Improvements in Equipment for the Spectrometric Determination of Oxygen in Metals," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 66.

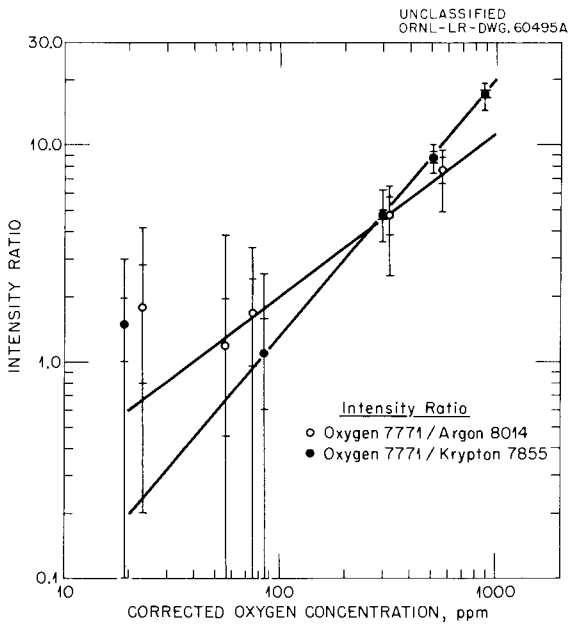

Fig. 5.2. Analytical Curves for the Spectrographic Determination of O_2 in Steels.

The application of this method to the determination of O_2 in various powdered inorganic salts is being studied, and initial results indicate that the application is feasible. Since a capsule-type sample electrode[14] is required, thus limiting the sample size, the residual O_2 blank poses a greater problem than is encountered in the analysis of steel.

Spark Solution Analysis

J. A. Norris

Use of the Paschen spectrometer has been extended to include the quantitative analysis of special calutron deposits, electrodeposited alloys, and alloying metals. The elements listed in Table 5.4 are determined.

Analysis of Clamshells

J. A. Norris

An emission spectrographic method was developed for the determination of Ba, Mn, Na, and Sr in clamshells ($CaCO_3$); a 4-amp arc and a 1-mg test portion of the sample are used. The ranges covered are: Ba, 10 to 300 ppm; Mn, 100 to 1000 ppm; Na, 200 to 4000 ppm; and Sr, 90 to 500 ppm. The Paschen spectrometer, equipped with a direct reader-computer readout, was used because a large number of samples were to be analyzed and because additional samples of the same type are anticipated in connection with ecological studies on natural systems that may contain Sr^{90}.

[14] E. J. Beck and F. E. Clark, "The Determination of Oxygen by an Inert-Gas Fusion Method," presented at the Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961.

Table 5.4. Elements Determined by Direct-Reading Spectrometry

Element Determined		Internal Standard		Concentration Range (μg/ml)
Element	Wavelength of Line (A)	Element	Wavelength of Line (A)	
Mn	2576	Fe	2599	1 to 100
Mg	2795	Fe	2599	0.2 to 20
Sr	4077	La	4333	1 to 100
Ba	4554	La	4333	0.1 to 10
Cd	3610	Be	2650	50 to 800
Ag	3280	V	3185	10 to 500
Mg	2795	Mn	2576	2 to 100
Sr	4077	Y	3710	2 to 200
Ca	3933	Y	3710	5 to 200
Ba	4554	Y	3710	2 to 100
Fe	3021	Pt	2997	20 to 1000
V	3185	Pt	2997	50 to 1000
Cu	3247	Mn	2794	5 to 200
Sn	3174	Mn	2794	20 to 400
Al	3082	V	3185	1 to 200

6. Mass Spectrometry

A. E. Cameron
J. R. Sites

It was found that the use of boron oxide, B_2O_3, together with $Pb(NO_3)_2$ on the sample filament gives thermal ions of Pb. Also, when B_2O_3 is used with WO_3, a more stable ion beam is realized.

A study was made of the effects of admitting a very small controlled amount of C_6H_6 into the source of a mass spectrometer while the U^+, UO^+, and UO_2^+ ions were watched. If there is no significant source of O_2 near the ionization chamber, a very clean beam of U^+ ions is obtained in the presence of the C_6H_6.

Aid was given in the checking of calculations for the revised values of the atomic weights of the elements.

Uranium standards were analyzed in special runs in which a high-intensity ion beam was used. The analyses were made in order to determine the U^{234} and U^{236} content (from 10 to 200 ppm) of the standard. The results agreed within a few percent with the values reported by the Referee Analysis Laboratory.

7. Optical and Electron Microscopy

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

ELECTRON MICROSCOPY OF RADIOACTIVE MATERIALS

The establishment in the high-radiation-level facility, now under construction, of a laboratory devoted exclusively to the study of radioactive material by electron microscopy has been proposed. The use of the electron microscope for this purpose requires new or modified preparation techniques. To this end, a procedure has been developed for the observation of radioactive particulate material in the electron microscope. By the isolation of a minimal portion of sample for observation and the encapsulation of the portion in a film of plastic, exposure of personnel to radiation and contamination of the electron microscope with radioactive particles are avoided. The procedure is as follows. By means of the "hot cell" facilities, a test portion is removed from the sample and is suspended in dichloroethane. A few drops of the suspension are dispersed ultrasonically in a 0.5% solution of Formvar in dichloroethane. A drop of the dispersion is flooded over a microscope slide and dried. The resulting film is crosshatched into $^1/_8$-in. squares, which are floated off onto water and collected on copper electromesh grids for subsequent electron microscopy. The method has been evaluated with both nonradioactive and radioactive samples. A typical electron micrograph of a ThO_2 sample from an in-pile loop is shown in Fig. 7.1.

Relative to this same purpose, a study is being made in cooperation with the Metallurgy Division to perfect techniques for replicating the surfaces of radioactive opaque materials.

Fig. 7.1. Electron Micrograph of Particles of ThO_2 Taken from an In-Pile-Loop Sample. 8000X.

Improved Filament for Electron Microscopy and Diffraction

Several Philips standard electron-microscope filaments were modified by welding a short tungsten wire of the same gage as the original filament to the hairpin tip of the filament. This wire was then reduced to a length of 0.5 to 0.8 mm and was sharpened to a point by electrolysis in a 20% solution of NaOH, the wire being the anode, and graphite the cathode. The method of Fernandez-Moran, discussed

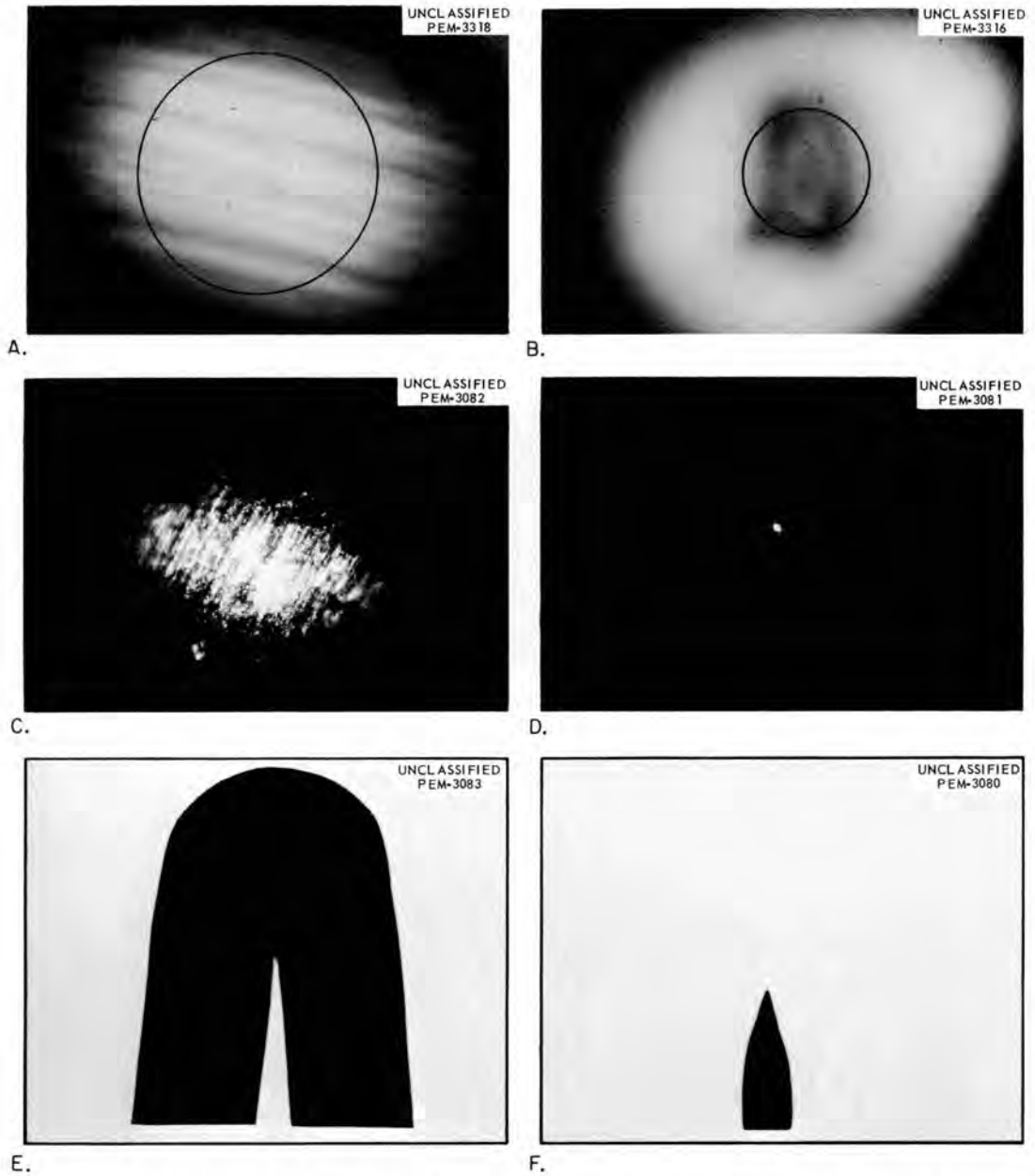

Fig. 7.2. Pictorial Comparison of Emission and Physical Characteristics of Unmodified and Modified Philips Filaments. (*a*) Emission area (circled) of an unmodified Philips filament. 1500X. (*b*) Emission area (circled) of a modified Philips filament. 1500X. (*c*) Photomicrograph of the tip of an unmodified Philips filament. 300X. (*d*) Photomicrograph of the tip of a modified Philips filament. 300X. (*e*) Profile of the end section of an unmodified Philips filament. 100X. (*f*) Profile of the pointed tip of a modified Philips filament. 100X.

previously,[1] was used. The modified filaments were tested in the Philips EM-100-B electron microscope. The large-bore pole piece was used; it usually gives a resolution of about 30 A. As a result of the modification to the filament, resolution was improved by a factor of about 2. It appears that the contribution to resolution made by the filament is largely a function of the cross-sectional area of the electron-emitting surface of the filament; that is, the more closely this area approaches a point, the better is the resolution. A pictorial comparison of some of the emission and physical characteristics of the two electron sources is given in Fig. 7.2. An electron micrograph of a ThO_2 sample taken with a modified filament is shown in Fig 7.3; the resolution achieved in this case is 15 to 20 A. Tips of much smaller cross-sectional area will be studied.

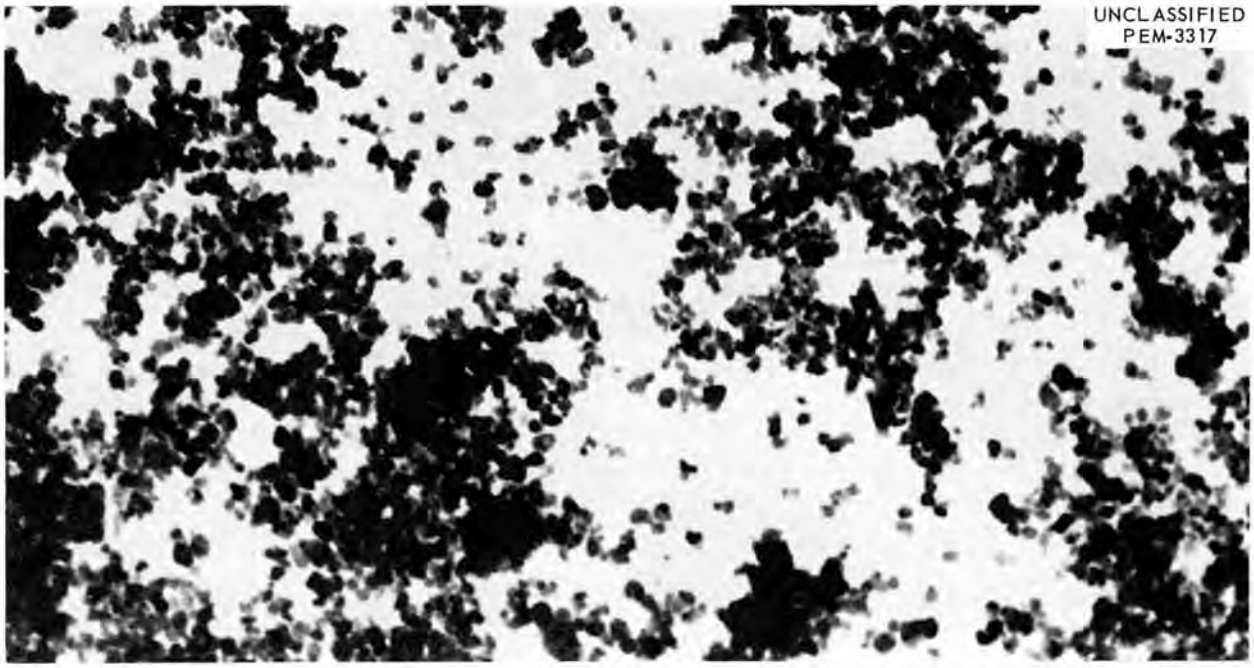

Fig. 7.3. Electron Micrograph of ThO_2 Crystallites Showing a Resolution of 15 to 20 A. 103,800X.

Replication of Particles of 0.1- to 1.0-μ Size

In the study by surface replication of particles of 0.1- to 1.0-μ size, the greatest difficulty is holding the particles in place while a negative replica is made of the exposed top surface. The embedding medium must hold the particles but must not flow over their edges. A procedure has been developed for anchoring such particles by use of cellulose acetate or styrene. At 150°C either material softens sufficiently that particles placed on its surface can be embedded to a suitable depth by covering the particles with a microscope slide and gently applying uniform pressure. The medium is then cooled, and the negative replicas of the particles are made with polyvinyl alcohol.

[1] T. E. Willmarth, H. W. Wright, and T. G. Harmon, "Optical and Electron Microscopy," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 53–57.

Instrumentation

An LKB ultramicrotome, which produces sections of 200-A thickness, has been acquired for use in the electron microscopic study of the ultrastructure of exchange resins, bulk oxide coatings, and animal bone. The studies of bone are being made in conjunction with the University of Tennessee–AEC Agricultural Research program.

A modified anode for the electron diffractograph that will improve pattern resolution has been designed and will be fabricated. This anode, together with the improved filament (see "Improved Filament for Electron Microscopy and Diffraction," this report), should provide maximum resolution from the diffractograph. Also, a comparator for measuring electron diffraction patterns that is much more accurate than the one now in use has been purchased.

Research Assistance

Assistance was given to research groups, particularly those in the Physics and Chemistry Divisions, by the application of optical electron microscopy, electron diffraction, and other similar techniques in the study of materials of interest in nuclear technology. Solid-state radiation detectors and cyclotron targets made of thin films of evaporated metals were studied and fabricated. Surface and other physical characteristics were determined for many materials, for example, pure metals, alloys, ceramics, and thin films of various compositions.

8. Radiochemical Analyses

J. C. White
W. S. Lyon

RADIOCHEMICAL STUDIES

Development of Analytical Radiochemical Methods for the Transuranium Program

F. L. Moore

Work was begun on the development of analytical radiochemical methods for application in the Transuranium (TRU) Program at ORNL. The tentative methods that have been developed and tested are: "gross alpha, direct method"; "gross alpha, LaF_3 method"; "gross alpha, amine extraction method"; "plutonium alpha, LaF_3 method"; "plutonium alpha, TTA method"; "transplutonium alpha, LaF_3 method"; "transplutonium alpha, amine extraction method"; and "alpha spectrometry, silicon diode detector." The methods have been distributed within ORNL for further evaluation.

O,O'-Dialkylphosphorodithioic Acids as Extractants for Metals

T. H. Handley J. A. Dean[1]

A survey has been made of reported liquid-liquid extractions with the *O,O'*-dialkylphosphorodithioic acids, in particular, with *O,O'*-di-*n*-butylphosphorodithioic acid, $(n\text{-}C_4H_9O)_2PS(SH)$. Extraction coefficients for many metals were determined as a function of the concentrations of $(n\text{-}C_4H_9O)_2PS(SH)$ and of either HCl or H_2SO_4 (0.05 to 9 *N*). The influence of various organic solvents was evaluated. Other *O,O'*-dialkylphosphorodithioic acids were studied in order to ascertain the effects of substituents in the ester group on the properties of this class of reagents. The relative stabilities of many of the metal complexes were determined, and in some cases the individual formation constants were calculated.

Phosphorodithioic acids resemble diethyldithiocarbamate in their applicability. However, unlike the latter reagent, they do not decompose rapidly in acid solutions of concentration even as high as 10 *M*, and they extract many metals from very acid solutions.

