

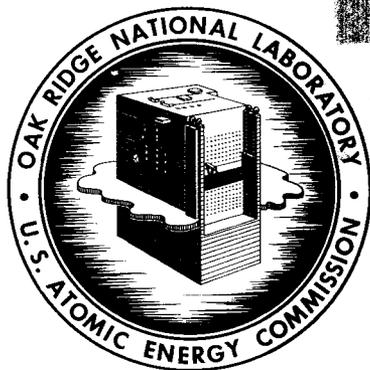
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ORNL-3060
UC-4-Chemistry
TID-4500 (16th ed.)

**ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
FOR PERIOD ENDING DECEMBER 31, 1960**



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

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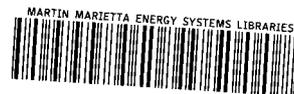
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For Period Ending December 31, 1960

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

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Oak Ridge, Tennessee
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ANALYTICAL CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

SUMMARY

RESEARCH AND DEVELOPMENT

Analytical Instrumentation (X-10)

Work was continued on in-line instrumentation. Gamma-absorptiometric techniques for the continuous determination of heavy elements in flowing streams were studied further. In order to perform the measurements with monochromatic radiation, an Am^{241} source has been used with a rapid-scanning gamma spectrometer that is equipped with a thallium-activated sodium iodide crystal transducer. Straight-line semilogarithmic plots of count rate vs concentration are obtained for uranium over the concentration range from 0 to 320 g/liter. A plant-type alpha-detecting instrument, designed to monitor for excessive product losses in chemical-processing waste streams, has been operated in the Power Reactor Fuel Processing Pilot Plant; U^{233} was used as the source of alpha activity at the levels expected. The instrument has sufficient sensitivity for the streams being considered at present, and the results correlate well with the results of laboratory analyses.

The work with two cathodic-stripping voltammetric techniques for the determination of chloride ion concentration was finished. The standard deviation (for one determination) of the results of the current-stepping technique over the range from 1.5×10^{-4} to 1×10^{-3} M is about 1.3×10^{-5} M; for the voltage-stepping technique over the range from 4×10^{-6} to 3×10^{-5} M, it is about 6×10^{-7} M. The null-point concentration-cell titration technique of Malmstadt and Winefordner for the determination of the concentration of chloride ion and the conditions necessary for its application have been studied. The relative standard deviations of the results of the determination of chloride ion in concentrations of 2×10^{-5} , 2×10^{-4} , and 2×10^{-3} M were 3.5, 0.4, and 0.1%, respectively.

Several instruments were modified to extend their usefulness or were developed. A precision chronopotentiometer is being developed that has regulated current and electronic readout of transition time. Two more ORNL model Q-1728 automatic titrators have been constructed. Control charts (for the period May 1955 through September 1960) for the titration of about 30 mg of uranium with ferric sulfate solution show that the limit of error for one determination at the 95% probability level is 0.2%. An absorption-cell attachment for a Welch Densichron reflection unit has been designed and fabricated so that either reflectance or absorbance measurements can be made remotely. An automatic-fill circuit and a plunger-position indicator were added to the control unit for the remotely servo-controlled pipetter. The indicator establishes when the pipet plunger has arrived at a new position demanded by the control dial and whether the servo system can maintain a position balance with an error no greater than 0.0002 in. Electronic readout instruments for the rapid spectrographic determination of oxygen have been designed, fabricated, tested electrically, and released for analytical evaluation. Development has continued of a high-resolution, high-sensitivity, scanning, recording flame spectrophotometer. The relative advantages of several alternative circuits for measuring the flame intensity and presenting the final result are to be evaluated, particularly at wavelengths up to 852 $\text{m}\mu$. A corrosion-resistant pipet has been designed and tested, and

one has been installed in a remotely servo-operated pipetter in the High-Radiation-Level Analytical Facility. Radioactive solutions that contain nitric acid, sulfuric acid, hydrochloric acid, hydrofluoric acid, or aqua regia can be pipetted with it. The pipet will function reliably for thousands of pipettings of corrosive liquids. The relative standard deviation of delivery is 0.2%.

Some new work in polarographic instrumentation and in polarography was done. The performance of the ORNL controlled-potential ac polarograph was studied. The peak heights of polarograms made of unsparged solutions of Cd^{2+} are reproducible to within about $\pm 1\%$. Further development of the phase-discriminator circuit is under way, and it is planned to also investigate a harmonic-measuring technique. Circuitry for counting drops from and measuring the rate of flow of mercury through a D.M.E. has been designed and built. With the ORNL model Q-1988-ES controlled-potential and derivative polarograph it is possible to measure concentrations in high- or low-conductivity solutions of the order of $10^{-7} M$ with a D.M.E.; this sensitivity is a hundredfold greater than that of conventional polarography. With this instrument, techniques for the measurement and interpretation of derivative polarograms consisting of either resolved waves or interfering waves have been established. It has been shown experimentally that derivative wave values must be measured at $E_{1/2}$ potentials rather than at potentials where maxima occur in the net derivative wave. Derivative polarography provides a rapid, easy, and accurate means of determining n values. A standard-addition method for the mathematical analysis of interfering derivative waves has been developed; the method makes possible the correct measurement from interfering derivative waves of concentrations of the reducible species. The method was tested experimentally by analyses of solutions of Cd^{2+} and In^{3+} whose derivative waves are separated by 38 mv; each interferes severely with the other. The results of analyses of these solutions by this technique were within $\pm 5\%$ of the concentrations known to be present.

Inorganic Preparations (X-10)

The preparation of the nitrides of the rare-earth metals for the Physics Division continued and was extended to include some compounds of the rare-earth metals with other members of the group V elements. The high-purity lithium iodide program for the Neutron Physics Division and the preparation of fused salts for the Chemistry and Metallurgy Divisions were continued.

Numerous preparations of interest were made for various divisions. Compounds of high purity, for example, magnesium oxide and potassium fluoride, are being prepared. An investigation into some phases of the chemistry of rhenium and technetium was begun.

Ionic Analyses (X-10)

The Ionic Research and Development Group has continued its work in electrochemistry, titrimetry, spectrophotometry, and gas chromatography. In electrochemistry the major effort has been on the application of controlled-potential coulometry to the determination of plutonium and uranium in various reactor-fuel-dissolver solutions. A new coulometric titration method for the determination of uranium in the presence of molybdenum was developed. The technique of generation and back-titration of intermediate reagents by means of controlled-potential coulometry has been studied. A

method for the coulometric titration of uranium(IV) has been investigated. The performance of a Teflon dropping mercury electrode for use in hydrofluoric acid media has been studied. An apparatus for the automatic simultaneous measurement of m , t , w , and drop count of a dropping mercury electrode has been fabricated.

In cooperation with the Health Physics Division, a study was made of the chemical reaction between Purex waste solutions and sodium chloride. A method has been developed for the titrimetric analysis of mixtures of monobutyl-, dibutyl-, and orthophosphoric acids.

Spectrophotometric studies have resulted in the development of two methods for the determination of technetium(VII). The chromogenic reagents are thioglycolic acid and toluene-3,4-dithiol. The spot-test equipment for control of isotope production has been modified for use in a hot cell. Spectrophotometric studies of the polymerization and hydrolysis of plutonium in uranyl nitrate and nitric acid solutions have been started.

Spectrophotometric techniques are being developed for the fundamental study, at high temperatures and pressures, of aqueous solutions of interest in high-temperature chemistry and in reactor technology. An ultraviolet-visible-near-infrared spectrophotometer, designed to be operated at temperatures as high as 330°C and pressures of at least 3000 psi in the presence of high levels of alpha radiation, is being designed for ORNL by the Applied Physics Corporation. The design is almost finished and the construction work will start in the near future. A miniature circulating loop system, under construction by the Chemical Technology and the Engineering and Mechanical Divisions, will be used to evaluate certain design features of the spectrophotometer and the possibilities of absorption spectrophotometry for the automatic control analysis of highly radioactive, high-temperature, circulating solutions.

A mathematical technique that uses high-speed digital computation has been developed to resolve seriously overlapping spectral bands and fine structure. By means of it, the visible and near-ultraviolet spectra of uranyl perchlorate and of uranyl sulfate have been resolved completely. The analysis of the spectrum of Pu^{4+} in perchloric acid from 8000 to 29,000 cm^{-1} is almost completed.

An automatic, digital, data-readout system has been designed for use with a Cary model 14 PM spectrophotometer.

The gas chromatographic work has been concerned with the analysis of gases from off-gases of dissolvers and of HRT shield gas, with studies of the recombination of deuterium and oxygen in thoria slurries, and with studies of radiolytic decomposition of water.

Mass Spectrometry (Y-12)

Uranium and boron isotopic standards have been obtained and checked. New preferred compounds for use in the analysis of separated stable isotopes have been designated. Samples of Sr^{90} have been analyzed successfully.

The retarding-potential-difference method for the study of gaseous ionization was modified to permit the use of ac signal detection. Data-collection time was thereby reduced from hours to minutes, and signal-to-noise ratio was greatly improved. The ionization of krypton was studied.

Nuclear Analyses (X-10)

Trace and macro quantities of many elements were determined in many types of materials by neutron-activation analysis; a summary of these applications is presented. In addition, other nuclear techniques, for example, neutron absorption, neutron transmission, and delayed-neutron counting, have been used to determine concentrations of elements. Neutron-activation analysis has also been used to determine particle-size distributions in a number of particulate materials. Radioactive tracers have been used in the study of molten salts and surface areas.

A low-level gamma spectrometer has been developed. Also, a preliminary investigation was made of the analysis of radionuclide mixtures by gamma spectrometry together with high-speed digital computer techniques.

ORNL Master Analytical Manual (X-10 and Y-12)

Two supplements to the *ORNL Master Analytical Manual* (one of methods issued in 1958 and the other of methods issued in 1959) are available in reprinted form (TID-7015, suppl 1 and suppl 2) from the Office of Technical Services, Department of Commerce, Washington. Forty-six new methods and 12 revised methods were issued. The Table of Contents for Sec 5, "Nuclear Analyses Methods," was brought up to date. The "ANP Project Methods," Subsection 9 09, were declassified. The *Manual* was issued to two new custodians.

Optical and Electron Microscopy (X-10)

Particles of many types of materials were studied to determine their size, shape, and surface characteristics. A variety of metals and ceramics that had been exposed in the Experimental Gas-Cooled Reactor, in molten salts, in thorium-oxide-slurry test loops, or that had been used in metallurgical experiments were examined to determine the chemical and physical nature of the surface layers. Metals and thin films of interest in corrosion studies were also investigated; one metal is illustrated. The Physics and the Chemistry Division were assisted in their work with single-crystal barrier-type alpha counters. Work was done for the Biology Division in connection with their studies of radiation damage of animal tissue. Improvements were made in the electron diffraction instrument. A device for measuring electron diffraction patterns was designed and is being built, and an improved filament for electron microscopy and diffraction is being studied.

Radiochemical Analyses (X-10)

The gamma branching of Kr^{85} was determined, and work on the decay scheme of Pm^{148} was completed. Neutron-capture cross sections for Os^{184} , Cd^{108} , and Au^{197} have been determined. Instrumental analyses by means of gamma and alpha spectrometry continue to be useful. Gas chromatography has been applied in the separation of the fission gases krypton and xenon. Increasing interest in several natural radionuclides has led to the development or adaptation of methods for determining them. New developments in solvent-extraction techniques include the separations of lanthanides and actinides, use of organophosphorus compounds, and preparation of a monograph on extractions with amines. Instruction of noncitizen guests and participation in the scientific programs of national organizations required the attention of some personnel.

Reactor Projects Laboratory (Y-12)

The Reactor Projects Laboratory continued its support program in analytical chemistry for the Gas-Cooled Reactor Project and the Aircraft Nuclear Propulsion Project. This work is reported in the appropriate progress reports of the projects.

Research was continued in the investigation of the absorption spectra of various molten-fluoride systems by use of the pendant-drop technique for confining the molten salts. Improved methods were also devised for obtaining pendant drops of molten fluorides for spectrophotometric study. Spectral studies of the 3d transition-element fluorides dissolved in pure alkali-metal fluorides were initiated. The spectrum of 0.25 mole % cobalt(II) fluoride in molten lithium fluoride was measured. Absorption maxima were found at 495 and 572 m μ . The spectra of the fluorides of praseodymium, neodymium, and samarium dissolved in molten lithium fluoride were obtained and compared with their spectra in aqueous and nonaqueous solvents. A graphite resistance heater was fabricated which permits the attainment of temperatures in the range of 1000 to 2000°C. The investigation and evaluation of chromogenic reagents for use in molten-salt media was extended to sulfonate derivatives of phthalocyanine.

Solvent-extraction studies with organophosphorus compounds, primarily tris(2-ethylhexyl)phosphine oxide, were continued. Pyrocatechol violet was used as a spectrophotometric reagent for the determination of tin following extraction of the tin with tris(2-ethylhexyl)phosphine oxide. A method was also developed for the determination of molybdenum in cyclohexane solutions of tri-n-octylphosphine oxide. The method is based on the measurement of the absorbancy of the yellow complex formed between molybdenum and thioglycolic acid; it is suitable for concentrations of molybdenum in the final solution from 2 to 20 μ g/ml. An improved procedure was established for the determination of thorium and uranium in granite and other siliceous rocks. The high-temperature fluorination technique, using potassium tetrafluorobromide for the determination of oxygen in metals and fluoride salts, was extended to the determination of oxygen in Be, Dy, Si, Nb, and Mo, as well as in miscellaneous inorganic compounds. In an effort to clarify the mechanism of the degradation of potassium bromate under gamma irradiation, a gas chromatographic method for the determination of oxygen released during the irradiation of alkali-metal bromates was developed. Also, infrared spectra of irradiated samples of potassium bromate were recorded between 660 and 1700 cm^{-1} . The Leco automatic sulfur titrator was modified to make possible the determination of as little as 0 to 10 μ g of sulfur in test portions of various metals. A simple rapid method was devised to determine boron trifluoride in helium; it is based on the reaction of boron trifluoride with calcium chloride.

Spectrochemical and X-Ray Analyses (X-10 and Y-12)

Chemical methods have been developed for dissolving high-fired beryllium oxide and for isolating traces of silicon from copper and traces of rare earths for spectrochemical determination. Porous cups prepared from National Carbon Company carbon stock were shown to give considerably better precision than porous cups made of graphite or from other types of carbon stock tested.

It was found that the loss of boron during the evaporation of hydrochloric acid and hydrochloric-hydrofluoric acid solutions of boric acid is prevented by the presence of excess mannitol. The x-ray absorption-edge method has been extended to include Zr, Mo, Hf, and Sn. The stability of the instrument has been improved. A new method of calculating results has been devised that permits an increase in sensitivity of the method. A tissue-ashing laboratory has been established in Building 4500. A new method of pulverizing dried tissue has been proved to be successful, and the container-cleaning procedure was shown not to cause cross-contamination. The precision and sensitivity of spectrographic analysis of tissue ash have been improved by thermally insulating the spectrometer and by essentially eliminating the turbulence of the arc.

An analog computer has been designed and built that will automatically calculate and print out analytical results from data produced by a direct-reading spectrometer.

Statistical Development (Y-12)

Special statistical services were provided in connection with nearly 200 individual problems. Three ASTM methods were reviewed for ASTM Subcommittee II of E-2; detailed recommendations were made.

Thermal Breeder Reactor Projects Analytical Chemistry Laboratory (Y-12)

The major portion of the work of the Thermal Breeder Reactor Projects Analytical Chemistry Laboratory is the analysis of solutions of thorium oxide, uranyl sulfate, mixtures of other metallic oxides, and a number of additives and/or corrosion products of materials used in reactor tests. Studies have been continued in order to develop or improve methods for these analyses.