Results of this investigation will be submitted for publication in the open literature.

Cyclotron Research

T. H. Handley

Studies of Neutron-Deficient Radionuclides. – In cooperation with members of the Electronuclear Research Division, the study of neutron-deficient radionuclides is being continued. A report of this work has been published.[2] Future results will be submitted for publication in the open literature.

Chemistry of Pressurized-Water In-Pile Loop of the Oak Ridge Research Reactor

T. H. Handley

A study is being made of the identity, nature, and methods of controlling the water-borne material (both soluble and insoluble) in the pressurized-water in-pile loop of the Oak Ridge Research Reactor (ORR). The material was found to be the products of the corrosion of stainless steel. Fission products were not detected in either the material or the water. The results of the radiochemical analysis of the water indicated wide variation in both the amount and type of radiochemicals present; this variation probably is caused by variation in operating conditions. The results of this investigation are discussed in the progress reports of the Reactor Chemistry Division; the work was done jointly with C. F. Baes, Jr., of that division.

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[1] University of Tennessee, Knoxville.

[2] B. Harmatz, T. H. Handley, and J. W. Mihelich, "Nuclear Levels in a Number of Even-Even Rare Earths ($150 \leq A \leq 184$)," *Phys. Rev.* 123, 1758 (1961).

MEASUREMENT OF RADIOACTIVITY

Assistance to the Radioisotope Production Program

The program of consultation and mutual assistance between the Radiochemical Analyses Group and the Isotopes Division was continued. A brief description follows of two typical problems in which assistance was given.

Chemical Species of P^{32} in Phosphorus Radioisotope Products (T. H. Handley). – Customer complaints to the Isotopes Division indicated that not all the P^{32} in phosphorus radioisotope products was present as orthophosphate, the desired form. By use of an ion exchange technique,[3] it was found that 7 to 17% of the P^{32} in the products was in the form of pyrophosphate. Conversion of the pyrophosphate to orthophosphate by heating the product solution in an oxidizing acid medium was recommended. Subsequent analysis indicated that, as a result of this recommended process, essentially 100% of the P^{32} was present as orthophosphate.

Study of Radionuclides Present in Tellurium Radioisotope Products (W. S. Lyon). – Samples of two tellurium radioisotope products, one enriched in Te^{122} in order to produce Te^{123m} and the other in Te^{126} to produce Te^{127m}, were irradiated in the ORR and were dissolved. Portions of each solution were analyzed for the radioactive constituents. A third product, Te^{125m}, was produced by a long irradiation of tin, the reactions being

$$Sn^{124}(n,\gamma)Sn^{125} \xrightarrow[10\ d]{} Sb^{125} \xrightarrow[2.7\ y]{} Te^{125m}.$$

After a cooling period of several months, Te was separated from the Sn-Sb mixture, and a portion was studied. Decay and gamma-ray spectrometric measurements were made over a period of nine months. Despite the use of enriched isotopes, the Te^{123m} and Te^{127m} product solutions contained several radionuclides. Because of the similarity in radiation characteristics of tellurium radioisotopes, the positive identification of the individual tellurium radioisotopes in a mixture of them is often difficult. The results of the decay and gamma-ray spectrometric measurements are given in Table 8.1.

[3] C. E. Higgins and W. H. Baldwin, "Dehydration of Ortho-phosphoric Acid," *Anal. Chem.* 27, 1780 (1955).

Table 8.1. Activities Identified in Tellurium Radioisotope Products

Product	Activity Identified	Measured Half-Life (d)	Relative Amount at End of Irradiation
Te^{123m}	Te^{123m}	118	
	Te^{127m} K x rays	95	
Te^{125m}	Te^{123m} (159-kev gamma)	120	4.5×10^{-4}
	Te^{125m} (100-kev gamma)	61	2.3×10^{-3}
	Te^{125m} K x rays	58	1.0
Te^{127m}	Te^{127m} K x rays	95	1.0
	I^{131}	8	0.1

The disintegration rate of Te^{123m} was obtained by measuring the 159-kev gamma ray and using a transition probability of 0.85 gamma ray per disintegration. The shorter half-life for the *K* x-ray peak is attributed to the presence of Te^{127m} (95 d) and/or Te^{125m} (58 d).

In the Te^{127m}, I^{131} was produced by decay of Te^{131}. After the I^{131} was removed, only 95-d Te^{127m} *K* x rays and the low-intensity 0.41-Mev gamma ray from 9-h Te^{127}, which is the daughter of 95-d Te^{127m}, were observed.

The agreement between the values for the half-life of Te^{123m} given in Table 8.1 is interesting, since the previously accepted value has been 110 d. The presence of Te^{123m} was somewhat surprising; it is surmised that Te^{123m} was produced indirectly from antimony impurity in the tin target according to the reaction sequence

$$Sb^{121}(n,\gamma)Sb^{122} \xrightarrow[2.8\ d]{} Te^{122}(n,\gamma)Te^{123m}.$$

Preparation of Large Liquid Scintillators (W. S. Lyon). – The program[4] of preparing and testing liquid scintillators for detection of gamma rays arising from neutron capture has continued. Difficulty has been experienced in obtaining a satisfactory preparation of gadolinium 2-ethylhexanoate; this difficulty has resulted in delay in the filling and use of the 300-gal liquid-scintillator tank. This work is being done jointly with G. DeSaussure, J. D. Kington, and L. W. Weston of the Neutron Physics Division.

Liquid Scintillators by Use of Glass Loading (W. S. Lyon). – Exploratory work at Harwell[5] indicates that α-methyl naphthalene may be useful as a liquid scintillator. Since the refractive indexes of several optical lead glasses overlap the refractive index of α-methyl naphthalene, a mixture of pulverized glass and organic scintillator together in the same container gives a potentially useful scintillator system having a higher density and hence a greater efficiency than a liquid system alone.

Samples of α-methyl naphthalene have been procured from several producers, and a program of purification, preparation of liquid-scintillator systems, and testing was begun. In addition, the effects of α-methyl naphthalene on materials required for the construction of a container for the scintillator are being studied. When satisfactory α-methyl naphthalene has been secured, samples of different lead glasses (pulverized to predetermined size) will be mixed with it, and attempts will be made to develop a satisfactory scintillator system. This study is being made with R. L. Macklin of the Physics Division.

Applications of Gamma Spectrometry (J. S. Eldridge, T. H. Handley, W. S. Lyon). – The use of gamma spectrometry for nondestructive assays has continued.[6] Some of the more novel aspects of this technique were used in the serial examination of tubes and pipes in which gamma activity had been deposited. For example, various regions of a loop through which heated water passed after having contacted pellets of ThO_2 were examined. Areas of deposition of Ra^{228} were distinguished and indicated that Ra^{228} was leached from the ThO_2 in the loop.

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[4] W. S. Lyon *et al.*, "Preparation of Large Liquid Scintillators," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 61.

[5] R. L. Macklin, *Naphthalene Derivative Scintillators and Glass Loading Possibilities*, AERE-R-3744 (June 1961).

[6] J. S. Eldridge *et al.*, "Applications of Gamma Spectrometry," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 61–63.

Gamma spectrometry was also used to study the release of fission products from fuels being considered for advanced reactors. In each case the fission products released from the fuel at high temperature were allowed to pass through a tube. A tube that contained deposited fission products released from UO_2 fuel was cut into 1-in. segments, and each segment was analyzed separately. Fission products were identified as Ba^{140}-La^{140}, Te^{132}-I^{132}, I^{131}, and Xe^{133}; in some segments Ru^{103} was also identified. In another determination of released fission products, a stainless steel pipe that had been exposed to a neutron flux and that contained fission products was examined with a collimated spectrometer system. By sliding the pipe over a collimator, it was possible to identify and measure the deposited fission products, as well as the products of the neutron activation of the stainless steel.

Gamma-ray spectrometry continues to be used in the analysis of fission-product-gas mixtures,[7] as well as of radioactively pure gases (e.g., Kr^{85}). Gas samples collected on charcoal or filters or in sealed containers have been studied.

A High-Level Gamma-Ray Spectrometer System (J. S. Eldridge). – A collimating system and gamma detector were assembled in a hot cell for use in high-level gamma-ray spectrometry. The collimator was built into a 6-in.-diam opening from which a zinc bromide window had been removed. With this arrangement, radionuclides present in various parts of an in-pile loop and subassemblies were identified on the basis of characteristic gamma spectra and, in some cases, of half-life values.

The spectrometer system consisted of a 256-channel transistorized analyzer and a 3×3 in. thallium-activated sodium iodide detector. The detector used in most of the preliminary determinations had a resolution of 7.5% for 0.663-Mev gamma rays of Cs^{137}. A camera attachment for the oscilloscopic display was devised, which greatly facilitated the collection and analysis of the data.

The collimating system consisted of a brass sleeve inserted into a 6-in.-diam opening in a 36-in.-thick concrete cell wall. The forward 15 in. of the sleeve was filled with No. 5 lead shot. A 1-in.-diam opening through the center of the plug of lead shot served as the collimator. On occasions when a higher degree of collimation was desired, auxiliary 1-in. lead sleeves having openings of various sizes were inserted into the collimator. To complete the collimation, a lead sleeve with a 1-in. wall thickness, 10-in. diameter, and 15-in. length was suspended within the cell. The in-pile loop was suspended from a crane and was passed through the opening in the lead sleeve. A 2×3 in. window was cut in the sleeve and was aligned with the collimator opening.

The collimator tube and sleeve window were aligned by means of a light beam that passed through the collimator and impinged on the window in the sleeve. With the collimating system fixed, the in-pile loops or subassemblies could be moved in a vertical direction by means of a mechanical hoist connected to the top of the loop or subassembly. Portions of the specimen outlined by the window in the sleeve were examined for characteristic gamma spectra.

An auxiliary system for the identification of gamma activity in small specimens was devised by using a pulley system lowered into the cell. A nylon rope that passed through the pulley and back up to the top of the cell permitted small specimens to be placed in cups attached to the rope and to be lowered into

[7] T. H. Handley *et al.*, "Gamma Scintillation Spectrometry," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 46–47.

position in front of the collimator. In this cell, source-to-detector distances could be varied from 30 in. to 6 ft. This auxiliary system has been used to examine corrosion coupons from the Homogeneous Reactor Test and to determine isotopic ratios in samples of activated europium control rods.

This work was done jointly with R. E. McDonald, J. R. Parrott, and B. W. McCollum of the Metallurgy Division.

Silicon Surface-Barrier Alpha-Particle Spectrometry (J. S. Eldridge, F. L. Moore). – A silicon surface-barrier alpha-particle spectrometer of the type described by Blankenship and Borkowski[8] was assembled and is being evaluated. It consists of a 2-cm-diam silicon surface-barrier detector, ORNL model Q-2069C-1RO linear amplifier for alpha analysis, charge-type preamplifier, and 256-channel analyzer. Compared with the conventional Frisch grid-chamber spectrometer, this spectrometer has the advantages of better resolution, higher tolerance for beta and gamma emitters, and higher counting rates. Its major disadvantage is its lower efficiency.

The instrument was used to determine directly Po^{210} on masking tape on which the alpha activity from a contaminated surface had been picked up. In this case it was possible to determine the alpha spectrum of the sample directly without ashing or leaching. In addition, the Ra^{226} in a mixture of natural radioactivities was determined. Five major alpha groups were present in the mixture. The energy spectra of many alpha emitters have been determined.

It is anticipated that the silicon surface-barrier spectrometer, in conjunction with the amine extraction technique when necessary, will be used for most of the alpha activity analyses required in the TRU program.

Natural Radionuclides. – *Uranium Ore Program* (C. L. Burros, S. A. Reynolds). – The Health Physics Division program[9] on the uptake of radioactive constituents from uranium ore deposited in the lungs of experimental animals has resulted in the submission of a few samples of wet-ashed tissues. Total uranium was determined spectrophotometrically, Ra^{226} by a U.S. Public Health Service method,[10] and Th^{230} (ionium) by a modification of two methods.[11,12] Results are shown in Table 8.2. The quality of the results can be appraised quickly by noting the near equality of the disintegration rates of Ra^{226}, Th^{230}, and U^{238}; at that stage of the studies the nuclides should have been in secular equilibrium.

Studies of Lake Silt (S. A. Reynolds, C. L. Burros). – Three samples of silt obtained from lakes in East Tennessee were examined by gamma spectrometry, the data being recorded overnight. The spectrum of one of these, together with the spectrum of a granite sample for comparison, is shown in Fig. 8.1; the element concentrations deduced from the spectra are given in Table 8.3.

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[8] J. L. Blankenship and C. J. Borkowski, "Silicon Surface-Barrier Nuclear Particle Spectrometer," *IRE, Trans. on Nuclear Sci.* NS-7(2–3), 190 (1960).

[9] S. A. Reynolds, "Uranium Ore Program," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 64.

[10] P. F. Hallbach, ed., *Radionuclide Analysis of Environmental Samples. A Laboratory Manual of Methodology, Procedure RC-88A*, "Radium-226," Taft Sanitary Engineering Centers Technical Report R59-6 (Nov. 16, 1959).

[11] F. L. Moore, "Radiochemical Determination of Ionium in Uranium Fluorination Ash," *Anal. Chem.* 30, 1020 (1958).

[12] M. H. Feldman and A. S. Goldin, *National Lead Co. Inc., Winchester Laboratory Quart. Rept. July 31, 1960–Sept. 30, 1960*, WIN-119 (Dec. 29, 1960).

Table 8.2. Results of Analysis of Animal Tissues

Sample	Total Uranium (mg)	U^{238} (dis/min)	Ra^{226} (dis/min)	Th^{230} (dis/min)
		$\times 10^3$	$\times 10^3$	$\times 10^3$
1	5.0	3.7[a]	5.7	5.1
2	4.7	3.5	3.7	3.4
3	6.0	4.4	4.7	4.6
4	35	26	28	30

[a]Loss of uranium-rich solution during wet-ashing.

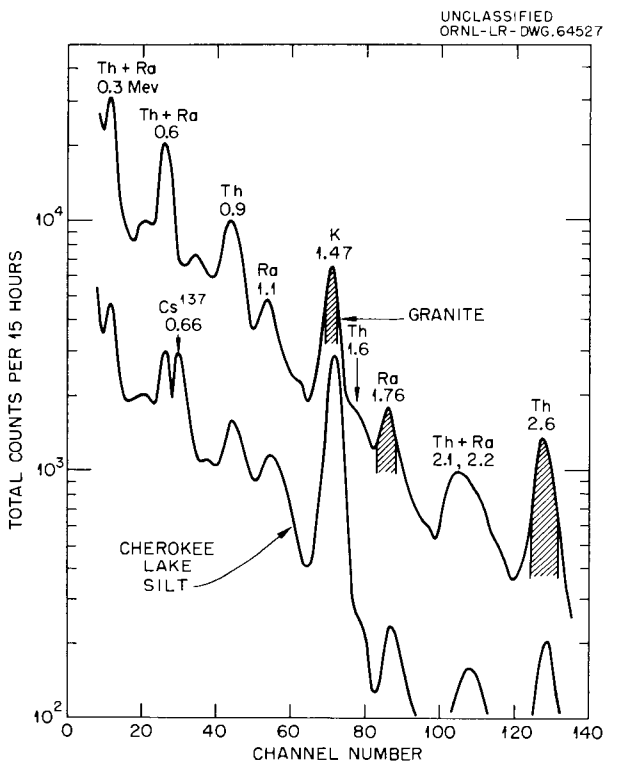

Fig. 8.1. Gamma Spectra of Silt Sample and Granite. (The peaks labeled Th, Ra, and Th + Ra are those characteristics of the short-lived daughters of the elements indicated; shading shows sections measured for Th, Ra, and K.)

Disintegration Rates of Radioisotope Standards (W. S. Lyon, H. A. Parker, S. A. Reynolds). – The program[13] of measurement of disintegration rates of radioisotope standards furnished by a commercial supplier has continued. The National Bureau of Standards also measures most of the standards. Results are shown in Table 8.4.

[13]W. S. Lyon *et al.*, "Disintegration Rates of Radioisotopes," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 59.

Table 8.3. Results of Analysis of Silt Samples

Sample	Natural Thorium		Ra^{226}			K		Cs^{137}	Other Data for Comparison
	ppm	β (dis min^{-1} g^{-1})[a]	g/g × 10^{13}	U (ppm)[a]	β (dis min^{-1} g^{-1})[a]	%	β (dis min^{-1} g^{-1})	β (dis min^{-1} g^{-1})	
Cherokee Lake silt	13	13	6	2	8	2.9	49	~1.3	0.3 to 7% K in various soils[c]
Douglas Lake silt	17	16	11	3	14	1.9	32	~2.0	
Loudon Lake silt	15	14	8	2	10	1.6	27	~2.0	
Granite G1	51		24	7		5.2			Th, 51 ppm[d]; K, 4.5%[c]
Granite GF	83		62	18		4.3			Th, 82 ppm[e]; U, 16 to 19 ppm[e,f]
Dunite[b]	<4		<3.5	<1		<0.2			Ra, 2.8 g/g × 10^{13}[g]; Th, <1 ppm[e]

[a] If whole series is in radioactive equilibrium.
[b] Short count (50 min).
[c] According to activation analysis made by G. W. Leddicotte.
[d] U.S. Geological Survey standard.
[e] ORNL.
[f] Rice University.
[g] AEC New Brunswick Laboratory.

Table 8.4. Disintegration Rates of Radioisotopes

Radioisotope	Date of Supplier's Measurement	Half-Life Used (ORNL)	Disintegration Rate (dis/sec × 10^{-3} to 10^{-6})			Mean Deviation (%)
			Supplier	NBS	ORNL	
Na^{24}	4/60	15.06 h	6.75		6.70	0.4
	10/60		4.66	4.72	4.69	0.4
	4/61		1.83	1.88	1.82	1.3
P^{32}	3/60	14.3 d	1.09[a]	1.09	1.09	0
	3/61		1.45[a]	1.45	1.44	0.3
	9/61		3.50	3.50	3.55	0.6
S^{35}	9/59	87 d	7.50[a]	7.50	7.33	1.1
K^{42}	8/60	12.47 h	3.37	3.48	3.56	2.0
	2/61		1.65	1.68	1.68	0.8
	8/61		4.15	4.10	4.15	0.5
Fe^{55}	1/61	2.9 y		5.20	5.12	0.8
Fe^{59}	10/59	45 d	6.86	6.70	7.03	1.6
	6/60		2.12	2.10	2.07	0.8
	12/60		1.49	1.51	1.45	1.6
Co^{60}	10/53	5.27 y	6.85[a]	6.85	6.85	0
Sr^{90}-Y^{90}	4/57	28 y	9.63[a]	9.63	9.95	1.6
Y^{90}	2/61	64.4 h	5.08[b]		5.17	0.9
	3/61		2.70[b]		2.70	0
I^{131}	1/60	8.08 d	1.36	1.32	1.37	1.5
	6/60		9.45	9.50	9.56	0.4
	1/61		3.10	3.11	3.15	0.6
	6/61		4.02	4.08	4.09	0.7
Cs^{137}	1/60	30 y	1.04	1.02_7	1.00	1.5
Ta^{182}	6/59	115 d	3.34	3.41	3.48	1.5
Au^{198}	5/60	2.69 d	2.27	2.30	2.28	0.4
	11/60		6.86	6.82	6.84	0.2
	5/61		1.08	1.10	1.08	0.8
Tl^{204}	6/57	3.56 y	1.91[a]	1.91	1.90	0.3
						Average 0.8

[a]Used NBS value.
[b]Supplied by U.S. Public Health Service, Cincinnati, Ohio.

Participation in National Organizations

ASTM Committee E-10, Radioactive Isotopes; Subcommittee III, Tracer Applications (W. S. Lyon). – W. S. Lyon has been named chairman of this subcommittee, which has as its scope "to promote the knowledge and use of radioisotopes in materials testing, and prescribe methods for the accurate testing and

measurement of radioisotopes." Two methods related to the second part of this scope were accepted as tentative methods by the ASTM at the 1961 annual meeting. An effort is being made to reactivate a number of projects necessary to the first part of the scope; in addition, a number of new applications are being pursued.

American Standards Association Committee N 5.4 (Use and Handling of Radioisotopes and High-Energy Radiations) (W. S. Lyon). – Work was continued on standard procedures for handling, packaging, shipping, and measuring unsealed sources of radiation. Work has also continued on the standardization of certain specifications for radiochemical laboratories and for equipment for use in handling radioisotopes.

Foreign Guest Program

W. S. Lyon J. S. Eldridge

Visitors from India, Switzerland, and Greece have studied methods of measurement and standardization of radioactivity. The program has been similar to that carried out in the past.[14]

[14]W. S. Lyon and S. A. Reynolds, "Foreign Guest Pragram," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 66.

9. Nuclear Analyses

J. C. White
G. W. Leddicotte

RESEARCH APPLICATIONS OF NEUTRON-ACTIVATION ANALYSIS

Trace Elements in Ultrapure Materials

G. W. Leddicotte J. F. Emery W. J. Ross
J. E. Strain L. C. Bate A. P. Grimanis[1]
W. T. Mullins F. F. Dyer M. M. Tuckerman[2]

Trace elements in ultrapure Be, Nb, and Zr, in crystalline MgO and SiO_2, and in commercial drugs were determined by neutron-activation analysis. The ultrapure metals are of interest in nuclear reactor technology. The drugs included hormones, vitamins, analgesics, and antacids. This is the first application of neutron activation in the analysis of drugs. The crystalline MgO and SiO_2 were to be used in solid-state studies. Results are summarized in Table 9.1. Both destructive techniques (as described

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[2]Research participant from School of Pharmacology, Temple University, Philadelphia, Pa.

Table 9.1. Applications of Neutron-Activation Analysis in the Assay of Ultrapure Materials

Element Determined	Induced Radionuclide	Technique[a]	Material Analyzed	Experimentally Determined Concentration of Element (μg/g)	Estimated Limit of Measurement for Element (μg)[b]
Al	Al^{28} (2.27 m)	ND	Beryllium	7 to 99	0.001 to 0.03
			Niobium	16	
			Zirconium	100 to 200	
Br	Br^{82} (35.87 h)	ND	Beryllium	0.001 to 0.1	0.001 to 1.0
		ND	Niobium	3 to 4	
		ND	Commercial drugs	0.5 (estd)	
Cd	Cd^{115} (53 h) or Cd^{115m} (43 d)	RC	Niobium	28 to 82	0.1 to 10.0
			Zirconium	10^3 to 10^4	
Cl	Cl^{38} (37.29 m)	ND	Beryllium	10^2 to 10^3	0.05
			Niobium	558 to 656	
			MgO	*c*	
			SiO_2	2 to 89	
			Commercial drugs	1 to 10	
Cr	Cr^{51} (27.8 d)	RC	Beryllium	0.1 to 1.0	
			Niobium	17 to 20	0.10
			Zirconium	6 to 7	
			MgO	*c*	
			SiO_2	0.6	
Co	Co^{60} (5.24 y)	ND	Beryllium	0.1 to 1.0	0.01
			Niobium	13 to 20	
Cu	Cu^{64} (12.80 h)	ND	Beryllium	1 to 10	0.001 to 0.002
			Niobium	1 to 2	
			Zirconium	2 to 3	
			Commercial drugs	0.1 to 0.5	
Au	Au^{198} (2.697 d)	ND	Beryllium	0.001 to 0.01	0.0001
			MgO	*c*	
			SiO_2	0.0007 to 0.006	
Hf	Hf^{179m} (19 s)	ND	Zirconium	140 to 150	0.001 to 0.05
Fe	Fe^{59} (45.1 d)	ND	Beryllium	8 to 40	2.0 to 5.0
			Niobium	200 to 700	
			Zirconium	60 to 75	
			MgO	*c*	
			SiO_2	38 to 160	
Mn	Mn^{56} (2.576 h)	ND	Beryllium	2 to 100	0.0001 to 0.75
			Niobium	0.75	
			MgO	*c*	
			SiO_2	0.03 to 0.04	
			Commercial drugs	0.5 (estd)	

Table 9.1 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Material Analyzed	Experimentally Determined Concentration of Element (μg/g)	Estimated Limit of Measurement for Element (μg)[b]
Hg	Hg^{197m} (24 h)	ND	Commercial drugs	<0.10	0.1
Mo	Mo^{99} (66.0 h)	RC	Zirconium	20 to 30	0.1
Ni	Co^{58} (71.3 d)[d]	ND	Niobium	22 to 24	
			MgO	*c*	1.0
			SiO_2	5 to 9	
P	P^{32} (14.22 d)	RC	Niobium	3 to 4	0.05
K	K^{42} (12.5 h)	ND	Beryllium	10^2	0.1
Sc	Sc^{46} (83.9 d)	ND	Beryllium	0.01 to 60	0.01
Si	Si^{31} (2.62 h)	RC	Beryllium	30 to 60	1.0
			Niobium	3 to 4	
			Zirconium	10 to 20	
Na	Na^{24} (15 h)	ND	Beryllium	0.01 to 0.9	0.007
			Niobium	1 to 10	
			MgO	*c*	
			SiO_2	0.04 to 1.3	
			Commercial drugs	1 to 10	
Ta	Ta^{182} (115.1 d)	RC	Niobium	10^3	0.002
Th	Pa^{233} (27.0 d)[e]	ND	Beryllium	0.07 to 700	0.01
W	W^{187} (24.0 h)	RC	Beryllium	0.01 to 0.1	0.001
			Niobium	11 to 12	
			Zirconium	7 to 10	
U	Np^{239} (2.346 d)[f]	ND	Beryllium	0.008 to 27	
			Niobium	2 to 5	0.001
V	V^{52} (3.76 m)	ND	Niobium	1	0.001 to 2.0
			Zirconium	2	
Zn	Zn^{69m} (13.8 h)	RC	Niobium	2 to 3	0.02
			Commercial drugs	0.1 to 1.0	
Zr	Zr^{97}(17.0 h)	RC	Niobium	10^2 to 10^3	0.2

[a] Nondestructive (ND) or radiochemical (RC).

[b] For use of different reactor flux areas; varied from 6×10^{11} to 6×10^{13} neutrons cm^{-2} sec^{-1}.

[c] Qualitative results only.

[d] Produced by the reaction $Ni^{58}(n,p)Co^{58}$.

[e] Daughter radionuclide of 22.12-m Th^{233}.

[f] Daughter radionuclide of 24.1-m U^{239}.

in the *ORNL Master Analytical Manual*) and nondestructive techniques (i.e., complement-subtraction gamma spectrometry[3]) were used; comparator samples were analyzed in each case.

Other Quantitative Applications

L. C. Bate
J. F. Emery
W. T. Mullins
A. P. Grimanis[1]
M. Constantinidis[1]
G. W. Leddicotte

Trace Elements in Ecological Systems. – The following elements in micro concentrations or less were determined in soils and in parts from pine trees: I, Br, Cl, Se, Th, Sc, Al, Zn, Cr, Ta, Cu, and Sb. Both destructive and nondestructive methods were used; the results have been reported.[4]

Ru in Aqueous Solutions. – Use of the reaction $Ru^{96}(n,\gamma)Ru^{97}$ in the assay of process solutions that contain stable Ru was shown to be feasible. Following its production, Ru^{97} (2.88 d) is separated from the sample by either distillation from $HClO_4$ solution[5] or by hydrolytic precipitation.[6] The separated ruthenium carrier and Ru^{97} are precipitated as Ru metal by reduction with Mg metal; the Ru^{97} radioactivity is measured by gamma counting. The limit of measurement under the conditions of a 60-hr irradiation at a flux of about 6.5×10^{11} neutrons cm^{-2} sec^{-1} is about 0.05 μg, which is at least 50 times lower than that achieved with most other methods.

Trace Elements in Tc^{99} Products. – The elements As, O, Br, and Mn were determined in Tc^{99} products by neutron-activation analysis. The Tc^{99} did not interfere. Typical data follow:

Element Determined	Concentration (nanograms/g)
As	1
Br	10
Mn	10
O	2.9 (mg/g)

Oxygen was determined by means of the reactions $Li^6(n,\alpha)H^3$ and $O^{16}(H^3,n)F^{18}$. The F^{18} (112 m) was removed by distillation and was measured by gamma counting. The other elements were determined by means of methods given in the *ORNL Master Analytical Manual.*

Trace Na in Solutions of Sr^{90} and of Other Fission Products. – Gamma scintillation spectrometric measurement of the 2.75-Mev gamma radiation from Na^{24} (14.97 h), the product of the $Na^{23}(n,\gamma)Na^{24}$ reaction, is now being used to determine nondestructively the Na^{23} content of radioactive solutions of

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[3]L. C. Bate and G. W. Leddicotte, *The Quantitative Analysis of Complex Radionuclide Mixtures by Gamma-Ray Spectrometry*, ORNL-2917 (in press).

[4]J. S. Olson *et al.*, "'Forest Ecology.' Biogeochemical Analyses of Plants and Soils," *Health Physics Div. Ann. Progr. Rept. July 31, 1961*, ORNL-3189, pp 110–13.

[5]R. E. Druschel, "Ruthenium Activity in Aqueous or Organic Solutions," Method No. 2 21731 (3-2-54), *ORNL Master Analytical Manual;* TID-7015, sec 2.

[6]R. R. Rickard, "Ruthenium Activity in Aqueous Solutions, Nondistillation Method," Method No. 2 21733 (6-31-60), *ORNL Master Analytical Manual;* TID-7015, suppl 3.

Sr^{90} and of mixed fission products. Aliquots of a dilute solution of the sample are irradiated in the ORNL Graphite Reactor for at least 1 hr; the gamma radiation from the induced Na^{24} is then measured.[7] As little as 0.1 μg of Na^{23} can be determined by this method.

P in Si and Its Compounds. – The nuclear reaction $P^{31}(n,\gamma)P^{32}$ has been used to determine traces of stable P in Si and in some compounds of Si. The half-life of P^{32} is 14.22 d; P^{32} emits 1.707-Mev beta radiations. Interferences from the reactions

$$Si^{30}(n,\gamma)Si^{31}\xrightarrow[2.62\ h]{\beta^-,\gamma}P^{31}$$

and the reaction $P^{31}(n,\gamma)P^{32}$ are minimized by use of a short irradiation time. The method consists in irradiating the sample no longer than 20 min at a flux of at least 5.0×10^{13} neutrons cm^{-2} sec^{-1} and then processing the sample radiochemically for P^{32}. The beta radioactivity from P^{32} is measured by means of a beta counter. Less than 10^9 atoms of P^{31} will be produced from the decay of Si^{31} during the irradiation. The lower limit of quantitative measurement of the method is 2.4 ng (nanograms) of P^{31} per gram of Si.

Ni in Tobacco. – A rapid procedure was developed for the determination of Ni in tobacco. The tobacco sample together with Ni carrier is ashed in the presence of benzenesulfonic acid; the ashing can be completed in 15 min without loss of Ni. Studies of other elements that may be present (Cu, As, Fe, Co, Sr, Mn, Na, and Zn) showed that only Cu, Na, and Fe interfere, but these interferences can be eliminated by precipitation of Ni with dimethylglyoxime. The neutron-activation analysis method for nickel[8] now in the *ORNL Master Analytical Manual* will be modified to include this rapid procedure.

Trace Elements in Raw Opium

J. F. Emery L. C. Bate G. W. Leddicotte

The results of the determination by neutron-activation analysis of trace elements in raw opium from various sources (see Table 9.2) show source-to-source variations in the composition. The complement-subtraction technique of gamma spectrometry was used. When more samples from the same sources are analyzed, it may be possible to correlate composition with source and thus to determine sample origin by means of neutron-activation analysis.

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[7] W. T. Mullins and G. W. Leddicotte, "Sodium, Neutron Activation Analysis (Direct Measurement) Method," Method No. 5 11791 (2-20-61), *ORNL Master Analytical Manual*; TID-7015, suppl 3.

[8] W. T. Mullins and G. W. Leddicotte, "Nickel, Neutron Activation Analysis (Isotopic-Carrier) Method," Method No. 5 11540 (7-31-59), *ORNL Master Analytical Manual*; TID-7015, suppl 2.

Table 9.2. Results of Determination of Trace Elements in Raw Opium by Neutron-Activation Analysis

Source of Sample	Concentration of Element (μg/g)								
	Al	Sb	Cs	Co	Fe	Mn	P	Sc	Zn
Greece	99	1.63	0.36	0.98	1980	25	1150	0.13	6.7
Indochina	135	1.31	0.34	0.36	77	18	1930	0.05	1.8
Turkey	98	<0.1	<0.07	0.40	675	25	2180	0.16	8.9
China	2,620	<0.1	0.46	0.53	976	29	2140	0.49	6.3
Yugoslavia	351	<0.1	<0.07	0.53	556	13	1790	0.06	62.2
Pakistan	41,600	0.87	0.13	0.76	601	24	3920	0.16	557.0
Burma	233	0.58	<0.07	0.37	476	17	2380	0.06	11.0
Afghanistan	409	<0.1	<0.07	0.19	421	9	2100	0.12	2.2
Japan	76	0.95	<0.07	0.11	412	9	2510	<0.004	14.0
Faizabad	303	<0.1	<0.07	0.14	280	5	1830	0.06	4.0

Quantitative Analysis with Radionuclides of Very Short Half-Life

J. F. Emery

Use of short-lived radionuclides in neutron-activation analysis was discussed earlier.[9] New applications of short-lived radionuclides are listed in Table 9.3, and the limits of measurement are indicated. The gamma spectrum of Y^{89m}, which is one of the short-lived radioelements used, is shown in Fig. 9.1.

Determination of Micro Concentrations of Be

J. F. Strain

Micro concentrations of Be can be determined by measuring the instantaneous (capture) gamma radiations that result from the interaction of alpha particles with Be. The high-energy gamma photons (3.5- to 4.5-Mev) of almost instantaneous half-life that are produced in the nuclear reaction $Be^{9}(\alpha,n)C^{12}$ are specific for Be. The number of gamma photons produced is a linear function of the Be concentration of a sample. This simple method consists in mixing the Be-containing material with milligram amounts of Am^{241} (458 y) as the alpha source, placing the container directly on the NaI crystal of a gamma-scintillation spectrometer, and counting. Typical data obtained in the analysis of liquid and solid samples show that Be in concentrations as small as 50 μg/ml (or μg/g) can be determined by this method.

[9] J. F. Emery and G. W. Leddicotte, "Use of Short-Lived Radionuclides in Neutron-Activation Analysis," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 42.