For the analysis of simulated HRT fuel solutions, a conductometric titration for free acid and an indirect nonaqueous titrimetric method for sulfate were developed. Both methods are applicable to the analysis of hot reactor solutions. An indirect polarographic method and an amperometric method for thorium and a means for the separation of macro quantities of thorium with thenoyltri-fluoroacetone were developed for the analysis of thorium oxides or mixtures thereof. Other methods developed or studies carried out were related to the determination of trace materials. Among these are a method for osmium, a spectrophotometric titration for samarium and neodymium, and the coulometry of molybdenum in nitrilotriacetic acid. The flame photometric determination of rare-earth elements was studied further. A very significant study of the effect of anions on the radiant intensity of calcium has been made in conjunction with flame photometric analyses of ecological materials. An apparatus for differential thermal analysis was assembled and used to study effects of radiation on alkali-metal bromates.

SERVICE ANALYSES

The number of Statistical Quality Control programs, maintained in nine service laboratories, was reduced nearly 50% in order to compensate for revisions in the projects of other ORNL divisions and for the subsequent decrease in the analytical services required by those divisions. However, the quality of the work exceeded the 92% level attained in 1959; a new level of 95% was achieved in 1960.

Some 3800 samples were analyzed in the Counting Laboratory. They consisted chiefly of nitric acid solutions or organic solutions that contained either organonitrogen or organophosphorus extractants. Radiochemical methods were used for approximately half the analyses, which included the determination of Pu, Am, Tc, Ru, Zr, Nb, and gross beta and gamma activities. Non-radiochemical methods (spectrophotometric, flame photometric, volumetric, and polarographic) were also used.

Some 2300 samples were analyzed in the Miscellaneous Analysis Laboratory. This work included the specification testing of samples of metals, alloys, oil, ink, paint, and other materials; the analysis of soils and plant materials; determination of oxygen in metals, oxides, and fluoride salts; and chromatographic analysis of gases.

In the Raw Materials Analytical Laboratory, 9200 samples were analyzed. These consisted principally of aqueous and organic solutions derived from solvent-extraction studies. However, approximately 10% of the samples were solids, for the most part granite that had been leached with sulfuric acid. Altogether, almost 40 different components were determined by means of spectrophotometric, volumetric, gravimetric, or fluorometric methods.

Ionic service analyses continued to be the same types as have been reported in the past.

The number and types of analyses made in the Low-Level Radiochemical Laboratory increased considerably. The samples originated primarily from ecological, waste-disposal, and area-monitoring studies.

The Analytical Mass Spectrometry Laboratory reported 35,096 analyses from 4301 samples. New techniques were developed for the isotopic analysis of elements that previously were very difficult to analyze.

The Spectrochemical Analyses Laboratory analyzed a large number of stable isotopes submitted by the Isotopes Division. Neodymium and samarium were determined in Pm^{147} . Many rare-earth-element mixtures were analyzed.

During the past year, a 25% reduction occurred in the number of analyses performed by the Process Analyses Laboratories because of the curtailment in the processing of highly radioactive materials since the various incidents occurred. One new group was formed during the past year. The number of persons in the process groups was reduced approximately 6%. A brief statement of new developments in each laboratory follows.

In the Special Analyses Laboratory, equipment for the measurement of surface area by krypton adsorption and by the continuous-flow method was put in operation. Analyses for oxygen in liquid metals and for dissolved oxygen and hydrogen in water from pressurized loops were made. Silicon,

molybdenum, boron, and sulfur were determined in metals and alloys. Neutron-capture cross section targets of 65 elements were prepared.

The Radioisotopes-Radiochemistry Laboratory developed a new analytical procedure for radio-antimony. The half-lives of five radionuclides were determined. A monograph on the radiochemistry of ruthenium is being prepared. A 256-channel transistorized scintillation spectrometer has been purchased. Specifications have been completed for construction of hot analytical cells in Building 3038.

The Process Development Service Laboratory developed a spectrophotometric method for the determination of ruthenium in nitric acid. Methods were adapted for the determination of zirconium in aqueous and in organic media.

The High-Alpha Analytical Laboratory has put into service two new instruments, a 256-channel analyzer and a single-channel gamma spectrometer. Twenty-one new glove boxes are being equipped and put into service in a new facility in the Laboratory.

The Pilot-Plant Control Laboratory has reviewed its operating rules and procedures for handling radioactive samples and has issued new rules that reflect lowered tolerances for radiation exposure and contamination. Special nonroutine work was done for Atomics International, REED, the Metallurgy Division, and the Radiochemical Processing Pilot Plant. The following new equipment was installed: a corrosion-resistant pipetter for the remotely controlled measurement of radioactive samples, mobile work benches, and a Fisher Gas Partitioner.

The Reactor Analyses Laboratory has modified and improved the conductometric titration method for free acid and sulfate in HRT solutions.

The High-Radiation-Level Analytical Facility was completely decontaminated. Modifications to the HRLAF were made in order to increase containment and to change the off-gas ducts. In an effort to gain closer control of contamination, modifications were made to the manipulators and in the operating procedures.

The Decontamination Studies Laboratory was formed this past year and at present is assembling equipment needed for the work in Building 3508.

The quality-control program was expanded to include 15 new control samples that contain from one to ten elements in known concentration.

The Radiochemical Analyses Group determined radioactive materials in filters and charcoal traps and fission product gases in mixtures, primarily by gamma spectrometric techniques. They also determined P^{32} , S^{35} , and H^3 by liquid-scintillation counting and made many analyses of unusual radioisotope products.

The Reactor Projects Laboratory analyzed many fused mixtures of fluorides that were received in connection with basic research on fused salts. The exact compositions of the salts were determined in many cases; also, single major constituents and corrosion products were determined.

A total of 31,300 analyses were performed on some 6500 samples in the Thermal Breeder Reactor Projects Analytical Chemistry Laboratory. The types of samples, methods of analysis, components determined, and physical measurements required are discussed.

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RESEARCH AND DEVELOPMENT
ANALYTICAL INSTRUMENTATION (X-10)

D. J. Fisher

Single-Beam Gamma Absorptiometer

R. W. Stelzner

Studies on gamma-absorptiometric techniques for the continuous determination of heavy elements in flowing streams have continued. The Am^{241} radiation sources, which were originally enclosed in aluminum containers, are now encapsulated in welded stainless steel cells ($\frac{1}{2}$ in. long by 1 in. in diameter) in order to decrease the hazard of a loss of Am^{241} . A flux of 2.6×10^8 photons/sec through a 10-mil-thick window is obtained from 20 mg of Am^{241} (as the oxide).¹

Attenuation of the collimated 60-kev gamma-ray beam is measured by a rapid-scanning gamma spectrometer that uses a 100-mil-thick thallium-activated crystal of sodium iodide as a radiation transducer. The rapid-scanning feature was achieved by installation of an electronic sweep circuit that integrates a specified constant current to the pulse-height-selection circuit of a single-channel discriminator. Linear plots on semilogarithmic paper of the count rate at 60 kev vs concentration are obtained for empirical calibration. Straight-line plots have been obtained for uranium over the concentration range from 0 to 320 g/liter and for cadmium chloride (as an example of light-element attenuation) over the range from 0 to 50 g/liter.

Chopping of the beam by a rotating lead attenuator does not appear feasible with the present electrical instrumentation because of the lag in response.

Efforts to measure the concentration of solutions directly through stainless steel piping have indicated some possibility for success if the thickness of the stainless steel can be kept at a minimum. Scattered radiation measured at 90° to the direction of the beam shows a peak at 60 kev, the intensity of which varies with concentration. It was not possible to detect characteristic x rays in the scattered radiation with the existing instrumentation.

Monitors of Alpha Radiation

T. S. Mackey² R. W. Stelzner

A plant-type instrument designed to monitor for excessive product losses in chemical-processing waste streams has been operated in the Power Reactor Fuel Processing Pilot Plant; U^{233} was used as the source of alpha activity at the expected levels. The principle of operation is based on the correlation of the number of alpha particles that escape from the surface of the process liquid with the alpha content of the stream. This scheme had been evaluated

¹Sources fabricated by J. E. Strain, Nuclear Analyses Group.