Table 9.3. Applications of Short-Half-Life Radionuclides in Neutron-Activation Analysis

Element Determined	Induced Radionuclide	Half-Life	Nuclear Reaction	E_γ (Mev)	Limit of Measurement[a] (ng/g)	Counting Conditions
Se	Se^{77m}	17.5 s	(n,γ) $(n,2n)$	0.162	0.2[b]	20-sec decay; on crystal[c]
Hf	Hf^{179m}	19 s	(n,γ)	0.160 0.217	0.02[b]	20-sec decay; on crystal[c]
F	F^{20}	10.7 s	(n,γ)	1.627	50[b]	20-sec decay; sample on 0.5-in.-thick absorber (1 g/cm^2 of plastic)
Nb	Nb^{94m}	6.6 m	(n,γ)	0.0415	5[d]	On crystal[e]
Y	Y^{89m}	16.1 s	(n,n')	0.913	200[b]	20-sec decay; sample at 5-cm geometry; 0.5-in. absorber (1 g/cm^2 of plastic) used at this position to reduce Y^{91} (57.5 d) beta-radiation interference
V	V^{52}	3.76 m	(n,γ)	1.44	0.08[d]	On crystal

[a]Based on collection of 100 counts of the gamma radiations used in the measurement after irradiation in the ORR.
[b]For a 20-sec irradiation at a flux of 6×10^{13} neutrons cm^{-2} sec^{-1}.
[c]NaI crystal, 3 × 3 in.
[d]For a 1-min irradiation at a flux of 6×10^{13} neutrons cm^{-2} sec^{-1}.
[e]NaI crystal, $\frac{3}{32}$ in. thick × $1\frac{1}{2}$ in. in diameter.

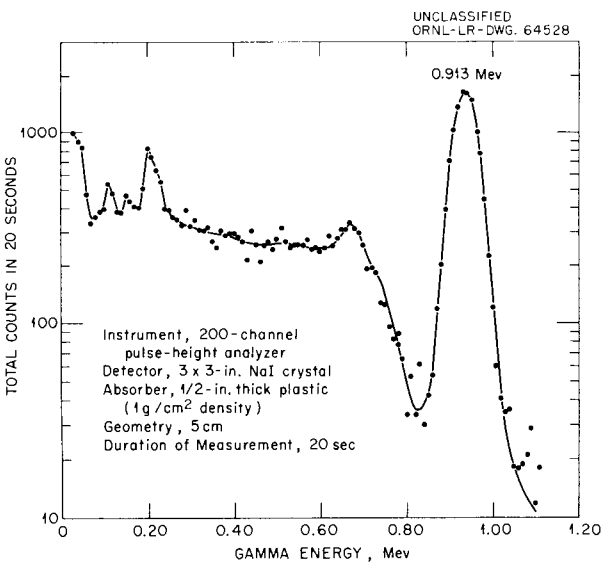

Fig. 9.1. Gamma Spectrum of 16.1-s Y^{89m}.

Determination of U^{235} by Delayed-Neutron Counting

F. F. Dyer J. F. Emery G. W. Leddicotte

The method of determining U^{235} by delayed-neutron counting[10] is now used routinely by the Nuclear Analyses Group to determine U^{235} in ores, alloys, solutions, and graphite, as well as to determine the isotopic composition of uranium in samples that contain known amounts of total uranium. Under the conditions of the analysis, 1 μg of U^{235} produces 10^6 delayed neutrons, and it has been possible to measure quantitatively 1 ng of U^{235}. A single determination of U^{235} requires 1 min of irradiation time and 2 min of counting time, additional time being required for weighing the sample, placing the sample in an irradiation "rabbit," and making the necessary calculations. The method is being written for inclusion in the *ORNL Master Analytical Manual.*

Particle-Size-Distribution Analysis

L. C. Bate G. W. Leddicotte

The method of particle-size-distribution analysis described previously[11] has been applied to a variety of materials other than ThO_2 and UO_2. The data for nickel shown in Fig. 9.2 are typical.

[10] F. F. Dyer and G. W. Leddicotte, "Analytical Application of Delayed-Neutron Counting," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 48.

[11] G. W. Leddicotte and H. H. Miller, "Particle-Size Distribution," *Anal. Chem. Div. Semiann. Progr. Rept. Oct. 20, 1954*, ORNL-1788, pp 21–23.

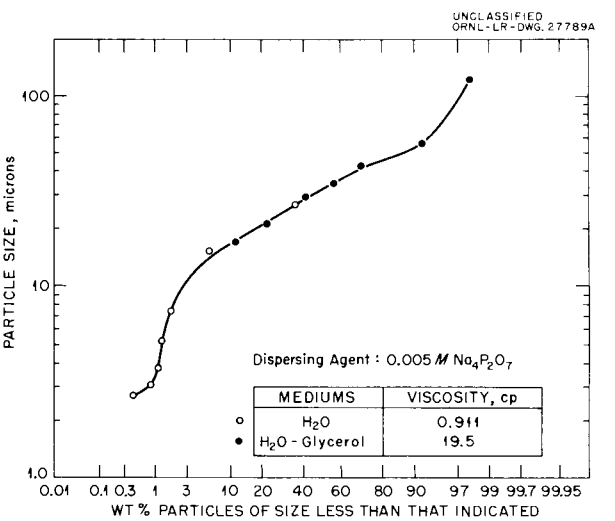

Fig. 9.2. Particle-Size Distribution of Ni by Neutron-Activation Analysis – Sedimentation Method.

Measurements of Spectra of Neutrons Produced in Reactors

G. W. Leddicotte F. F. Dyer

Techniques described previously[12] for monitoring neutron flux are being used to monitor many reactor areas and experiments by means of thermal- and fast-neutron threshold detectors (activation foils). Measurement of the fast flux in the ORR core is typical.[13]

Nondestructive Automatic Assay of Radioactivity in Neutron-Flux-Monitor Wires

F. F. Dyer G. W. Leddicotte

A device for continuously scanning the radioactivity of neutron-flux-monitor wires that contain one radionuclide has been described previously.[14] For a number of reasons, the method of continuous scanning has not been entirely satisfactory. The device has been modified to automatically take counts on a scaler for predetermined lengths of counting time at predetermined positions equally spaced along the wire. The data are recorded on a Streeter-Amet traffic counter in terms of counts min^{-1} $segment^{-1}$. Comparison of the data from a test wire with the data from a comparator wire for which the specific activity is known makes possible the calculation of the specific activity of the test wire. Results obtained by this method agree within about ±3% with the results obtained by cutting a wire into short segments (usually 1 in.) and measuring the specific activity of each segment.

Radiochemical Separations Applicable to Neutron-Activation Analysis Separation of Se from Te by Liquid-Liquid Extraction

A. P. Grimanis[15] G. W. Leddicotte

A study was made of the extraction into benzene of Se, as hexabromoselenic acid, from different aqueous solutions of $HClO_4$ and of H_2SO_4. Accordingly, a method was developed for the separation, at both the submicrogram and milligram levels, of Se^{4+} from Te^{4+} by extraction of Se^{4+} into benzene from 1 *M* HBr–7 *M* $HClO_4$ or from 1 *M* HBr–6 *M* H_2SO_4 solutions. For both extraction systems, more than 98% of the Se^{4+} and less than 0.1% of the Te^{4+} are extracted. Of the elements Ga, Sb, As, Fe, Cr, Pa, Au, Cu, Sn, and Mg, 99% of the As is extracted and 1% of the Sb; less than 0.5% of each of the others is extracted. At optimum extraction conditions, the solvents toluene and xylene are equally effective.

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[12]G. W. Leddicotte and W. T. Mullins, "Measurement of Reactor Neutron Spectra," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1958*, ORNL-2662, p 10.

[13]P. Dragoumis, J. R. Weir, and G. W. Leddicotte, *Fast-Flux Measurements in the ORR Core*, ORNL-3028 (Jan. 16, 1961).

[14]G. W. Leddicotte *et al.*, "Measurements of Reactor Neutron Spectra," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 31.

[15]Temporary employee from Nuclear Research Center, Greek Atomic Energy Commission, Athens.

Radiochemical Separation for 87-d S^{35}

L. W. Balmer[16]

The distillation of the S^{35} and inactive carrier S as H_2S and the development of the methylene blue complex form the basis of a radiochemical procedure for the determination of S^{35}. The chemical yield of the complex can be determined colorimetrically, and the complex can be used in a liquid scintillation counter to measure the beta radiations of S^{35}. The method has been applied in several analyses. However, some interferences exist in the determination of chemical yield by the colorimetric method, and some exist as a result of the presence of other volatile radionuclides, particularly Se^{75} (121 d). Further work on the method is being done.

RADIOACTIVITY MEASUREMENTS

"Differential-Count" Technique of Gamma Spectrometry

J. F. Emery L. C. Bate

The usefulness of "complement-subtraction" ("subtract-logic") in applications of multichannel gamma-scintillation spectrometry to nondestructive activation analysis has been discussed.[17] It was found convenient to establish another way of interpreting gamma spectral data. The "differential-count" method consists in measuring the gamma-ray spectrum on the analyzer for 1 min and then immediately counting the sample for 1 min in the complemented (subtract) mode of the analyzer. The resulting composite gamma-ray spectrum consists of the spectra of only those radionuclides that have decayed in 1 min. For instance, in the analysis of Zr for trace Hf by use of Hf^{179m} (19 s), the sample is irradiated in the pneumatic-tube system of the ORR for 20 sec and allowed to decay 20 sec. A 1-min count is made, the data in the magnetic memory of the analyzer are complemented immediately, and another 1-min count is started. The resulting spectrum is that obtained for the decay of Hf^{179m} for 3.16 half-lives, which is equivalent to the decay of 89% of the Hf^{179m}. The need for extensive mathematical manipulations to show the relationship of this amount of activity to the concentration of stable Hf is eliminated by counting an Hf^{179m} comparator sample under identical conditions and then relating the observed Hf^{179m} radioactivity to that shown in the spectral data for the test sample. This "differential-count" method is most applicable to those radionuclides that have a half-life of 30 s or less, but it has been used successfully for radionuclides of half-life as long as 10 m.

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[16]Research participant from Pennsylvania State University, Erie Branch, Erie, Pa.

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

Low-Cost Gamma Counter for Samples of Large Mass or Volume

J. F. Emery G. W. Leddicotte

As a consequence of the work in low-level gamma counting cited earlier,[18] a low-cost radiation shield (see Fig. 9.3) was developed for use with a gamma scintillation counter or spectrometer in order to measure the gamma activity of samples of large mass or volume. Typical examples of the use of this shield with the gamma spectrometer are given in Figs. 9.4 and 9.5. The whole-body spectrum displayed in Fig. 9.5 suggests the possibility of using the counter for economical whole-body counting.

[18] J. F. Emery, L. C. Bate, and G. W. Leddicotte, "Low-Level Gamma Counting," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 50.

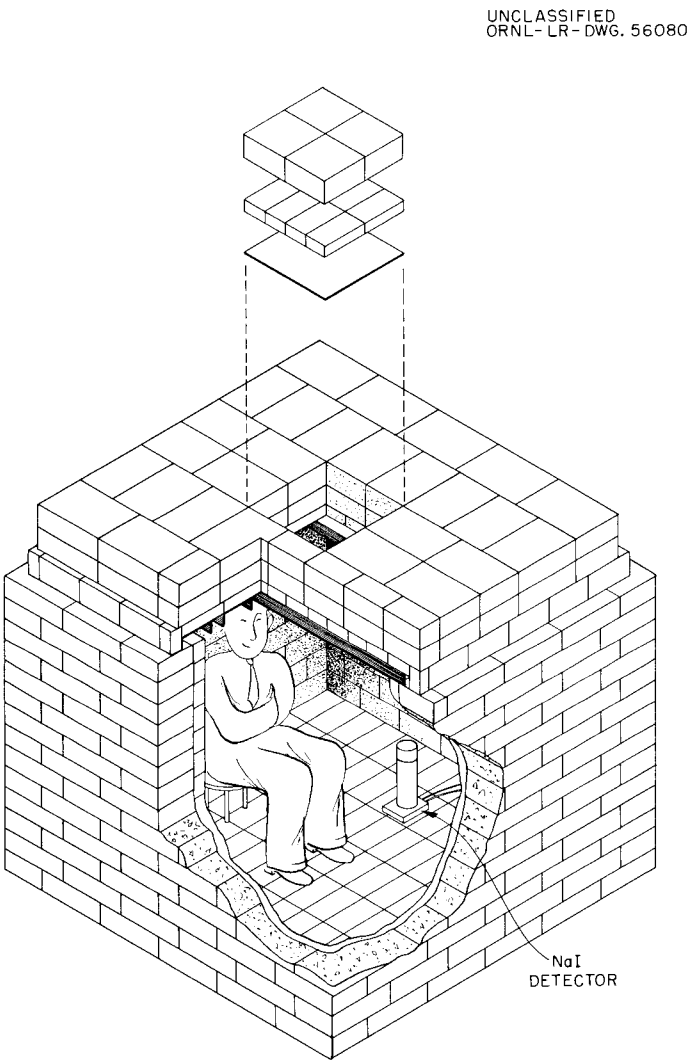

Fig. 9.3. Gamma Counter for Samples of Large Mass or Volume.

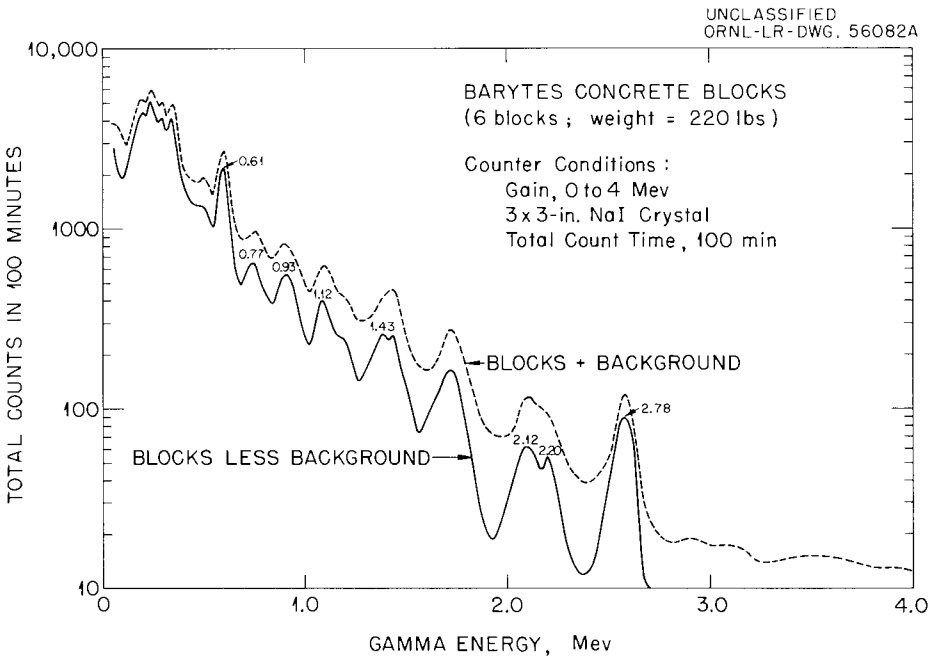

Fig. 9.4. Gamma Spectrum of Barytes Concrete Blocks.

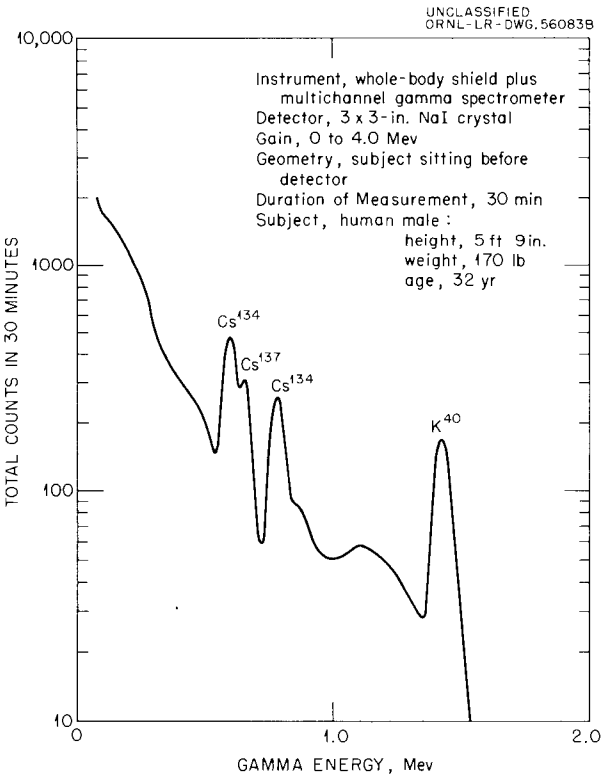

Fig. 9.5. Gamma Spectrum of Human Male Whole Body.

Beta-Ray Spectra from Anthracene Scintillation Crystals

J. F. Emery R. R. Rickard[19]

An anthracene scintillation detector and a multichannel pulse-height analyzer have been used to obtain beta spectra of radioisotopes for quality-control purposes. These spectra are used to indicate whether beta-emitting impurities are present in purified radioisotopes. In addition, the technique should be suitable for the identification of induced radionuclides obtained in neutron-activation analysis. A report of this work is being prepared.

APPLICATIONS OF RADIOACTIVE TRACERS

Studies of Valence States of Radioisotopes

F. F. Dyer G. W. Leddicotte

Interest has been expressed by the Isotopes Division in determining the valence states of radioisotopes in radioisotope products. The valence states of As^{76} and Sb^{125} have been determined. Solvent extraction and ion exchange were used to separate As^{3+} from As^{5+}, and Sb^{3+} from Sb^{5+}, and thus to distinguish the valence states of these elements.

The valence of As^{76} was determined by extracting the As from concentrated HCl into benzene; 2.3% of the As was extracted. A corresponding extraction of neutron-activated As^{5+} resulted in 2.5% of the As going into the benzene layer, whereas neutron-activated As^{3+} gave an extraction of 99%. It was concluded that at least 97 to 98% of the As^{76} was present as As^{5+}.

The valence state of Sb in a solution that contained Sb^{125} was determined by solvent extraction and ion exchange. According to Edwards and Voigt,[20] 99.5% of Sb^{5+} extracts into isopropyl ether from a 6.5 to 8.5 *M* HCl solution, whereas only 1.6% of Sb^{3+} extracts. An extraction of a sample of Sb^{125} was carried out from 7 *M* HCl into isopropyl ether; 83% of the Sb extracted. By use of this value and the data of Edwards and Voigt, the valence-state composition of the Sb^{125} was calculated to be 83% Sb^{5+} and 17% Sb^{3+}.

In the ion exchange study, an aliquot of the Sb^{125} solution was placed on a 1 × 10 cm Dowex 1 column that had been pretreated with 2 *M* HCl. Elution was carried out with 2 *M* HCl until Sb ceased to be eluted. In this manner, 20% of the Sb was removed and 80% remained on the column. According to Kraus and Nelson,[21] the distribution coefficient of Sb^{5+} for the system Dowex 1–2 *M* HCl is about 1, whereas the distribution coefficient of Sb^{3+} in this system is about 1000. Thus, by use of 2 *M* HCl as an eluent, it is

[19] Radioisotopes-Radiochemistry Laboratory.

[20] F. C. Edwards and A. F. Voigt, "Separation of Antimonic Chloride from Antimonous Chloride by Extraction into Isopropyl Ether," *Anal. Chem.* 21, 1204 (1949).

[21] K. A. Kraus and F. Nelson, "Metal Separations by Anion Exchange," *ASTM Spec. Tech. Publ.*, No. 195, 27–57 (1956).

easy to remove Sb^{5+} from Dowex 1 and to leave Sb^{3+} on the resin. On the basis of the results of the ion exchange separation, it was concluded that about 20% of the Sb^{125} was Sb^{3+} and 80% was Sb^{5+}. This result agrees fairly closely with the values obtained by solvent extraction.

FOREIGN GUEST PROGRAM

G. W. Leddicotte

Visitors to the Nuclear Analyses Group from Greece, Spain, Indonesia, Thailand, Vietnam, and Yugoslavia have studied activation analysis methods for times ranging from one to ten months. In this training, the applications of activation analysis and the use of radiochemistry and radioactivity measurements, particularly gamma-ray spectrometry, were emphasized. This program is continuing.

PARTICIPATION IN NATIONAL ORGANIZATIONS

National Academy of Sciences–National Research Council Subcommittee on Radiochemistry

G. W. Leddicotte

Monographs on the radiochemistry of the elements have been issued as a part of the work of this committee. In addition, special studies were undertaken relative to establishing the levels of radioactivity in chemical reagents and in materials to be used in the construction of low-level counting equipment.

Semiconductor Analyses Group

J. F. Emery

This group is evaluating methods for determining trace elements in ultrapure metals and alloys used as semiconductors. Formal meetings are held periodically to review the progress of the work.

ASTM Committee E-3, Lithium Task Force

L. C. Bate

This committee was activated recently to develop and evaluate methods for the determination of trace elements in Li and its compounds. The scope of the work of the committee is now being reviewed in order to determine what areas of study will be undertaken.

U.S. Atomic Energy Commission–Measurement-Evaluation Seminars

G. W. Leddicotte

The AEC is evaluating existing procedures for determining uranium and other fissionable elements. G. W. Leddicotte is chairman of the Radiochemistry Group, which is evaluating nuclear-analysis and radiochemical methods suitable for these determinations. The methods selected will be published during the next year.

10. Inorganic Preparations

M. T. Kelley
D. E. LaValle

In the work for the Nuclear Physics and Neutron Diffraction Group of the Physics Division, the general program of preparation of nitrides and other compounds of the rare-earth metals with group-five elements was almost completed, and attention was then given to some specific related problems. Among these were the preparations of high-purity HoP and the subsulfide HoS in 20-g quantities. Both these problems were solved by the use of a plunger-type bomb arrangement in which the elements, compressed in a stainless steel cylinder between two snugly fitting piston-like plungers, are rapidly brought to reaction temperature in a stream of inert gas.

For the same group, 60 g of Cr^{52} metal was purified by treatment at 1000°C for one week with highly purified hydrogen to remove about 1% of the oxygen. The method used was adapted from that of Kroll, Hergert, and Yerkes.[1]

For the Nuclear Physics and Low-Temperature Group of the Physics Division, a series of gold compounds was made; they were AuF_3, $AuCl_3$, $AuBr_3$, $KAuF_4$, $KAuCl_4$, $KAuBr_4$, and $KAuI_4$. Attempts to prepare the monohalide AuCl gave products that always contained as much as 10% free gold. For this same group, a sample of alum, $NH_4Al(SO_4)_2 \cdot 12H_2O$, was made in which 1 mole % of the Al was replaced by Fe^{57}.

In the preparation of fused salts, several more 100-g quantities of the bismuth halides and about 50 g of anhydrous $La(NO_3)_3$ were prepared for the High-Temperature Reactions Group of the Metallurgy Division. In connection with other fused-salt programs, about 2 kg of LiCl-KCl eutectic was produced for the Molten Salts Systems Group of the Reactor Chemistry Division. For the High-Temperature and Structural Chemistry Group of the Chemistry Division, the following anhydrous salts were prepared in 100-g quantities: $CaCl_2$, $SrCl_2$, $BaCl_2$, SrI_2, KI, CsI, $CdCl_2$, $NdCl_3$, NdI_3, and $PrCl_3$.

In work for the Chemical Physics Group of the Chemistry Division, 20 g of KO_2 was prepared. In regard to the preparation of deuterated hydrazine, numerous attempts were made to duplicate the work of Bulgozdy and Wagner[2] without success.

A program to attempt to prepare K_2O free from other oxides of potassium was begun for the Spectroscopy of Ionic Media Group of the Metallurgy Division. Thus far, attempts by three different methods have given products of only 90 to 95% purity.

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[1] W. J. Kroll, W. F. Hergert, and L. A. Yerkes, "Ductile Chromium," *J. Electrochem. Soc.* 97, 258 (1950).

[2] E. L. Bulgozdy and E. L. Wagner, "The Preparation of Anhydrous Hydrazine and Deutero-hydrazine from Hydrazine Dihydrochloride," *J. Am. Chem. Soc.* 73, 5866 (1951).

The investigation of the chemistry of rhenium and technetium, begun last year, solved some problems. The pink salt prepared here as K_2ReF_6 has been amply identified as the compound despite the description given elsewhere that K_2ReF_6 is white.[3] The analogous compound of technetium, K_2TcF_6, which is pale lavender, has also been prepared and identified, and from it H_2TcF_6 and $(NH_4)_2TcF_6$ were obtained by ion exchange and neutralization. The decomposition of $(NH_4)_2TcF_6$, in vacuum and in inert gas, has not led to the anticipated lower fluorides of technetium but instead to a mixture of the metal and unidentified substances.

Another 100 g of K_2ReBr_6 was prepared in order that an attempt could be made to resolve the anomalies in the heat-capacity curve of this compound. The method of Weise[4] was followed in which no outside reductant for $KReO_4$, such as $CrBr_2$, is used.

A series of surface-active agents, that is, the sodium alcohol sulfates of 12, 16, and 22 carbon atoms, were prepared in 100-g quantities for the Chemical Engineering Research Studies Group of the Chemical Technology Division.

In the preparation of compounds of high purity, the MgO program, as described in previous annual reports, continues to be the major problem. The contamination by platinum incident to the ignition of magnesium precipitates in the presence of NH_4Cl is of concern at present.

Osmium was purified by distillation as OsO_4 for the 63-Inch Cyclotron Operations Group of the Electronuclear Research Division. For the Nuclear Physics and Neutron Diffraction Group of the Physics Division, 70 g of $NiCl_2$ was treated by ion exchange to bring the Co content down to less thon 1 ppm.

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[3]D. E. LaValle, "Inorganic Preparations," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 15–16.

[4]E. Weise, "Fluorokomplexe des vierwertigen Rheniums," *Z. anorg. u allgem. Chem.* **283**, 377 (1956).

11. Organic Preparations

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

Most of the organic compounds prepared were for the Chemical Technology Division. Compounds were also synthesized or purified for the Analytical Chemistry, Chemistry, and Physics Divisions. They were either not readily available from commercial sources or were available in impure form only and required purification. A summary of this program follows.

Isonitroso Compounds

At the request of Chemical Development Section C of the Chemical Technology Division, methods were studied for nitrosating compounds having active methylene groups to form isonitroso (oximino) derivatives. Several such compounds were synthesized. Illustrative of these was the preparation of isonitrosopropiophenone by reaction of methyl nitrite with propiophenone in the presence of gaseous HCl.

The method by which 50 g of isonitrosoacetone was synthesized is to be described in detail in a formal report. First, the potassium salt of acetoacetic ester is formed at a temperature below 45°C; the reaction is

$$CH_3COCH_2COOC_2H_5 + KOH \rightarrow CH_3COCH_2COOK + C_2H_5OH .$$

Then the reaction vessel is cooled in an ice-salt mixture, and the nitrosation to isonitrosoacetone is carried out. The reaction is

$$2CH_3COCH_2COOK + 2NaNO_2 + 2H_2SO_4 \rightarrow 2CH_3COCHNOH + K_2SO_4 + Na_2SO_4 + 2CO_2 + 2H_2O .$$

A practically pure product was obtained which, after purification by sublimation, had the melting point and composition indicated in Table 11.1.

Table 11.1. Composition of Isonitrosoacetone

Melting point, 69°C (theoretical)
68°C (found)

Component	Mole Percent	
	Theoretical	Found
Carbon	41.4	41.6
Hydrogen	5.79	5.85
Nitrogen	16.1	15.6

n-Alkylbenzenes

Chemical Development Section C of the Chemical Technology Division requested the preparation of several of the higher *n*-alkylbenzenes. *n*-Hexylbenzene was synthesized by treating the proper Grignard reagent with the alkyl ester of *p*-toluenesulfonic acid according to the method reported by Gilman and Beaber.[1] The ester, *n*-amyl-*p*-toluenesulfonate, was prepared by adding slowly two equivalents of powdered KOH to a well-stirred ether solution that contained equivalent weights of *p*-toluenesulfonyl chloride and *n*-amyl alcohol and keeping the temperature of the mixture below 4°C. The reaction mixture was poured into ice water and then extracted with ether. An equivalent amount of ester in ether was added to

[1]H. Gilman and N. J. Beaber, "The Preparation of Hydrocarbons by the Reaction Between Alkyl Sulfonates and Organomagnesium Halides," *J. Am. Chem. Soc.* 47, 518 (1925).

benzyl magnesium chloride, refluxed for 3 hr, and poured on crushed ice to which was added dilute HCl. The ether extract was washed, dried, and filtered. The ether was then evaporated on a steam bath, and the resulting oil was distilled at 226°C.

n-Nonylbenzene

n-Nonylbenzene was prepared[2] by suspending 2.6 moles of Na in 800 ml of toluene at 72°C and adding 0.52 mole of octyl bromide dropwise over a 1-hr period.

Work is continuing on the preparation of homologs of benzene. *n*-Heptylbenzene and *n*-octylbenzene will be synthesized by methods similar to those used for *n*-nonylbenzene. The methods and the results of synthesizing *n*-alkylbenzenes will be described in detail in a formal report.

N-Methylacetamide

Six kilograms of *N*-methylacetamide was synthesized at the request of the Chemical Separation of Isotopes Group of the Chemistry Division. The procedure consisted in heating equal amounts by weight of methylamine hydrochloride and acetamide to 190°C for several minutes until NH_4Cl was completely precipitated; the reaction is

$$CH_3NH_2 \cdot HCl + NH_2COCH_3 \rightarrow CH_3NHCOCH_3 + NH_4Cl \downarrow .$$

After the solution was cooled, chloroform was added, and the NH_4Cl was filtered off. Following removal of the chloroform by distillation, the product was collected as the fraction distilling at 203 to 206°C. Liquid *N*-methylacetamide was obtained in a 12.6-kg yield from which 6.1 kg (48% of theoretical) was recovered as crystals (mp 29 to 30°C).

Alkali-Metal Salts of *p*-Ethylbenzenesulfonic Acid

Small quantities (less than 100 g each) of the sodium, potassium, lithium, and cesium salts of *p*-ethylbenzenesulfonic acid were prepared. First, *p*-ethylbenzenesulfonic acid was prepared by the reaction of excess ethylbenzene with concentrated sulfonic acid, according to the method reported by Sempotowski,[3] under conditions that permit the removal of the water formed during the reaction as the ethylbenzene-water azeotrope. The reaction was continued until the theoretical amount of water was

[2]A. A. Morton, J. B. Davidson, and R. J. Best, "Condensations by Sodium. XXI. *n*-Octyl- and *n*-Decylsodium," *J. Am. Chem. Soc.* 64, 2239 (1942).

[3]L. Sempotowski, "Ueber isomere Derivate des Aethylbenzols," *Chemische Berichte* 22, 2662 (1889).

collected. The *p*-ethylbenzenesulfonic acid was then isolated as the barium salt, according to the directions of Paquette, Lingafelter, and Tartar.[4] The barium *p*-ethylbenzesulfonate was purified by recrystallization and was converted to the corresponding sodium, potassium, or cesium salt with a slight excess of the appropriate alkali-metal carbonate. The alkali-metal *p*-ethylbenzenesulfonate was then purified by several crystallizations from alcohol. The lithium *p*-ethylbenzenesulfonate was formed by use of lithium sulfate instead of lithium carbonate because of the insolubility of lithium carbonate. The salts obtained had the compositions indicated in Table 11.2.

Table 11.2. Compositions and Molecular Weights of Alkali-Metal *p*-Ethylbenzenesulfonates

Salt	Composition			Molecular Weight	
	Component	Mole Percent		Theoretical	Found
		Theoreticol	Found		
$C_8H_9SO_3Li$	Carbon	50.0	49.1	192	192
	Hydrogen	4.7	4.7		
	Lithium	3.6	3.5		
$C_8H_9SO_3Na$	Carbon	46.2	45.7	208	207
	Hydrogen	4.4	4.4		
	Sodium	11.0	10.9		
$C_8H_9SO_3K$	Carbon	42.8	42.1	224	226
	Hydrogen	4.0	4.1		
	Potassium	17.4	17.5		
$C_8H_9SO_3Cs$	Carbon	30.2	29.7	318	317
	Hydrogen	2.9	2.9		
	Cesium	41.8	41.8		

α-Methylnaphthalene

Three liters of α-methylnaphthalene was purified for use in organic scintillator solutions. Whereas this compound is water-white immediately following vacuum distillation, it becomes colored on standing, apparently as a result of oxidation that takes place on exposure to air. However, it was found that aeration of α-methylnaphthalene for 48 hr with a stream of oxygen followed by vacuum distillation gave an essentially water-white compound suitable for use in a liquid scintillator.

[4]R. G. Paquette, E. C. Lingafelter, and H. V. Tartar, "Studies of Sulfonates. VII. Conductances and Densities of Sodium Ethyl-, *n*-Butyl-, *n*-Octyl-, and *n*-Dodecylbenzene-*p*-sulfonate Solutions," *J. Am. Chem. Soc.* 65, 686 (1943).

Part II. Analytical Development

J. C. White
P. F. Thomason

12. Ionic Analyses

H. Kubota

DETERMINATION OF RADIOLYTIC DECOMPOSITION PRODUCTS OF DOWEX 50

C. C. White

It was desired to identify and determine the anionic products from the radiolytic decomposition of a Dowex 50 column that had been placed in the radiation field of a Co^{60} source. The column had been eluted continuously while in the field. The anionic products were isolated by passing the effluent through a column of Dowex 1 and eluting them from the column. The eluate from the Dowex 1 column was treated to remove any sulfates and sulfonates before it was submitted for analysis. The primary constituent of the remaining solution was identified as oxalic acid by a paper chromatographic technique.[1] The presence of oxalic acid was confirmed by means of a spot test that consisted in converting the oxalic acid to glyoxalic acid by reduction with nascent hydrogen and reacting the glyoxalic acid with phenylhydrazine and an oxidant in the presence of a mineral acid to form a colored product.[2]

The oxalic acid was determined quantitatively in successive fractions of the eluate by an indirect titration. A slight excess of standard $KMnO_4$ solution ($\sim$0.01 *N*) was added to a warm acidified solution of the eluate, the solution was cooled, a small crystal of KI was added, and the excess permanganate

[1] A. G. Long, J. R. Quayle, and R. J. Stedman, "The Separation of Acids by Paper Partition Chromatography," *J. Chem. Soc.* 1951, 2197.

[2] F. Feigl, *Spot Tests in Inorganic Analysis*, 6th ed., p 383, Elsevier, New York, 1960.

was back-titrated with standard ~0.01 *N* $Na_2S_2O_3$ solution. The oxalic acid concentration in the fractions was in the range from <0.01 to 2.2 mg/ml.