²Chemical Technology Division.

earlier in the laboratory³ but had not been adopted because of the large amount of maintenance required to replace contaminated phosphors. A re-evaluation of the permissible amount of maintenance has made possible the continued development of the instrument. The surface-monitoring method, in spite of its low efficiency (0.1%), has sufficient sensitivity for the streams being considered at present; the results obtained by means of it correlate well with the results of laboratory analyses.⁴

The results of tests on the disk-type monitor³ indicate that the drying operation involving the hot-air stream leads to severe contamination. The etched stainless steel surface of the rotating disk is not wet uniformly; other materials of construction will be tried in reworking the instrument.

An effort to increase the sensitivity of alpha monitoring of waste streams by measurement of the neutrons emitted in (α, n) reactions on fluorine-rich materials was not successful.

Cathodic-Stripping Voltammetry of Chloride Ion

W. L. Maddox

The work described previously⁵ has been completed. The current-stepping method was studied at chloride ion concentrations from 1×10^{-5} to 1×10^{-3} M. The standard deviation of a determination by this method in the concentration range from 1.5×10^{-4} to 1×10^{-3} M is about 1.3×10^{-5} M. The voltage-stepping method was studied at chloride ion concentrations from 2×10^{-6} to 4×10^{-5} M. In the range from 4×10^{-6} to 3×10^{-5} M, the standard deviation is about 6×10^{-7} M. The work is described in a thesis accepted in June 1960 by the University of Tennessee in partial fulfillment of the requirements for the MS degree.

Null-Point Potentiometric Titration of Chloride Ion

W. L. Maddox

Chloride ion in dilute solutions can be titrated with good precision by the method of "precision null-point potentiometry." Malmstadt and Winefordner have described this method in detail.^{6,7}

In brief, a concentration cell in chloride ion is set up; identical Ag/AgCl electrodes are used in both sides of the cell. A solution of known chloride concentration is placed in one side of the cell. This side consists of an isolation compartment, such as the L & N pH

³J. W. Landry, T. S. Mackey, and R. W. Stelzner, "Monitors of Alpha Radiation," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 1.

⁴T. S. Mackey, *Status of Pilot Plant Section Equipment Development Program*, ORNL CF-60-10-36 (Oct. 14, 1960).

⁵W. L. Maddox, "Cathodic-Stripping Voltammetry of Chloride Ion," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 5.

⁶H. V. Malmstadt and J. D. Winefordner, "Precision Null-Point Potentiometry. A Simple, Rapid and Accurate Method for Low Concentration Chloride Determinations," *Anal. Chim. Acta* 20, 283 (1959).

⁷H. V. Malmstadt and J. D. Winefordner, "Determination of Chloride by Precision Null-Point Potentiometry," *J. Am. Water Works Assoc.* 51, 733 (1959).

(S.C.E.) electrode sleeve. The isolation compartment dips into a beaker that forms the other half-cell. The beaker is provided with a stirrer and two burets. A null-point potential for the cell is determined with identical dilute chloride reference solutions in both halves of the cell. Then the beaker is removed and replaced with a beaker that contains the sample. A solution is added from the buret to adjust the chloride concentration of the sample until it matches that of the reference solution. The polarity of the cell voltage when the sample is in the beaker indicates whether to deliver a chloride-concentrating solution (e.g., a solution of NaCl) or a chloride-diluting solution (the supporting medium). A titration is concluded when the cell voltage reaches the previously established null point.

Electrodes that are stable in potential and that respond quickly to changes of chloride ion content can be made by electroplating stiff platinum flag electrodes with silver and then depositing silver chloride on the surfaces in a controlled cyclic process. Electrodes made in this manner are much superior to those made from silver wire. In solutions that are $2 \times 10^{-3} M$ in chloride ion, commercial Ag/AgCl electrodes (e.g., from E. H. Sargent & Company) have drift rates and speeds of response that are similar to those of the type electrode described above. The procedure does not work with a low-resistance null-point detector; good titrations are obtained when the input resistance of the detector is 1 megohm or greater. The null detector must be stable and should have a full-scale sensitivity of ~ 10 mv. Best results are obtained when the solution is stirred vigorously with a nonmagnetic stirrer and the titrant is delivered directly onto the indicator electrode.

The precision of the titration of standard solutions of chloride by this method is indicated by the data of Table 1.

It was planned to apply the null-point method to the determination of water uptake by ion exchange resins. When a dry resin is equilibrated with a dilute salt solution (e.g., NaCl), the resin removes water from the solution, thus causing an increase in the salt concentration. The amount of water taken up is determined from the before-and-after salt concentrations. Unfortunately, some of the resins appear to contribute poisons to the solutions, thus making detection of the null point impossible because of drift of potentials or sluggish response of the electrodes. In spite of the disappointing results with some of the resins, the null-point potentiometric method is generally satisfactory.

Table 1. Precision of Null-Point Potentiometric Titration of Chloride for Various Chloride Concentrations

Number of Samples	Volume of Solution Titrated (ml)	Cl ⁻ Concentration of the Solution Titrated (M)	Cl ⁻ Concentration of Reference Solution (M)	Relative Standard Deviation (%)
11	25	2.00×10^{-3}	1.00×10^{-3}	0.1
18	25	2.00×10^{-4}	1.00×10^{-4}	0.4
9	20	2.00×10^{-5}	1.00×10^{-4}	3.5

Precision Chronopotentiometer

W. L. Maddox D. J. Fisher

Development of a precision chronopotentiometer has been continued. The amount of current available for electrolysis and the degree to which this current is regulated have been increased by use of a USA-3 amplifier in the current-supply circuit. The electromechanical transition timer formerly used (capable of accuracy no better than ± 0.01 sec) has been replaced by an all-electronic timer, which is capable of millisecond accuracy. The constant-current and cutoff circuits are unaffected by high resistance in the test solution. This instrument is to be used in the investigation of nonaqueous chronopotentiometry and of chronopotentiometry in stirred solutions.

ORNL Model Q-1728, Automatic, Recording, Velocity-Servo Potentiometric Titrator

M. T. Kelley W. R. Laing B. J. Ginocchio D. J. Fisher

Two more of the ORNL model Q-1728, automatic, recording, velocity-servo potentiometric titrators⁸ have been constructed, one for use at the Y-12 Plant and the other (serial No. 6) at ORNL. Various revisions and refinements were made to several of the drawings contained in the Q-1728 series of drawings. No design change was made to the instrument. A paper that describes the titrator has been published.⁹

One of the principal uses by the Special Analyses Laboratory of three titrators of this design has been the titration with ferric sulfate solution, for accountability purposes, of test samples that contained about 30 mg of uranium. There is about 12 in. of chart travel between end points for this titration. Control data for the period May 1955 through September 1960 are given in Table 2. The constancy and low value of the limit of error over the five-year period indicate that the performance of the ORNL model Q-1728 titrator is adequate for this uranium determination.

Absorption-Cell Attachment for a Welch Densichron Reflection Unit

H. C. Jones D. J. Fisher

An absorption-cell attachment for a Welch Densichron reflection unit has been designed and fabricated.¹⁰ Either reflectance or absorbance measurements can be made remotely with the Welch Densichron by use of this attachment.

The cell attachment is machined from linen-base laminated Bakelite and consists of a collimated light source, a slot for a 2×2 in. interference filter, and a cell compartment for a Beckman square absorption cell of 1-cm light-path length. The attachment is bolted to a Lucite case that surrounds the reflection unit. When the absorption cell is being used, the collimated light

⁸J. P. Phillips, *Automatic Titrators*, pp 63-65, Academic Press, New York, 1959.

⁹M. T. Kelley, D. J. Fisher, and E. B. Wagner, "Automatic Recording Velocity-Servo Potentiometric Titrator," *Anal. Chem.* 32, 61 (1960).