DETERMINATION OF Cl^- IN K METAL

H. Kubota J. R. Lund

Potassium metal was dissolved in *n*-hexane under a blanket of Ar by the slow addition of methanol. When dissolution was complete, water was added, and the organic constituents were removed by vaporization. The chloride content of the residual solution was determined by the iodometric permanganate method.

PRECISE ANALYSIS OF HBr-KBr SOLUTIONS

H. Kubota

It was desired to know the acid and Br^- contents of HBr-KBr solutions with a relative standard deviation of 0.1% or better. The determinations were made by titrating with dilute standard solutions of base and $AgNO_3$ respectively. At least 90% of the calculated amount of titrant solution required was weighed into the test solution, and the last phase of the titration was performed with an automatic titrator. The desired precision can be obtained with quantities of reactants as small as 0.1 meq.

POTENTIOMETRIC TITRATION OF Al^{3+} WITH ETHYLENEDIAMINETETRAACETIC ACID

R. F. Apple

A potentiometric titration method was devised that is applicable to the determination of Al^{3+} in an HF solution that contains zirconium. Since F^- interferes seriously in this titration, it is expelled by fuming with H_2SO_4, after which the zirconium is removed by extraction into a 0.1 *M* solution of tri-*n*-octylphosphine oxide in cyclohexane. The Al^{3+} in the aqueous phase is then determined by adding an excess of ethylenediaminetetraacetic acid and potentiometrically back-titrating the excess with a standard solution of $ZnSO_4$.

DETERMINATION OF PO_3^{3-} IN H_3PO_4-HNO_3

R. F. Apple

A procedure by Scott[3] was modified for the determination of PO_3^{3-} in 0.1 to 1 *M* H_3PO_4–6 *M* HNO_3 solutions. The PO_3^{3-} is oxidized to PO_4^{3-} by the use of Br_2 water. After the excess Br_2 is removed

[3] N. H. Furman, ed., *Scott's Standard Methods of Chemical Analysis*, 5th ed., p 191, Van Nostrand, New York, 1939.

by boiling, the Br^- is converted to BrO_3^- with ClO^-. Any excess ClO^- is reduced with HCOONa. The BrO_3^- is then reacted with excess KI. The resulting I_2, which is six times the PO_3^{3-} equivalence, is determined by titration with a standard solution of $S_2O_3^{2-}$.

DETERMINATION OF Tl IN CsI

H. Kubota

Cesium iodide was dissolved in water, and the I^- was removed by oxidation with HNO_3. Since the large quantity of cesium affected the subsequent polarographic determination of the Tl, the Tl was oxidized with Cl_2 water to Tl^{3+} and fixed on a Dowex 50 column as the chloro complex. The Tl^{3+} was then eluted as Tl^+ with water that contained a small amount of H_2SO_3, which was later removed by boiling. The polarographic determination of Tl^+ was performed in 0.1 *M* H_2SO_4.

SPECTROPHOTOMETRIC CURCUMIN METHOD FOR B

H. Kubota J. G. Surak[4]

Use of the curcumin-boron complex provides a spectrophotometric procedure that is one of the most sensitive tests for B; by means of it, as little as 0.05 μg of B can be determined. The conditions under which the color is developed were investigated, and several changes were made in existing methods. An hour-long drying and developing stage in a forced-draft oven at 75°C was found to give reproducible results and maximum sensitivity. Large amounts of alkali and alkaline-earth metals decrease the sensitivity; however, the small degree of attenuation by these substances is essentially constant over a wide range of their content.

The procedure has been used to determine B in reactor-grade graphite as well as in nitric acid. The graphite is burned in a stream of moist O_2 at 1200°C; the volatilized B is caught in an alkaline solution and is determined. A determination of B is also made on the ash following fusion with Na_2CO_3. When B is determined in HNO_3, the HNO_3 is destroyed with HCOOH prior to the color development.

STRIPPING RATE FOR CO_2 FROM WATER IN A MOLTEN-SALT REACTOR EXPERIMENT PUMP DEMONSTRATION SYSTEM

R. F. Apple

Relative to the removal of Xe from the Molten-Salt Reactor Experiment (MSRE), the rate of removal of CO_2 from water in an MSRE pump demonstration system was followed by means of pH determinations. In the initial experiments, the rate of removal of CO_2 was about 10% of the maximum theoretical rate

[4]Temporary employee from Marquette University, Milwaukee, Wis.

based on the volume fraction used. After suitable modifications were made to the system in order to increase the area of the liquid-gas interface, the CO_2-removal rate was increased to about 95% of theoretical. Although CO_2 is approximately 10^4 times more soluble in water than Xe is in MSRE fuel, the data obtained from these experiments will be useful in predicting the rate of Xe removal during normal MSRE operation.[5]

DETERMINATION OF CARBON IN STAINLESS STEEL BY DIRECT COMBUSTION

R. F. Apple

A study was made to learn whether an accelerator is necessary in the determination of carbon in high-alloy steel by combustion analysis and also to establish the minimum time required to complete the combustion and to sweep the CO_2 from the combustion tube. No accelerator is required if the combustion is carried out at 1300°C or higher. Furthermore, the combustion of carbon and the complete removal of CO_2 can be effected in 7 min.

PREPARATION OF ESSENTIALLY PURE LiF: REMOVAL OF Mg

R. F. Apple

A method was devised for preparing essentially pure LiF in which LiOH is used as the starting material. Magnesium is removed from a solution of the LiOH by extraction as a magnesium–perfluorooctanoic acid complex into ethyl ether, after which the Li^+ is precipitated as LiF that contains less than 15 ppm Mg. Precautions are given for preventing contamination by Mg introduced as an impurity in reagents.

[5]R. B. Briggs, *MSR Progr. Rept. Aug. 1, 1960, to Feb. 28, 1961*, ORNL-3122, p 134.

13. Infrared Spectral Studies

C. A. Horton

The infrared spectra of a variety of materials were obtained in order to identify functional groups; to study states of purity; to detect changes in structure due to radiation damage, reaction, or chelation; to detect adsorbed ions; and to determine band-pass regions. The samples included several substituted purines; unirradiated and irradiated $CsBrO_3$, ThO_2, and ethylenediaminetetraacetic acid; K_2ReBr_6; borate-doped KCl; organophosphorus extractants; some oximes; ceramics used to insulate thermocouple

wire; uranium oxides; plastics; and ion exchange resins. A Perkin-Elmer model 112 spectrometer with CsBr optics was used for the 15- to 40-μ region, a Beckman model IR7 for the 2.5- to 16-μ region, and a Cary model 14M for the 0.4- to 2.6-μ region.

Liquids were studied in absorption cells either directly or in solution in carbon tetrachloride, benzene, hexane, cyclohexane, or carbon disulfide. Solids were examined as mulls in mineral or fluorocarbon oil, as pellets with KBr prepared by grinding or freeze-drying, or directly in the infrared beam. Gases were examined in cells of 10-cm optical path.

14. Anodization of Sector Coils for the Analog II Cyclotron

H. L. Holsopple, Jr.

Sixteen sector coils to be used in the Analog II cyclotron were anodized to meet specifications set by the Electronuclear Research Division. Anodization was carried out in 10% H_2SO_4 in a plastic-lined 30-gal drum at 20 to 22°C with a current density of 16 amp/ft^2 for 35 min per part. Cooling was provided by use of a 55-gal drum as a water-cooling jacket for the smaller drum. The anodized surfaces showed no voltage breakdown at voltages less than 50 v when tested with a Simpson voltage test meter.

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

Group Making Analyses	Av No. in Group		Number of Results Reported																										
			For ORNL																			For Others							
	Scientists	Technicians	Analytical Chemistry	Biology	Chemical Technology	Chemistry	Electronuclear Research	Engineering and Mechanical	Health Physics	Instrumentation and Controls	Isotopes	Metallurgy	Neutron Physics	Operations	Physics	Reactor	Reactor Chemistry	Solid State	Thermonuclear	Inspection Engineering	AEC	G.E.	K-25	Miscellaneous	Paducah	University of Tennessee	Y-12	Total
Ionic Analyses[a]	15	0	18		959	35			315		10						607											1,944
Low-Radiation-Level Radiochemical Analytical Laboratory	2	2	2		135				3,649				174	157		48										76	27	4,268
Mass Spectrometry Analyses[a]	10	7	869	155	548	214					10,111	5,618		72	22	6,716	2,963	460	20				1622			2130	31,520
Nucleor Analyses[a]	8	4	194	1	781	20	5		360		268	590	30	1,780	3	1,063	382	1231								3	6,711
Optical and Electron Microscopy[a]	3	2	112		727	509			148		21	371			57	103	594	5								291	2,938
Process Analyses																												
General Analyses Laboratory	11	16	113	44	35,155	628			1,425		1,400	6,284	113	610	129	402	955	227										47,485
General Hot Analyses Laboratory	9	12			5,615				58		2,366	555		12,398		9,868	638	200					2				31,700
High-Level Alpha Radiation Laboratory	3	4	22		8,933			5	17		392	15	11	1			13	1					11	12		82	9,515
Materials Testing Laboratory	5	12	149		12,904	1322	20		24		203	1,346	155	11	20	1,206	4,677		2	49						231	22,319
Radioisotopes-Radiochemistry Laboratory	5	14			2,750	1430			1,245	21	14,123	208	1921	4,632	10	329	1,378	34				40	19	115	83	487	28,825
Radiochemical Analyses[a]	5	1			407				125		325	319	2		19	603	18	376				3					2,197
Spectrochemistry Laboratory[a]	3	2	30		801	493	150	89	898		22,199	3,202	133		75	1,430	3,581		65							2064	35,210
Thermal Breeder Reactor Projects Analytical Chemistry Laboratory[a]	1	4	15		404	13			2,540		29	1,792				3,807	7,601	4	4	33	760					132	17,134
X-Ray and Spectrochemical Analyses[a]	9	3	22		772	220	8	52	3,941	4	576	2,140	12		80	522	540	134								128	9,151
Total	89	83	1546	200	70,891	4884	183	146	14,745	25	52,023	22,440	2551	19,661	415	26,097	23,947	2672	91	82	760	43	19	1750	95	76	5575	250,917

[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
J. R. Lund
R. L. McCutchen[1] B. J. Ginocchio

Many of the Statistical Quality Control (SQC) programs that were operative in eight service laboratories of the Analytical Chemistry Division until the end of June 1961 had been partially or completely curtailed in order to compensate for revisions in the projects of other divisions and for the subsequent reduction in the analytical services required by those divisions. All the SQC programs were terminated by the end of June 1961 so that the needs of the various service laboratories, which were undergoing adjustments due to their relocation, could be re-evaluated. Revised SQC programs are now in effect. About 2800 results were obtained for control purposes in 1961, as compared with some 4300 in 1960.[2] The distribution of the results, by laboratory, is shown in Table 15.1; a similar compilation, by analysis, is presented in Table 15.2.

The quality of the work of these laboratories and the Division was about the same as that attained in 1960 (see Table 15.1).

[1]Present address, Aeroproducts Inc., Westchester, Pa.

[2]R. L. McCutchen and B. J. Ginocchio, "Quality Control," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 95.

Table 15.1. Distribution by Laboratory of Control Results for October 1960 Through June 1961

Laboratory	Number of Control Results		Quality Level (%)[a]	
	Total	Outside Fixed Limits	1960	1961
Pilot Plant Control	381	32	95	92
Reactor Analyses	723	40	96	94
Special Analyses	454	31	91	93
Process-Development Analytical	830	47	96	94
Reactor Projects Analytical	124	0	100	100
Thermal Breeder Reactor Projects Analytical Chemistry	58	1	99	98
Raw Materials	302	12	98	96
Miscellaneous Analyses	8	0	98	100
	2880	163	Av 97	Av 96

[a]Percent of control data inside fixed limits.

Table 15.2. Distribution by Analysis of Control Results for October 1960 Through June 1961

Type of Method	Constituent	Number of Control Programs		Number of Control Results	
Colorimetric (spectrophotometric)	Chromium	4		103	
	Iron	4		106	
	Nickel	4		96	
	Nitrate	1		8	
	Thorium	4		477	
	Uranium	6		603	
	Vanadium	1		1	
			24		1394
Conductometric	Free acid	2		93	
			2		93
Coulometric	Copper	2		158	
	Nickel	2		152	
	Uranium	4		291	
			8		601
Electrogravimetric	Copper	1		10	
			1		10
Fluorometric	Uranium	7		399	
			7		399
Photometric	Sulfate	2		100	
			2		100
Potentiometric	Free acid	1		56	
	Sulfate	2		56	
	Uranium	1		78	
			4		190
Volumetric	Thorium	1		4	
	Uranium	3		71	
	Vanadium	1		1	
			5		76
Total			53		2863

16. Ionic Analyses

J. C. White
P. F. Thomason

Ionic service analyses continued to be of the same types they have been in past years.

17. Low-Level Radiochemical Laboratory

M. T. Kelley
C. L. Burros

The Low-Level Radiochemical Laboratory reported 4268 analyses. Approximately 85% of them were made for the Health Physics Division in connection with their environmental study on White Oak Creek and their area-monitoring, ecological, and waste-disposal programs. Samples continued to be of the same types as those submitted in past years.

18. Mass Spectrometric Analyses

A. E. Cameron
J. R. Sites

The Analytical Mass Spectrometry Laboratory reported 31,520 determinations from 3845 samples. About one-third of these were relative to the expanded program of electromagnetically separated stable isotopes. Another third were for the Metallurgy and Reactor Divisions in support of their reactor-development programs.

Several hundred determinations were made for the Isotopes Division on samples enriched in Ar^{36}, Ne^{21}, Ne^{22}, and C^{13} by thermal diffusion.

A number of fission product gases were analyzed. One gas mass spectrometer was modified so that about one-fiftieth as much sample as is usually required can be analyzed.

The number of determinations of stable isotopes increased 63%, whereas the charge per sample decreased 20%.

Several hundred cylinders of He, Ar, and N_2, as well as numerous special mixtures in cylinders, were certified.

19. Spectrochemical Analyses Laboratory

C. D. Susano
J. A. Norris
Z. Combs

More than 2500 samples were analyzed in the Spectrochemical Analyses Laboratory, and approximately 35,000 results were reported. The majority of the samples originated in the Isotopes Division and included the stable isotopes of Pb, Os, Ag, Pd, Nd, Ti, Lu, Te, C, Cl, Rb, Dy, Zr, Ru, Mg, Ga, Ca, Si, Ba, B, Cd, K, Ir, Cr, Li, Fe, W, V, Ni, Se, Sm, Yb, Zn, Tl, and Gd. The Development Group of the Stable Isotopes Department submitted samples of Ca, Sn, and Mg taken from various experimental collector pockets to determine retention and scatter patterns of the ion beam. The Reactor Chemistry Division submitted miscellaneous materials for analysis, including numerous samples of BeO, graphite, and Li compounds.

New standards consisting of various common impurities in matrices of NiO and Mn_2O_3 were prepared and were used to establish that the limit of detection of these impurities is about 10 ppm.

20. Process Analyses

L. T. Corbin

High-Level Alpha Radiation Laboratory

J. H. Cooper

Most of the analyses performed by the High-Level Alpha Radiation Laboratory were for the Chemical Technology Division relative to the processing of transuranium elements. Alpha emitters, such as Am^{241}, Cm^{242}, Cf^{252}, and Es^{253}, were determined by gross alpha counting and alpha pulse-height analysis. In mixtures of Cm^{242} and Cf^{252}, each of which emits 6.11-Mev alpha particles, the Cf^{252} was determined by counting the spontaneous fissions. The alpha count rate of the Cf^{252} was calculated from the fission rate and was subtracted from the gross-alpha count rate to give the Cm^{242} alpha count rate.

Berkelium-249 was determined by counting the 0.10-Mev beta radiation in a windowless gas-flow proportional counter.

Determinations of plutonium alpha activity were made on solutions in which the uranium alpha activity was 10^4 times the plutonium activity. After the plutonium was separated from the uranium, alpha pulse-height analyses showed that only about 0.002% of the uranium was counted with the plutonium.

A solid-state detector has been acquired for alpha-energy analyses in conjunction with the multichannel analyzer.[1] This detector is more suitable than the ionization chamber, because higher count rates of alpha and beta activity can be tolerated.

One room in the High-Level Alpha Radiation Laboratory has been decontaminated thoroughly and remodeled in order to provide a place for reagent preparation and for low-level-activity analyses.

General Analyses Laboratory

W. R. Laing

Several new methods were put into use in the General Analyses Laboratory. A total of 47,485 analyses were made. Among the new methods are the determination of nitrogen in sol-gel ThO_2; measurements of density by displacement of toluene, of mercury, or of He; vibratory compaction tests; and the determination of Tc in Tc metal and in NH_4TcO_4. Other analyses were made for Sn and Mo in salts from the Volatility Process, S in nonirradiated and irradiated resins, H_2O in tributyl phosphate, Cl^- in insulating material, and U^{4+} and U^{6+} in UO_2 and ThO_2-UO_2. Also, attrition rates and surface area measurements were made on irradiated ThO_2. Gases evolved from alloys and oxides were measured and were submitted for mass assay.

The quality-control program was expanded to include the preparation of 15 new control samples that contain from one to eight elements in known concentrations.

General Hot Analyses Laboratory

C. E. Lamb

The General Hot Analyses Laboratory was formed by combining the Pilot-Plant Control Laboratory with the Reactor Analyses Laboratory. The work requirements of each group were reviewed, and work areas were reorganized to reduce duplication of equipment and services, to permit consolidation of work requiring similar methods of analysis, and to suitably equip the laboratories and the HRLAF work cells for greater versatility in the analysis of highly radioactive materials. The staff of the new group is 20% smaller than the total staff of the two former groups.

A remotely controlled conductometric titration[2] was used to determine free acid in the feed solutions from the HRT during its final six months of operation. The relative error for the method was −1.1% for 55

[1] J. H. Cooper, "High-Alpha Analytical Laboratory," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 101.

[2] U. Koskela, "Reactor Analyses Laboratory," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 104–5.

core control samples. The relative error for all samples was −2.4%.[3] The range of free-acid concentration in the control samples was 0.0089 to 0.0640 *N*. In addition, the method[2] was tested for applicability to the determination of sulfate in HRT samples, but mechanical difficulties that developed during the tests prevented sufficient investigation. However, the relative error for eight control samples before the trouble developed was −0.4%.

A technique for removing radioactive NaF-LiF-ZrF_4 salt samples from copper sample ladles from the Volatility Process was devised for use in the HRLAF. The ladle ($\frac{1}{2} \times 1$ in.) is heat-sealed within a thick-walled polyethylene tube and is crushed in the jaws of a vise operated by compressed air. The polyethylene sleeve is cut open, and the powdered salt is poured into a bottle for analysis.

Small plates cut from irradiated fuel elements were submitted by the Solid State Division for analysis to determine burnup. Two types of alloys, Al-Si-U and Al-UC_2, required dissolution by refluxing with 9 *M* H_2SO_4 for 16 hr, with periodic additions of H_2O_2. Sections of irradiated stainless-steel-clad Eu_2O_3 samples were submitted for europium determination.[4] They were dissolved by refluxing for 16 to 40 hr in 2.5 *M* HNO_3–5 *M* HCl.

A method for determining the oxygen-to-uranium ratio[5] in irradiated UO_2 pellets received from the Solid State Division was adapted for use in the HRLAF. The method requires that an atmosphere of Ar be maintained over the sample during dissolution and analysis.

Three chemists from India, on a six-month assignment at ORNL, were trained in the use of the analytical methods needed in the Purex Process.

Materials Testing Laboratory

L. J. Brady

The Materials Testing Laboratory, which began operation in June 1961, is a unit comprised of five laboratories in which five chemists and twelve analysts work. This unit was formed when the following laboratories, formerly located at Y-12, were consolidated and moved into new facilities in Building 4500 at ORNL: the Counting, the Raw Materials, the Reactor Projects, and the Miscellaneous Analyses Laboratories. The Materials Testing Laboratory works in close cooperation with the General Analyses Laboratory and shares a sample-receiving and reporting facility with it.

In addition to the types of analyses that were done before the reorganization, the Materials Testing Laboratory is now analyzing metal oxides and fused fluoride salts for oxygen by the $KBrF_4$ method and is also using a Perkin-Elmer vapor fractometer in the chromatographic analysis of gas mixtures. Work of the type done previously by the Counting Laboratory on the analysis of samples for Pu, Am, and other alpha emitters has been transferred to the High-Level Alpha Radiation Laboratory.

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[3]From D. M. Richardson, Reactor Chemistry Division, to U. Koskela, private communication (October 1961).

[4]W. D. Shults, "Controlled-Potential Coulometric Determination of Europium," *Anal. Chem.* 31, 1095 (1959).

[5]H. Kubota, "Determination of the Stoichiometry of Uranium Dioxide. Polarographic Determination of Uranium(VI) in Uranium Dioxide," *Anal. Chem.* 32, 610 (1960).

Prior to the move from Y-12 in June, the four laboratories that were consolidated into the Materials Testing Laboratory analyzed some 6000 samples and reported about 16,000 results. Since then, about 22,300 results have been reported.

Radioisotopes-Radiochemistry Laboratory

E. I. Wyatt

About half the work of the Radioisotopes-Radiochemistry Laboratory was for the Isotopes Division. The group is now doing some of the radioactivation work formerly done by the Nuclear Analyses Group. The radioactivation work together with the general radiochemistry and low-level work was moved to Building 3550. New multichannel spectrometers were purchased and are in service in Buildings 3038 and 3550. These instruments are used for alpha, beta, and gamma work by interchanging detectors. A catalog of beta spectra for most of the radioisotope products was compiled. To obtain a spectrum, an anthracene crystal is used as the detector, and the spectrum that appears on an oscilloscope is photographed with a Polaroid camera. This type of identification requires only a small fraction of the time required for beta-absorption studies. The half-life values for some 20 radionuclides were determined and published.[6] A monograph on the radiochemistry of ruthenium[7] and a paper on the determination of radioantimony[8] were published. Another paper on the determination of promethium and radioyttrium was accepted for publication in *Analytical Chemistry*.

The contract for construction of analytical "hot" cells in Building 3038 has been let; construction of the cells should be completed by May 1962.

A special analytical hot cell for use in assaying I^{131} products was put into service in Building 3026-C. Metals in radioisotope products are now being determined flame photometrically in the same laboratory.

High-Radiation-Level Analytical Facility

L. G. Farrar

The improvement of containment continues to have high priority in the work of the High-Radiation-Level Analytical Facility (HRLAF). The number of penetrations in the cell faces was reduced in order to decrease the pressure inside the cells. Pressure gages were installed on each cell to indicate when the working conditions are safe.

A new filter system for the ventilation system was put in operation, and closer control of air flow was established. In connection with the new filter system, local alarms and indicators are being installed in the HRLAF operating area.

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[6] E. I. Wyatt *et al.*, "Half-Lives of Radionuclides – II," *Nuclear Sci. and Eng.* 11, 74 (1961).

[7] E. I. Wyatt and R. R. Rickard, *The Radiochemistry of Ruthenium*, NAS-NS-3029 (February 1961).

[8] R. W. Lowe *et al.*, "Determination of Radioantimony by Extraction into Diisobutylcarbinol," *Anal. Chem.* 33, 874 (1961).

Several minor improvements have been made on the model 8 manipulators. The introduction of spring-loaded turnbuckles for the azimuth cables has decreased manipulator down time and boot replacement. Teflon disks were added to the manipulator boom tubes to minimize boot failure and to decrease the cost of initial installation of stainless steel parts.

Modifications were made to the carrier cart to make possible the use of heavier casks for unloading radioactive material in the storage cell.

Three work cells and the equipment used for the analyses of HRT materials were decontaminated completely. The equipment was stored, and the work cells were re-equipped for analyses required in current radioactive processes. A flame photometer for the analysis of radioactive solutions was installed in one of the work cells.

In order to comply with the recommendations of Radiation Safety and Control, modifications continue to be made in the operating procedures for waste disposal and for the transfer of radioactive materials. The amount of radioactive materials stored in the facility was decreased.

21. Radiochemical Analyses

J. C. White
W. S. Lyon

Special or unusual samples continue to be handled by the Radiochemical Analyses Group; a large number of air, filter, and radioisotope product samples have been turned over to the service laboratories together with procedures for analyzing them. Cooperation between the research group and the service organizations has made possible the smooth transfer of established methods and responsibility for analyses to the service laboratories; the Radiochemical Analyses Group retains responsibility for method development.

22. Thermal Breeder Reactor Projects Analytical Chemistry Laboratory

C. D. Susano
H. E. Zittel C. K. Talbott

The Thermal Breeder Reactor Projects Analytical Chemistry Laboratory made over 17,000 analyses on some 4200 samples. Of these, about 45% were submitted by the Reactor Chemistry Division, 20% by the Health Physics Division, and 15% by the Reactor Division; the remainder were derived from 15 other sources. The samples consisted principally of solutions of UO_2SO_4 (many of which contained $CuSO_4$),

water, solutions of NH_4F, clamshells, HNO_3 solutions, ThO_2 and slurries thereof, mixtures of fluoride salts, and high-alloy steel. Analyses were made less frequently on a wide variety of materials including plant materials; soils; and solutions of HCl, LiCl, $K_2Cr_2O_7$, NH_4OH, and fluorescein. Methods of analysis included volumetry, gravimetry, spectrophotometric and potentiometric titrimetry, spectrophotometry, flame spectrophotometry, polarography, thermogravimetry, and gasometry. Physical measurements were made on many samples; the measurements included pH, conductivity, particle-size distribution, specific gravity, and zeta potential.

Part IV. ORNL Master Analytical Manual

23. ORNL Master Analytical Manual

M. T. Kelley
Helen P. Raaen H. P. House
Authors of Methods

The third supplement has been issued to the reprinted form of the *ORNL Master Analytical Manual.* It contains the new and revised methods issued in 1960. This supplement is available from the Office of Technical Services, Department of Commerce, Washington 25, D.C., for $7.75; it is designated TID-7015 (suppl 3).

Twenty-three new methods were added to the *Manual* (see "Presentations of Research Results"); of these, eight were for the purpose of record only. Nine revised methods were issued. The subsection 9 08, "Homogeneous Reactor Project (HRP) Methods," and a number of other methods no longer in current use were recalled. The Table of Contents for the entire *Manual* was revised to bring it up to date. The *Manual* was issued to three new custodians.

A survey was made to determine from the authors of each method what revisions to methods are needed; those needed are being made.

Presentations 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
Kelley, M. T., D. J. Fisher, W. D. Cooke,[1] H. C. Jones	"Controlled-Potential and Derivative Polarography," pp 158–82 in *Advances in Polarography*, vol 1, ed. by I. S. Longmuir	Pergamon, New York, 1960
Miller, H. H.,[2] M. T. Kelley, P. F. Thomason	"Polarographic Studies of the Reduction of Pertechnetate Ion in Aqueous Solutions," pp 716–26 in *Advances in Polarography*, vol 2, ed. by I. S. Longmuir	*Ibid.*
Zittel, H. E., M. T. Kelley, F. L. Conover,[3] G. R. Wilson	"Effect of Phosphate and Other Anions in the Polarography of Uranium in Acid Media," pp 530–37 in *Advances in Polarography*, vol 2, ed. by I. S. Longmuir	*Ibid.*
Bate, L. C., G. W. Leddicotte	*The Radiochemistry of Cobalt*, Nuclear Science Series Report NAS-NS-3041, September 1961	National Academy of Sciences – National Research Council, Washington, D.C.
Dyer, F. F., G. W. Leddicotte	*The Radiochemistry of Copper*, Nuclear Science Series Report NAS-NS-3027, April 1961	*Ibid.*
Emery, J. F., G. W. Leddicotte	*The Radiochemistry of Gold*, Nuclear Science Series Report NAS-NS-3036, April 1961	*Ibid.*
Leddicotte, G. W.	*The Radiochemistry of Iridium*, Nucleor Science Series Report NAS-NS-3045, October 1961	*Ibid.*
	The Radiochemistry of Manganese, Nuclear Science Series Report NAS-NS-3018, October 1960	*Ibid*

[1] Cornell University, Ithaca, N. Y.

[2] USAEC, Washington, D.C.

[3] Vanderbilt University, Nashville, Tenn.

	The Radiochemistry of Osmium, Nuclear Science Series Report NAS-NS-3046, October 1961	*Ibid.*
	The Radiochemistry of Platinum, Nuclear Science Series Report NAS-NS-3044, October 1961	*Ibid.*
	The Radiochemistry of Rhenium, Nuclear Science Series Report NAS-NS-3028, April 1961	*Ibid.*
	The Radiochemistry of Selenium, Nuclear Science Series Report NAS-NS-3030, April 1961	*Ibid.*
	The Radiochemistry of Tellurium, Nuclear Science Series Report NAS-NS-3038, July 1961	*Ibid.*
Moore, F. L.	*Liquid-Liquid Extraction with High Molecular-Weight Amines*, Nuclear Science Series Report NAS-NS-3101, December 1960	*Ibid.*
Mullins, W. T., G. W. Leddicotte	*The Radiochemistry of Tungsten*, Nuclear Science Series Report NAS-NS-3042, September 1961	*Ibid.*
White, J. C., W. J. Ross	*Radiochemical Techniques. Separations by Solvent Extraction with Tri-n-octylphosphine Oxide*, Nuclear Science Series Report NAS-NS-3102, February 1961	*Ibid.*
Wyatt, E. I., R. R. Rickard	*Radiochemistry of Ruthenium*, Nuclear Science Series Report NAS-NS-3029, February 1961	*Ibid.*

Articles

Author(s)	Title	Publication
Apple, R. F., J. C. White	"Separation and Colorimetric Determination of Trace Quantities of Magnesium in High-Purity Beryllium Oxide"	*Talanta* 8, 419 (1961)
Belew, W. L., G. R. Wilson, L. T. Corbin	"Spectrophotometric Determination of Ruthenium by Thiocyanate"	*Anal. Chem.* 33, 886 (1961)
Boyd, C. M., O. Menis[4]	"Coulometric Determination of Uranium(IV) by Oxidation at Controlled Potentials"	*Ibid.*, p 1016
Cooke, W. D.,[1] M. T. Kelley, D. J. Fisher	"Capillary Behavior in High Sensitivity Polarography"	*Ibid.*, p 1209
Dean, J. A.,[5] J. C. Burger,[5] T. C. Rains, H. E. Zittel	"Flame Spectrophotometric Study of Barium"	*Ibid.*, p 1722
Eldridge, J. S., S. A. Reynolds	"Analytical Radiochemistry and Nuclear Incidents"	*Nuclear Safety* 2(4), 41 (1961)

[4]Nuclear Materials and Equipment Corp., Apollo, Pa.

[5]University of Tennessee, Knoxville.

Eldridge, J. S., W. S. Lyon	"Promethium-148"	*Nuclear Phys.* **23**, 131 (1961)
Feldman, C.	"Evaporation of Boron from Acid Solutions and Residues"	*Anal. Chem.* **33**, 1916 (1961)
Fisher, D. J., M. T. Kelley, W. L. Belew	"A Corrosion-Resistant Pipetter for Remote Measurement of Radioactive Samples"	*Proceedings, Fourth Conference, Analytical Chemistry in Nuclear Reactor Technology*, TID-7606, p 311 (January 1961)
Goldstein, G., D. L. Manning, O. Menis,[4] J. A. Dean[5]	"Spectrophotometric Methods for the Determination of Osmium – I. Extraction and Ultraviolet Spectrophotometric Determination of Osmium Tetroxide"	*Talanta* **7**, 296 (1961)
	"Spectrophotometric Methods for the Determination of Osmium – II. Extraction and Determination of Osmium in Situ with 1·5-Diphenylcarbohydrazide"	*Ibid.*, p 301
	"Spectrophotometric Methods for the Determination of Osmium – III. Reaction of Osmium Tetroxide with 1:5-Diphenylcarbohydrazide in Aqueous Solutions Followed by Extraction of the Complex"	*Ibid.*, p 307
Goldstein, G., O. Menis,[4] D. L. Manning	"Indirect Determination of Sulfate by Nonaqueous Titrimetry"	*Anal. Chem.* **33**, 266 (1961)
Handley, T. H., J. A. Dean[5]	"Triphenyl Phosphite, a Selective Extractant for Copper(I) Halides"	*Ibid.*, p 1087
Harmatz, B., T. H. Handley,* J. W. Mihelich[6]	"Nuclear Levels in a Number of Even-Even Rare Earths ($150 \leq A \leq 184$)"	*Phys. Rev.* **123**, 1758 (1961)
Horton, C. A., J. C. White	"Infrared Spectra of Some Organophosphorus Extractants"	*Talanta* **7**, 215 (1961)
Lowe, R. W.,[7] S. H. Prestwood, R. R. Rickard, E. I. Wyatt	"Determination of Radioantimony by Extraction into Diisobutylcarbinol"	*Anal. Chem.* **33**, 874 (1961)
Lyon, W. S.	"Gamma Branching in Kr^{85}"	*Nuclear Sci. and Eng.* **9**, 148 (1961)
	"Reactor Neutron Activation Cross Sections for a Number of Elements"	*Nuclear Sci. and Eng.* **8**, 378 (1960)
Lyon, W. S., J. S. Eldridge, L. C. Bate	"3.1-Hour Y^{90m}"	*Phys. Rev.* **123**, 1747 (1961).
Miller, F. J., H. C. Jones	"Absorption Cell Attachment for a Welch Densichron Reflection Unit"	*Anal. Chem.* **33**, 651 (1961)
Miller, F. J., P. F. Thomason	"Spectrophotometric Determination of Technetium with Toluene-3,4-dithiol"	*Ibid.*, p 404

[6] University of Notre Dame, Notre Dame, Ind.

[7] Vanderbilt University Medical School, Nashville, Tenn.