¹⁰F. J. Miller and H. C. Jones, "Absorption-Cell Attachment for a Welch Densichron Reflection Unit," a paper accepted for publication in *Anal. Chem.*

Table 2. Control Data for the Determination of Uranium by Means of the ORNL Model Q-1728 Titrator

Period	Number of Control Standards Analyzed	L.E., ^a Limit of Error (%)	Number of Results Outside the L.E.
May-Dec. 1955 ^b	139	0.2	6
Jan.-Dec. 1956 ^c	199	0.2	6
Jan.-Dec. 1957 ^d	197	0.2	5
Jan.-Dec. 1958 ^e	204	0.2	7
Jan.-Dec. 1959 ^f	152	0.2	3
Jan.-Sept. 1960 ^g	91	0.2	1

^aL.E. = 2S, where S is relative standard deviation.

^bM. T. Kelley, *Statistical Quality Control Report, Analytical Chemistry Division, October through December, 1955*, ORNL CF-56-1-180, Table VIII and Fig. 20 (Jan. 31, 1956).

^cM. T. Kelley, *Statistical Quality Control Report, Analytical Chemistry Division, October through December, 1956*, ORNL CF-57-1-153, Table 1-3 (Jan. 25, 1957).

^dM. T. Kelley, *Statistical Quality Control Report, Analytical Chemistry Division, October through December, 1957*, ORNL CF-58-1-127, Table 1-3 and Fig. 1-14 (Jan. 31, 1959).

^eM. T. Kelley, *Statistical Quality Control Report, Analytical Chemistry Division, 1958 Ann. Summary*, ORNL CF-59-1-152, Table 1-3 and Fig. 1-12 (Jan. 23, 1959).

^fM. T. Kelley, *Ann. Statistical Quality Control Report, Analytical Chemistry Division, 1959*, ORNL CF-60-1-111, Table 1-6 and Fig. 1-27 (Jan. 15, 1960).

^gM. T. Kelley, *Statistical Quality Control Report, Analytical Chemistry Division, January through September, 1960*, ORNL CF-60-10-129, Table 1-1 and Fig. 1-3 (Oct. 15, 1960).

beam passes, in order, through the following: a $\frac{3}{16}$ -in.-diam hole, the interference filter, another $\frac{3}{16}$ -in.-diam hole, the Beckman cell, another $\frac{3}{16}$ -in.-diam hole, and then through a $\frac{3}{8}$ -in.-diam hole in the Lucite case and on into the reflection unit. A slot is provided in the Lucite case for reflectance measurements.

Automatic-Fill Circuit and Plunger-Position Indicator for the Remotely Servo-Controlled Pipetter

H. C. Jones D. J. Fisher

An automatic-fill circuit and a plunger-position indicator have been incorporated into the control unit for the remotely servo-controlled pipetter.¹¹ The improved unit is designated ORNL model Q-1348-A.

The automatic-fill circuit is used to bypass the manual "pipet-operate" switch. The switch is thrown to the *off* position, and the control dial is advanced from the fill setting (50) to the closed setting (250). The plunger remains at the fill position. When the liquid being drawn into the pipet makes contact with the platinum conductivity probe in the side arm of the pipet, the conductivity of the liquid causes the bias to be lowered on the grid of a 12AX7 vacuum tube in the control unit. The current through the tube increases, thus causing a plate relay to operate

¹¹M. 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).

whose normally open contacts bypass the "pipet-operate" switch. The bypassing of the switch permits the position servo to drive the plunger to the position corresponding to the dial setting of 250 and closes off the opening to the side arm. For subsequent deliveries, the automatic-fill circuit is switched out, and the manual "pipet-operate" switch is used as it was in the original control unit, which did not have the automatic-fill circuit.

The plunger-position indicator is an NE-51 neon lamp assembly connected across the output of the amplifier. When the servosystem is not balanced, the neon lamp is on. When the system is balanced, the lamp goes off. The indicator establishes when the plunger has arrived at the new position demanded by the control dial and also establishes whether the servosystem is able to maintain a position balance with an error of less than 0.0002 in.

Spectrographic Intensity-Ratio Analog Computer

H. C. Jones D. J. Fisher M. T. Kelley R. E. Weekley

A readout instrument for use in the rapid spectrographic determination of oxygen and other gases in certain samples has been described previously.¹² This instrument has been tested and was found to perform satisfactorily. A second model was designed and fabricated in order to incorporate several improvements. Each channel now consists of a current amplifier followed by two parallel-T, tuned, ac amplifiers that are stagger tuned to give a band-pass amplifier system. This voltage-amplifier system is followed by a synchronous rectifier that uses a transistor driven by an in-phase signal from the light-beam chopper. An incandescent light source, a Clairex type CL-3 crystal photocell, and a GAP/R K2-X operational amplifier provide the drive signal for the transistor. The response of the synchronous rectifier is linear and is more efficacious at low signal levels than is a diode rectifier. The rectifier system is followed by a GAP/R USA-3, printed-circuit, chopper-stabilized operational amplifier, which is used as an inverting amplifier or as a time integrator. The remainder of the circuit, that is, the ratio or instantaneous readout, is essentially the same as previously described.¹² The results of electrical tests on the completed instrument were satisfactory, and the instrument has been released for evaluation as an analytical instrument.

High-Resolution, High-Sensitivity, Scanning, Recording, Flame Spectrophotometer

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

A new high-resolution flame spectrophotometer was discussed previously.^{13,14} This instrument, at present, uses a chopped-light-beam system. The output from the multiplier phototube is amplified by a GAP/R K2-X operational amplifier that is used as a current amplifier.

¹²H. C. Jones *et al.*, "Spectrographic Intensity-Ratio Analog Computer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 3.

¹³D. 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, 1958*, ORNL-2662, p 17.

¹⁴D. 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, 1959*, ORNL-2866, p 2.

The current amplifier is followed by two tuned ac-voltage amplifiers, of which K2-X operational amplifiers are components. The voltage amplifiers are followed by a solid-state rectifier. The output of the rectifier system is then amplified or integrated by a chopper-stabilized operational amplifier (GAP/R USA-3), and its output is fed into a 10-mv Brown recorder.

At wavelengths up to 852 $m\mu$, the performance of the system in which a diode rectifier is used will be compared with that of the system in which a transistor is used as a synchronous rectifier. The performance of the system that contains the best rectifier, an ac-voltage amplifier, and a beam chopper will then be compared with that of a straight dc-voltage amplifier system that does not contain a beam-chopping device. With whichever system is best, the relative merits of instantaneous and integrated outputs will also be studied.

Corrosion-Resistant Pipetter for Remotely Controlled Measurement of Radioactive Solutions

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

In the pipettors used in the High-Radiation-Level Analytical Facility (HRLAF), a position servo remotely operates a positive-displacement pipet so designed that it can be cleaned and dried remotely with solvents such as water followed by acetone. The original pipettors were designed for pipetting solutions that contained nitric acid, for quantitative dilutions, and for density determination by the falling-drop method; the pipets were constructed of stainless steel and Teflon. It is now necessary to have a pipet suitable for pipetting radioactive solutions that contain one or more of the following corrosive chemicals: organic solvents, nitric acid, sulfuric acid, hydrochloric acid, hydrofluoric acid, or aqua regia. Very few materials of construction will resist the combined attrition from these sources. The plastic-lined pipet discussed previously¹⁵ was not developed further because it did not have a reliable seal design.

A new pipet was designed and constructed; B. Cook of the Engineering and Mechanical Division assisted in this work. It has a dynamic seal both above and below the intersection of the side arm and the displacement-plunger passages. The seal is confined and can be re-compressed if leakage develops as a result of wear. The pipet will quantitatively deliver organic solutions, as well as the other corrosive solutions indicated above. When the pipet is replaced in the servo assembly, or when one of these pipets is substituted for one of the pipets constructed from stainless steel and Teflon, the correlation between the displacement-plunger position and control-dial setting is not changed; the replacement can be made quickly. The delivery capacity of the pipet is about 700 μ l, but it would presumably be possible to build smaller or larger ones of the same design. Its cost is estimated to be less than that of the original stainless steel-Teflon pipet. The pipet is described in detail in a paper that has been submitted for publication.¹⁶

¹⁵D. J. Fisher, "Plastic Pipet for Remotely Servo-Controlled Pipetter," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 4.