Moeller, D. W.,[8] G. W. Leddicotte, S. A. Reynolds	"Behavior of Radionuclides on Ion-Exchange Resins"	*J. Am. Water Works Assoc.* 53, 862 (1961)
Moore, F. L.	"New Technique for the Separation of Trivalent Actinide Elements from Lanthanide Elements"	*Anal. Chem.* 33, 748 (1961)
Rains, T. C., Marion Ferguson, H. P. House	"Separation of Macro Quantities of Thorium with 2-Thenoyltrifluoroacetone"	*Ibid.*, p 1645
Ross, W. J., J. C. White	"Application of Pyrocatechol Violet as a Colorimetric Reagent for Tin"	*Ibid.*, p 421
	"Extraction of Tin with Tris-(2-ethylhexyl)-phosphine Oxide and Its Determination in Nonaqueous Medium with Pyrocatechol Violet"	*Ibid.*, p 424
Shults, W. D.	"Coulometric Generation and Back-Titration of Intermediate Reagents at Controlled Potential. Application to the Determination of Plutonium"	*Ibid.*, p 15
Stelzner, R. W.	"Single-Beam Gamma Absorptiometer"	*Proceedings, Fourth Conference, Analytical Chemistry in Nuclear Reactor Technology*, TID-7606, pp 276–90 (January 1961)
Weston, L. W., W. S. Lyon*	"Neutron Capture Cross Section of Gold at 30 kev and 64 kev"	*Phys. Rev.* 123, 948 (1961)
Wyatt, E. I., S. A. Reynolds, T. H. Handley, W. S. Lyon, H. A. Parker	"Half-Lives of Radionuclides – II"	*Nuclear Sci. and Eng.* 11, 74 (1961)
Zittel, H. E., L. B. Dunlap, P. F. Thomason	"Determination of Uranium in the Presence of Molybdenum by Controlled-Potential Coulometric Titration"	*Anal. Chem.* 33, 1491 (1961)

Reports

Author(s)	Title	Report No.
Apple, R. F., H. P. House	"A Study of Some Factors Affecting the Combustion Analysis of Carbon in High-Alloy Steel"	ORNL CF-61-9-61 (Sept. 8, 1961)
Apple, R. F., J. C. White	"Preparation of Essentially Pure Lithium Fluoride: Removal of Magnesium"	ORNL CF-61-6-31 (June 5, 1961)
Biggers, R. E.,* R. G. Wymer	"Design and Development of a High-Temperature High-Pressure Spectrophotometer System: Status Report"	ORNL CF-60-11-96 (Nov. 12, 1960)
	"Fabrication, Testing, and Installation of a High-Temperature, High-Pressure Recording Spectrophotometer System"	Specification No. CTD-4 (Sept. 27, 1961)

[8]U.S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

Dragoumis, P.,[9] J. R. Weir, G. W. Leddicotte*	"Fast-Flux Measurements in the ORR Core"	ORNL-3028 (Jan. 16, 1961)
Emery, J. F.	"Evaluation of 'Pickle-Band' Counting Shields"	ORNL CF-61-7-68 (July 25, 1961)
Fisher, D. J., H. C. Jones	"Check Out and Test Procedure for the ORNL Model Q-1988-ES or Q-1988A Controlled-Potential and Derivative Polarograph with Electronic Scan"	ORNL Test Specification ST-175A (July 21, 1961)
Goldstein, G.	"Sorption of Uranium on Zirconium Oxide"	ORNL-3177 (Aug. 28, 1961)
Goldstein, G., H. E. Zittel	"Amperometric Titrations with EDTA Using Iron(II) as the Indicator. Application to the Determination of Thorium"	ORNL CF-61-2-34 (Feb. 6, 1961)
Kelley, M. T.	"Statistical Quality Control Report Anal. Chem. Div. January through June, 1961"	ORNL CF-61-8-93 (Aug. 31, 1961)
Maddox, W. L.	"Modified Motorizing Assembly for Lab-Jack"	ORNL CF-61-4-52 (Apr. 21, 1961)
White, J. C.	"Synthesis of Dimethyl Telluride"	ORNL CF-61-2-7 (Feb. 2, 1961)
Wymer, R. G., R. E. Biggers*	"Čerenkov Radiation Intensity Calculations for Sr and Co in Water"	ORNL-3180 (Sept. 5, 1961)
Young, J. P.	"Spectrophotometry of Molten Salts Status Report, September through December, 1960	ORNL CF-60-12-83 (Dec. 21, 1960)
	"Spectrophotometry of Molten Salts Status Report, January through March, 1961"	ORNL CF-61-3-61 (Mar. 14, 1961)
Zittel, H. E.	"Anionic Interferences in the Flame Spectrophotometric Determination of Calcium: Use of Ethlene Glycol as a Releasing Agent"	ORNL-CF-61-2-82 (Feb. 21, 1961)
	"Conductometric Titrations of Sulfate by the Nonaqueous Barium Acetate Method"	ORNL CF-61-3-41 (Mar. 3, 1961)
Zittel, H. E., T. C. Rains, Marion Ferguson, H. P. House	"Separation of Macro Quantities of Thorium with 2-Thenoyltrifluoroacetone"	ORNL CF-61-3-62 (Mar. 7, 1961)

New Methods Issued to *ORNL Master Analytical Manual*

Author(s)	Title	Number(s)	Date
Emery, J. F., G. W. Leddicotte	"Fluorine, Neutron Activation Analysis (Direct Measurement) Method"	5 11281	2-17-61
	"Gold, Neutron Activation Analysis (Direct Measurement) Method"	5 11331	2-21-61
	"Niobium, Neutron Activation Analysis (Direct Measurement) Method"	5 11551	2-20-61
	"Vanadium, Neutron Activation Analysis (Direct Measurement) Method"	5 11931	2-23-61

[9] American Electric Power Service Corp., New York, N. Y.

Horton, A. D.	"Oxides of Carbon and of Nitrogen, Gas Chromatographic Method"	1 220019 9 00720019	9-19-61
Leddicotte, G. W.	"Selenium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11760	3-3-61
Mullins, W. T., G. W. Leddicotte	"Silicon, Neutron Activation Analysis (Isotopic Carrier; Distillation Precipitation) Method"	5 117701	9-28-61
	"Sodium, Neutron Activation Analysis (Direct Measurement) Method	5 11791	2-20-61
Pritchard, C. A.	"Other Alkali Metals in Cesium Compounds, Flame Spectrophotometric Standard Addition Method"	1 230009 9 073008	7-20-61
Ross, W. J.	"Thorium in Solutions that Contain Sulfate and Phosphate, Tri-*n*-octylphosphine Oxide Extraction – Spectrophotometric Thoron Method"	1 218711 9 00718711	6-30-61
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Author(s)	Title	Number(s)	Date
Bate, L. C., G. W. Leddicotte	"Particle-Size Distribution in Thorium Oxide, Neutron Activation–Sedimentation Method"	5 10200	R. 10-10-61
Cooper, J. H.	"Density of Uranium and Plutonium Product Solutions, Direct Weighing Method"	9 043100	R. 9-6-61
Koskela, U., C. E. Lamb	"Uranium, Spectrophotometric Ammonium Thiocyanate Method"	1 219210 9 00719210	R. 10-9-61
Wyatt, E. I.	"Antimony-124, HSA, Product Analysis Guide"	9 0733041	R. 2-24-61
	"Antimony-125, CF, Product Analysis Guide"	9 0733042	R. 2-23-61
	"Arsenic-77, Product Analysis Guide"	9 0733064	R. 9-15-61
	"Iridium-192, Product Analysis Guide"	9 0733401	R. 9-15-61
	"Molybdenum-99, Product Analysis Guide"	9 0733501	R. 9-21-61
	"Nickel-63, Product Analysis Guide"	9 0733541	R. 9-21-61

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Author(s)	Title	Number(s)	Date
Gaitanis, M. J., U. Koskela	"Preparation of Homogeneous Reactor Test Fuel for Mass Spectrometric Analysis"	9 082204	10-4-61
Horton, A. D.	"Reactor Off Gas and Shield Gas from the Homogeneous Reactor Test, Gas Chromatographic Method"	9 082227	10-4-61
Koskela, U.	"Hydrazine in Water, Iodimetric Titration Method"	9 082223	6-8-61
Manning, D. L.	"Sulfate in Solutions of High Ionic Strength, High-Frequency Titrimetric Method"	1 218122 9 00718122	6-1-61
	"Free Acid in Solutions of High Ionic Strength, High-Frequency Titrimetric Method"	1 220018 9 00720018	6-1-61
Musick, W. R., C. Feldman	"Metallic Impurities in Homogeneous Reactor Test Fuels, Spectrographic Method"	9 082224	9-25-61
Zittel, H. E.	"Free Acid in Homogeneous Reactor Test Fuels, Conductometric Titration Method"	9 082225	9-26-61
	"Total Sulfate in Homogeneous Reactor Test Solutions, Automatic Photometric Barium Perchlorate Titration Method"	9 082226	9-21-61

ORAL PRESENTATIONS

The Analytical Chemistry Division sponsored a Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology at Gatlinburg, Tennessee, on October 10–12, 1961. The committee consisted of C. D. Susano (chairman), H. P. House, S. A. Reynolds, T. E. Willmarth, and H. E. Zittel. Forty-six papers were presented.

This conference was held concurrently with the Second Conference on Nuclear Reactor Chemistry. There were 321 registrants: 175 from Oak Ridge, 57 from industrial organizations, 34 from other AEC installations, 23 from foreign countries, 9 from colleges and universities, 15 from governmental agencies other than the AEC, 5 from the AEC, and 3 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; and those of the Fourth Conference as TID-7606.

A Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology has been tentatively scheduled to be held at Gatlinburg, Tennessee, on October 9–11, 1962.

At Meetings of Professional Societies

Author(s)	Title	Presented at
Bate, L. C.,[10] G. W. Leddicotte	"Minor Elements in Water by Neutron Activation"	140th Meeting, American Chemical Society, Chicago, Ill., Sept. 3–8, 1961
Biggers, R. E.	"Mathematical Resolution of Complex Overlapping Spectra and Spectral Fine Structure by Means of High-Speed Digital Computing"	XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, Aug. 6–12, 1961
Costanzo, D. A.,[10] A. Timnick[11]	"A Resonant Cavity High Frequency Oscillometer"	9th Detroit Anachem Conference, Detroit, Mich., Oct. 16–18, 1961
Costanzo, D. A.,[10] W. D. Shults	"Applications of Controlled-Potential Coulometric Titrimetry to the Determination of Europium"	5th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961
Dunlap, L. B.,[10] W. D. Shults	"Determination of Sb by Controlled-Potential Coulometry"	5th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961
Feldman, C.	"Evaporation of Boron from Acid Solutions and Residues"	12th Annual Symposium on Spectroscopy, Society for Applied Spectroscopy, Chicago, Ill., May 15–18, 1961
	"The Excitation of Liquids for Spectrochemical Analysis"	Symposium, Society for Applied Spectroscopy and Instrument Society of America, Cincinnati, Ohio, Apr. 11–12, 1961
	"Fundamental Processes in Flame Photometry"	Monthly Meeting, Spectroscopy Society of Pittsburgh, Pittsburgh, Pa., Apr. 19, 1961
Fisher, D. J.,[10] M. T. Kelley, W. L. Belew	"Quantitative Derivative Polarography"	140th Meeting, American Chemical Society, Chicago, Ill., Sept. 3–8, 1961
Goldberg, G.	"Determination of Oxides and Nitrides in Salts and Metals by High-Temperature Fluorination with $KBrF_4$"	5th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961
Goldstein G., D. L. Manning,[10] H. E. Zittel	"Amperometric Titrations with Ethylenediaminetetraacetic Acid (EDTA) using Iron(II) as the Indicator Ion"	Southwest and Southeast Regional Meeting, American Chemical Society, New Orleans, La., Dec. 7–9, 1961

[10] Speaker.

[11] Michigan State University, East Lansing.

Handley, T. H.,[10] J. A. Dean[5]	"*O,O'*-Dialkyl Phosphorodithioates as Extractants for Metals"	Southwest and Southeast Regional Meeting, Americal Chemical Society, New Orleans, La., Dec. 7–9, 1961
Kelley, M. T.	"Microanalytical Techniques in the Analysis of Highly Radioactive Materials"	1961 International Symposium on Microchemical Techniques, University Park, Pa., Aug. 13–18, 1961
Kelley, M. T., D. J. Fisher, H. C. Jones[10]	"High-Resolution, High-Sensitivity, Scanning, Recording, Flame Spectrophotometer"	5th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961
Kelley, M. T.,*[10] J. W. Landry, T. S. Mackey, R. W. Stelzner*	"Inline Applications of Gamma Monitoring and Uranium Colorimetry"	Joint Nuclear Instrumentation Symposium, North Carolina State College, Raleigh, N. C., Sept. 6–8, 1961
Leddicotte, G. W.	"Neutron Activation Analysis"	Southern California Industrial Radioisotopes Conference, Los Angeles, Calif., January 1961
	"New Techniques Using Radioisotopes in Analytical Chemistry"	Colloquium, U.S. Naval Research Laboratory, Washington, D.C., Mar. 15, 1961
	"Radioactivation Analysis"	Asilomar Conference, California Association of Chemistry Teachers, Monterey, Calif., August 1961
	"Radioactivation Analysis: A Sensitive and Specific Method for Metal Analysis"	64th Annual Meeting, American Society for Testing Materials, Atlantic City, N. J., June 25–30, 1961
	"Radioisotopes in Analytical Chemistry"	Asilomar Conference, California Association of Chemistry Teachers, Monterey, Calif., August 1961
	"Useful Applications of Radioactivation Analysis"	Seminar, Chemical Sciences Division, Georgia Institute of Technology, Atlanta, Ga., Apr. 28, 1961
Leddicotte, G. W. L. C. Bate[10]	"Neutron Activation Analysis"	R. A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Apr. 6, 1961
Leddicotte, G. W., D. W. Moeller,[8] M. T. Kelley[10]	"Determination of Trace Elements in Water by Neutron Radioactivation"	139th Meeting, American Chemical Society, St. Louis, Mo., Mar. 21–30, 1961
Lyon, W. S.,[10] J. S. Eldridge, L. C. Bate	"A New Isomer of Yttrium (3.1-hr Y^{90m})"	5th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 10–12, 1961
Moeller, D. W.,[8] G. W. Leddicotte, S. A. Reynolds[10]	"Behavior of Radionuclides on Ion-Exchange Resins"	139th Meeting, American Chemical Society, St. Louis, Mo., Mar. 21–30, 1961

Moore, F. L.	"New Techniques for the Separation of Trivalent Actinide Elements from Lanthanide Elements"	139th Meeting, American Chemical Society, St. Louis, Mo., Mar. 21–30, 1961
Mullins, W. T.	"The Determination of Silicon by Neutron Radioactivation Analysis"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 27–Mar. 1, 1961
Mullins, W. T., F. F. Dyer[10] J. F. Emery, L. C. Bate, G. W. Leddicotte	"The Determination of Stable Trace Elements in Radioactive Materials by Neutron Radioactivation Analysis"	Southwest and Southeast Regional Meeting, American Chemical Society, New Orleans, La., Dec. 7–9, 1961
	"The Determination of Thorium and Uranium in Beryllium Metal by Neutron Activation and Gamma Spectrometry"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 27–Mar. 1, 1961
Norris, J. A.	"Spectroscopy Can Do Everything"	6th Annual Conference, Cleveland Section, Society for Applied Spectroscopy, Cleveland, Ohio, May 24, 1961
	"Stable Isotope Analysis"	Fall Meeting, Southeastern Section Society for Applied Spectroscopy, Birmingham, Ala., Sept. 16, 1961
Pruitt, M. E.,[10] R. R. Rickard, E. I. Wyatt	"Radiochemical Determination of Yttrium and Promethium – A Precipitation Method"	Southwest and Southeast Regional Meeting, American Chemical Society, New Orleans, La., Dec. 7–9, 1961
Rains, T. C.,[10] H. E. Zittel	"Anionic Interferences in the Flame Spectrophotometric Determination of Calcium: Use of Glycerol as a Releasing Agent"	140th Meeting, American Chemical Society, Chicago, Ill., Sept. 3–8, 1961
Rains, T. C., H. E. Zittel, Marion Ferguson[10]	"Flame Spectrophotometric Determination of Trace Quantities of Strontium in Macro Quantities of Calcium"	Southwest and Southeast Regional Meeting, American Chemical Society, New Orleans, La., Dec. 7–9, 1961
Reynolds, S. A.	"Basic Radiochemical Techniques"	R. A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Feb. 20–24, Nov. 13–17, 1961
	"Determination of Significont Radionuclides"	
	"Measurement of Radioisotope Standards"	National Research Council Subcommittee on Radioactivity Measurements and Standards, Washington, D.C., Nov. 2, 1961
	"Half-Lives of Radionuclides – II"	
	"Methods and Standards in Radioanalysis of Water"	139th Meeting, American Chemical Society, St. Louis, Mo., Mar. 21–30, 1961

	"Radioisotopes in Chemical Analysis"	R. A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Nov. 13–17, 1961
Strain, J. E.	"Neutron Activation Analysis"	Nuclear Application Symposium, U.S. Department of Interior, Bureau of Mines, Reno, Nev., Sept. 19–23, 1961
Weekley, R. E.	"The Spectrographic Determination of Oxygen in Metals"	XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, Aug. 6–12, 1961
White, J. C.	"Separations in Analytical Chemistry by Solvent Extraction with Organophosphorus Compounds"	Society for Analytical Chemists of Pittsburgh, Pittsburgh, Pa., Apr. 14, 1961
Young, J. P.	"Recent Developments in the Spectrophotometric Study of Molten Salts"	Gordon Research Conference on High Temperature Chemistry – Molten Salts, Meriden, N. H., Aug. 28–Sept. 1, 1961
Zittel, H. E., L. B. Dunlap, P. F. Thomason[10]	"Determination of Uranium in the Presence of Molybdenum by Controlled-Potential Coulometric Titration"	140th Meeting, American Chemical Society, Chicago, Ill., Sept. 3–8, 1961

Under the ORNL Traveling Lecture Program

Lecturer	Lecture Title	Presented at
Cameron, A. E.	"Geological Age Determinations by Isotopic Measurements"	Trinity College, Washington, D.C., March 1961
		West Virginia Wesleyan College, Buckhannon, W. Va., Apr. 26–27, 1961

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