¹⁶D. J. Fisher, M. T. Kelley, and W. L. Belew, *A Corrosion-Resistant Pipetter for Remote Measurement of Radioactive Samples*, a paper presented at the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960.

Three pipets of this new design were tested extensively at room temperature for resistance to corrosion, durability, and precision of delivery. A single servodrive and control unit was used for all tests. The relative standard deviation of delivery of 100- μ l volumes is 0.2%. The pipets, servodrive, and control unit functioned reliably with no maintenance for a total of about 24,000 pipetting cycles. Various liquids that contained one or more of the corrosive chemicals were pipetted. The caps that, by compression, form the dynamic seal did not have to be retightened, no leakage of the seal developed, and there was no evidence of appreciable wear. The working surfaces of the plungers became highly polished. In a 62-day static test, there was no evidence of uncontrolled cold flow of the confined dynamic seal. It was concluded that pipets of the new design are satisfactory for their intended purposes. One is now in use in the HRLAF.

AC Polarography

R. W. Stelzner

Evaluation studies of ac polarography using the controlled-potential ac polarograph¹⁷ have been carried out, principally on solutions of cadmium. The lowest concentration level achieved, with no sparging of the solution with nitrogen to remove residual oxygen, was 5×10^{-6} M. The half-width of the output wave form for this concentration is 60 mv, as compared with a theoretical half-width of 45.3 mv for true differentiation. The peak heights of the polarograms are reproducible to within about $\pm 1\%$.

Frequency studies indicate that the instrumentation operates best at low frequencies (the lowest frequency available for sinusoidal alternating current is 10 cps), most probably because of the reduction in amplitude of the capacitive component of the alternating current. At high frequencies this component can cause the current amplifier to limit.

Very large current spikes of short duration have been observed during the period of drop fall. These currents change polarity near the potential of the electrocapillary maximum for mercury, indicating a correspondence with the polarographic "condenser current." These current spikes also can cause the current amplifier to limit.

A phase-discriminator circuit that operates linearly at low voltage levels would minimize the problem of current limiting. A transistorized chopper that is located at a relatively low level in the amplification chain is being investigated as a possible replacement for the higher-level diode phase discriminator. The PNP type transistor appears to be superior to the NPN type for this application.

Rapid-scan circuits, based on electrical integration, operate satisfactorily at rates of electrical scan of 0.4 and 1.0 v/sec. These circuits make possible the oscilloscopic observation of the polarographic discharge currents of Pb^{2+} , Cd^{2+} , and Zn^{2+} on a single mercury drop. A more precise scheme for the synchronization of the start of electrical scan with a definite time in the

¹⁷J. W. Landry, T. S. Mackey, and R. W. Stelzner, "A-C Polarography," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 1.

growth cycle of the mercury drop is needed to ensure better precision. This synchronization can be supplied by a red-sensitive photoconductive cell whose light-excitation path is opened by the fall of the mercury drop.

Distortion of the sinusoidal wave form in the output of the current amplifier is apparently caused by the nonlinear electrical behavior of the D.M.E. The wave form of the output current varies as the polarizing voltage sweeps through the half-wave potential; this effect indicates a change in the harmonic content of the wave form. The amplitude of the harmonics generated may be related to the concentration of the discharging species and may offer a superior measuring technique. An investigation of a harmonic technique that uses the existing instrumentation is proposed.

Ac polarograms have been obtained by use of a three-electrode system that consists of the D.M.E., a control electrode (platinum wire), and a quasi-reference electrode (platinum wire). The polarograms are reproducible with respect to the height of the wave, but the half-wave potential is subject to small and unpredictable deviation from the accepted value.

Drop-Counting and Timing Devices for a Polarographic Dropping Mercury Electrode

H. C. Jones H. P. Raen D. J. Fisher

A device for counting drops from a polarographic dropping mercury electrode and a timing device for measuring the flow of mercury in a standtube above the electrode have been designed and fabricated and are now being tested (see "Apparatus for the Automatic Simultaneous Measurement of m , t , w , and Drop Count of a Dropping Mercury Electrode," this report). The drop-counting device is constructed so that a collimated beam of light is interrupted by the growing drop of mercury on the bottom of a capillary. The interrupted light beam falls on a Clairex type CL-3 crystal photocell, which drives a transistor amplifier circuit. A relay in the transistor collector circuit switches power to a Veeder-Root counter in such a way that one count is registered as each drop falls. The counter circuit can be turned on and off by a timing circuit, which measures the time required for a mercury column to fall between any two preselected points in the standtube. The timing circuit consists of two Clairex type CL-3 photocells and a separate light source for each. The upper photocell triggers a sensitive plate relay when the mercury falls past the photocell allowing the light to fall on its surface. The relay starts a timer and, if desired, starts the drop-counting circuit. When the column of mercury falls past the lower photocell, another relay is actuated thereby stopping the timer and shutting off the drop counter.

Sensitivity of Analysis with the ORNL Model Q-1988-ES Controlled-Potential and Derivative Polarograph

W. D. Cooke¹⁸ D. J. Fisher
W. L. Belew M. T. Kelley

An investigation of high-sensitivity polarography^{19,20} has been described in a paper that will be presented for publication in *Analytical Chemistry*. It was concluded that the lower limits of qualitative detection and quantitative measurement of polarography are restricted principally by the magnitude of "noise" components, that is, imperfect reproducibility of the total current at a D.M.E. This restriction becomes evident when current measurements are made by means of sensitive, stable circuitry.^{21,22} With the ORNL model Q-1988-ES polarograph and a drawn-out D.M.E. capillary, it is possible to work at concentrations of the order of 10^{-7} M in low- or high-conductivity solutions, which is a hundredfold increase in sensitivity over conventional polarography.²⁰ It is planned to do more work on the effect of mechanical dimensions of the D.M.E. on the ultimate sensitivity of polarographic measurements with a D.M.E. The hanging-drop-concentrating technique²³ presumably would be more sensitive with a given instrument than the technique of using a D.M.E.; however, it has not been studied with the Q-1988-ES polarograph.

As a practical example of the sensitivity of analysis with the ORNL model Q-1988-ES controlled-potential and derivative polarograph, some urine samples were analyzed for lead by derivative average-current polarography; an unmodified Sargent 2- to 5-sec D.M.E. capillary was used. These samples had been analyzed by regular average-current polarography with an ORNL model Q-1160 polarograph, which is more sensitive than conventional commercial polarographs. For this analysis, the model Q-1988-ES polarograph is about 50 times more sensitive than the model Q-1160 instrument.

Derivative Polarography

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

Measurement and Interpretation of Derivative Polarograms. – Derivative polarography done with the ORNL model Q-1988-ES controlled-potential and derivative polarograph^{21,22} has resulted in clarification of the method of measurement and the interpretation of derivative polarograms. The resolution of controlled-potential average-current derivative polarography is much

¹⁸Research participant from Cornell University, Ithaca, N.Y.

¹⁹W. D. Cooke, D. J. Fisher, and M. T. Kelley, "Investigation of High-Sensitivity Polarography," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 3.

²⁰W. W. Brandt, "Trace Analysis. Summer Symposium of the Analytical Division, Houston, Texas, 1960," *Anal. Chem.* **32**, 1595 (1960).

²¹M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," *Anal. Chem.* **31**, 1475 (1959).

²²M. 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).

²³J. W. Ross, R. D. DeMars, and I. Shain, "Analytical Applications of the Hanging Mercury Drop Electrode," *Anal. Chem.* **28**, 1768 (1956).

greater than that of controlled-potential undamped regular polarography. In some cases where consecutive regular polarographic waves cannot be measured independently, the corresponding consecutive derivative waves can be. The work done to date is summarized herein and will be published after it is completed.

The peak height of a single, resolved derivative polarographic wave of the reducible species should be measured from the base line to the maximum value of the peak, which, for a derivative wave of theoretical form, occurs at $E_{1/2}$ if the electrochemical reduction is rapid and reversible. The peak height is directly proportional to the product of i_d , n , and scan rate, or of concentration, n^2 , and scan rate.²⁴ For reactions at 25°C and for which mass transfer is predominantly controlled by diffusion, the peak width (in mv) at half-peak height is equal to $90.6/n$. This relationship provides a rapid and easy method of determining n values of such reactions by means of derivative polarography when the derivative waves are resolved. If the waves interfere, n cannot be determined without mathematical correction for the overlapping. The peak width may be increased and the maximum value of the derivative wave may be displaced from $E_{1/2}$ if iR losses are appreciable or if there is a time lag in the current-averaging filter²⁵ that precedes the derivative computer. With the ORNL Q-1988-ES polarograph, iR losses are negligible, even at high concentrations or in high-resistance media, because potential-control circuits are included in the instrument. With this polarograph, the time lag through the current-averaging filter (designed for drop time as long as 5 sec) becomes negligible if a slow scan rate (of the order of 0.02 v/min) is used. Accurate values of $E_{1/2}$ and n can be obtained if derivative polarograms are made at slow scan rates.

At each potential, the output (measured from the base line) of the derivative computer in the Q-1988-ES polarograph is directly proportional to the summation of the derivative values of two geometrically overlapping constituent waves. Geometrically overlapping derivative polarographic waves may or may not interfere. If they do not interfere, the methods of measurement and the interpretation are the same as for single waves. If the waves interfere mutually, then the values of the net derivative wave at the $E_{1/2}$ positions are both greater than the heights of the constituent waves, and neither derivative wave can be measured independently of the other.

The following consideration is vital to the correct measurement of concentrations of the reducible species from interfering derivative waves. When two derivative waves interfere, the potentials at which the maxima occur in the net derivative wave may no longer be at the corresponding $E_{1/2}$ values for the constituent derivative waves. Derivative wave values must therefore always

²⁴M. T. Kelley and D. J. Fisher, "Instrumental Methods of Derivative Polarography," *Anal. Chem.* **30**, 929 (1958).

²⁵M. T. Kelley and D. J. Fisher, "Unique Polarographic Damping Circuit for Selective Elimination of Current Fluctuations Due to Dropping Mercury Electrode," *Anal. Chem.* **28**, 1130 (1956).

be measured at $E_{1/2}$ potentials obtained from derivative polarograms (made under the same instrumental conditions as was the net wave) of solutions each of which contains only one of the reducible species. Wave values must not be measured at potentials at which the net derivative wave exhibits maxima unless these happen to coincide with the $E_{1/2}$ potentials.

It is possible, if certain necessary conditions are met, to resolve mathematically each of the two measured values into its two components by means of two simple simultaneous equations in which four proportionality constants will appear. This mathematical analysis is valid even when the two constituent derivative waves interfere so severely that only one broad maximum occurs on the net derivative polarogram and when a constituent suspected to be present in the sample is actually absent. This mathematical analysis of overlapping derivative polarographic waves is somewhat similar to a method reported by Breyer, Gutman, and Hacobian²⁶ for the mathematical analysis of overlapping ac polarographic waves; however, in their method, measurements are made at summit potentials rather than at $E_{1/2}$ potentials.

Standard addition is a simple and straightforward method of determining experimentally the values of the proportionality constants needed for the mathematical analysis of the interfering derivative waves. This method has the important advantages that the constants are obtained by use of the test solution of the sample itself and that the specific equation which describes the wave obtained under these conditions need not be known. If only one derivative wave interferes with the other, the calculations are simplified considerably.

Resolution of Polarographic Waves of Close $E_{1/2}$ Values and Various n Values with the ORNL Model Q-1988-ES Polarograph. – The resolution of polarographic waves of close $E_{1/2}$ values and various n values is being investigated with the ORNL model Q-1988-ES controlled-potential and derivative polarograph. Derivative polarograms were measured and interpreted by means of the methods discussed above. A brief summary of the work done to date is given herein; the work will be published after the investigation is completed.

Effect of Rate of Polarization (Scan Rate). – Time lag of a signal through the quadruple, parallel-T, current-averaging circuit (designed for drop times as long as 5 sec) of this polarograph has two effects on the form of the derivative polarogram that is obtained: the width of the derivative wave is increased, and the potential at which the peak occurs is delayed beyond the $E_{1/2}$ value. Both effects influence the degree of resolution. In order to measure the amount of lag in the quadruple filter, derivative polarograms of 0.1 M KCl solutions that contained only Tl^+ , Cd^{2+} , or In^{3+} were made at different rates of polarization of the D.M.E. (drop time ~ 4.5 sec) and both effects were observed as a function of scan rate. The potentials at which the derivative peak values occur were compared with values of $E_{1/2}$ reported in the literature.²⁷ Values of n were calculated by measurement of these average-current polarograms and were compared with

²⁶B. Breyer, F. Gutman, and S. Hacobian, "Polarography with Alternating Currents. I. Outline of Theory, Apparatus, and Technique. II. A. C. Polarography of Cadmium, Zinc, Lead, Thallium, Indium, Bismuth, and Antimony," *Australian J. Sci. Research, Ser. A* 3, 558 (1950).

²⁷I. M. Kolthoff and J. J. Lingane, *Polarography*, 2d ed., pp 198 and 519, Interscience, New York, 1952.

theoretical values and values reported in the literature.²⁸ The results of these studies are summarized in Table 3. When the scan rate is 0.02 v/min, the potentials at which the derivative peaks occur are in good agreement with the $E_{1/2}$ values; however, at a scan rate of 0.1 v/min, the potentials at which the peaks occur are about 30 mv more negative than the $E_{1/2}$ values. The values of n calculated from $W_{1/2}$ measurements taken from average-current derivative polarograms made at a scan rate of 0.02 v/min are in good agreement with the theoretical values of n . The method of calculating n from average-current derivative polarograms made at a sufficiently slow scan rate is much faster and easier than, and at least as accurate as, that method in which the conventional log plot from regular polarograms is used. The results of the measurements of both potentials of maximum peak heights and n values indicate that the time lag through the current-averaging quadruple filter is negligible at a scan rate of 0.02 v/min. In order to obtain maximum resolution of average-current derivative polarographic waves, it is necessary to use polarization rates of the order of 0.02 v/min.

Qualitative Comparison of Resolution Obtained with Various Polarographs. – Solutions that contained Tl^+ , Cu^{2+} , Pb^{2+} , Cd^{2+} , and ln^{3+} ions, each at the same concentration, were analyzed polarographically. The degree of resolution of the constituent waves of the controlled-potential average-current derivative polarogram achieved with the Q-1988-ES polarograph was about the same as that obtained with the Brookhaven incremental polarograph and as that reported for the Barker²⁹ and the Hamm³⁰ square-wave polarographs and for the Breyer, Gutman, and Hacopian²⁶ ac polarograph.

Examples of the Degree of Resolution of Consecutive Derivative Waves by the ORNL Model Q-1988-ES Polarograph. – The controlled-potential average-current derivative peaks obtained by means of the Q-1988-ES polarograph for a 0.1 M KCl solution that contains Pb^{2+} and ln^{3+} in concentrations of 50 and 20 $\mu g/ml$, respectively, are separated by 170 mv when a scan rate of 0.1 v/min is used. The two peaks are completely resolved; therefore the peak heights can be measured independently of each other.

Undamped regular and average-current derivative polarograms were made at a scan rate of 0.1 v/min of several 0.1 M KCl solutions that contained ln^{3+} and Eu^{3+} , each in concentration of about 10^{-4} M. Since the n values are 3 and 1, respectively, the Eu^{3+} derivative wave, which occurs at the more negative potential, is theoretically three times broader than that of ln^{3+} . The two maxima in the net derivative wave occur about 90 mv apart, which is also the difference between the $E_{1/2}$ values. The undamped regular polarograms interfere severely; it is not possible to measure the wave height of either of the two constituent regular waves. For the controlled-potential average-current derivative polarogram, the ln^{3+} wave does not interfere with the Eu^{3+} peak, but the Eu^{3+} wave does interfere with the ln^{3+} peak. From the derivative polarogram,

²⁸*Ibid.*, p 194.

²⁹G. C. Barker and I. Jenkins, "Square Wave Polarography. Part I. General Introduction," *Analyst* **77**, 685 (1952).

³⁰R. E. Hamm, "Square-Wave Polarograph," *Anal. Chem.* **30**, 350 (1958).

Table 3. Effect of Filter Lag at Various Polarization Rates on Values of Derivative Peak Potentials and Peak Widths for Reversible Reductions

Quadruple, parallel-T, current-averaging filter

Supporting electrolyte: 0.1 M KCl

Drop time: ~ 4.5 sec

Single Reducible Ion Present	Polarization Rate (v/min)	Potential of Maximum Peak Height (v vs the S.C.E.)	Literature $E_{1/2}$ Values* (v vs the S.C.E.)	n		
				Calculated from $W_{1/2}$	Literature Values** Calculated from $\log [i/(i_d - i)]$ vs E	Theoretical Value
Tl ⁺			-0.460		1.00	1
	0.02	-0.463		1.00		
	0.05	-0.476		0.964		
	0.10	-0.490		0.906		
Cd ²⁺			-0.599			2
	0.02	-0.604		1.92		
	0.05	-0.616		1.76		
	0.10	-0.630		1.51		
In ³⁺			-0.561		2.57	3
	0.02	-0.566		2.75		
	0.05	-0.582		2.42		
	0.10	-0.595		1.97		

*I. M. Kolthoff and J. J. Lingane, *Polarography*, 2d ed., pp 198 and 519, Interscience, New York, 1952.***Ibid.*, p 194.

the concentration of Eu^{3+} can be measured directly and that of In^{3+} can be measured by the method of standard addition.

Mathematical Analysis of Severely Interfering Derivative Waves by the Method of Standard Addition. – The mathematical analysis of severely interfering, controlled-potential, average-current derivative waves is being studied quantitatively. The Q-1988-ES polarograph and the method of standard addition are used. The concentrations of Cd^{2+} and In^{3+} in 0.1 M KCl were calculated. The $E_{1/2}$ values are separated by only 38 mv, and the constituent derivative polarograms interfere severely with each other in the net derivative polarogram of a solution that contains both ions. Solutions that contained various concentrations of Cd^{2+} and In^{3+} at $\text{In}^{3+}:\text{Cd}^{2+}$ ratios up to 1:10 were measured by this derivative polarographic method. The calculated concentrations of Cd^{2+} and of In^{3+} were within $\pm 5\%$ of the concentrations known to be present.

INORGANIC PREPARATIONS (X-10)

D. E. LaValle

The preparation of the nitrides of the rare-earth metals for the Nuclear Physics and Neutron Diffraction Group of the Physics Division was extended to include phosphides, arsenides, and antimonides of some rare-earth metals. Nitrides of ytterbium and of dysprosium, phosphides and antimonides of terbium and of holmium, and terbium arsenide were prepared.

The preparation of fused salts for the High-Temperature Reactions Group of the Metallurgy Division was continued; numerous preparations of the bismuth halides were made.

In the fused-salt work for the High Temperature and Structural Chemistry Group of the Chemistry Division, anhydrous CeCl_3 , NdCl_3 , LiCl , LiBr , LiI , AlCl_3 , and CsF were prepared.

The anhydrous lithium iodide program for the Neutron Spectroscopy Group of the Neutron Physics Division was continued; several preparations of normal LiI and Li^{61}I were made. The program was extended to include CsI . At the present time, purification methods are being limited to multiple crystallizations.

The preparation of bromates for use by the Radiation Chemistry Group of the Chemistry Division in Szilard-Chalmers reactions was continued. The bromates included $\text{Ba}(\text{BrO}_3)_2$, CsBrO_3 , TlBrO_3 , and the anhydrous forms of normal LiBrO_3 and Li^7BrO_3 .

An investigation into some aspects of the chemistry of rhenium and technetium began; some preparations of potassium hexafluororhenate, K_2ReF_6 , were made. All the products are pink, whereas the K_2ReF_6 prepared by Peacock was described by him as being white.³¹

Numerous other preparations of interest were made. Relative to scintillation counter work, cadmium octoate (the cadmium salt of 2-ethylhexanoic acid) was prepared for the group in the Physics Division who are working with the fast-chopper time-of-flight spectrometer; lithium-6 octoate was made for the Reactor Physics-Experimental Group of the Neutron Physics Division.

³¹R. D. Peacock, "The Quadrivalent Fluororhenates," *J. Chem. Soc.* 1956, 1291.

Platinum phthalocyanine was prepared for the Irradiation Effects on Oxidation of Metals Group of the Solid State Division. For the Nuclear Chemistry Group of the Chemistry Division, another preparation of Li_3^{15}N was made.

In the preparation of high-purity compounds, the magnesium oxide program was resumed, the goal being 10 lb of MgO containing less than 10 ppm of each transition-element impurity. This program is now activated under the Fundamental Investigation of Radiation Effects in Nonmetallic Materials Group of the Solid State Division. Potassium fluoride is being purified by zone-refining for the Chemical Research for Advanced Fluid-Fueled Reactors Group of the Reactor Chemistry Division.

IONIC ANALYSES (X-10)

P. F. Thomason

Controlled-Potential Coulometric Titration of Plutonium

W. D. Shults

The determination of milligram quantities of plutonium by controlled-potential coulometric titration has been described.³² The method was improved slightly and then evaluated thoroughly for analysis of "product" samples from the PRFP Pilot Plant. The work has been reported,³³ and the method has been incorporated in the *ORNL Master Analytical Manual*.³⁴

Analysis of Dissolver Solutions. – Work on the application of controlled-potential coulometry to the analysis of dissolver solutions for plutonium³² has continued. The optimum titration conditions for analysis of Purex type samples were established. In 0.5 M HCl–0.02 M $\text{NH}_2\text{SO}_3\text{H}$, the best supporting electrolyte solution of those tested, the $E_{\text{P}_U}^{\circ}$ is 0.705 v and the $E_{\text{F}_e}^{\circ}$ is 0.465 v vs the S.C.E. Consequently, preliminary reduction is made at $E_{\text{P}_U}^{\circ} - 0.120$ (i.e., 0.585 v) when iron is present or at $E_{\text{P}_U}^{\circ} - 0.180$ (i.e., 0.525 v) when iron is absent; oxidation of plutonium(III) to plutonium(IV) is then made at $E_{\text{P}_U}^{\circ} + 0.180$ (i.e., 0.885 v) and is the measured electrolysis. Each of these electrolyses is terminated when the current decreases to 10 μa . The relative standard deviation of this procedure is 0.3% when $\sim 250 \mu\text{g}$ of plutonium is titrated under ideal conditions. Highly radioactive solutions (from dissolution of irradiated dekad uranium metal rod) were analyzed remotely in the HRLAF by this procedure with success; the relative standard deviation was $\sim 0.6\%$. The results by this method agree with those by the thenoyltrifluoroacetone extraction–alpha counting method to within $\pm 1\%$.

³²W. D. Shults, "Controlled-Potential Coulometric Titration of Plutonium," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 5–6.

³³W. D. Shults, *Controlled Potential Coulometric Titration of Plutonium – Application to PRFR Samples*, ORNL-2921 (Apr. 11, 1960).

³⁴W. 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.

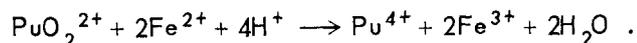
The separation procedure for plutonium discussed earlier,³² that is, adsorption of plutonium(IV) on an anion exchange resin from 10 M HNO₃, was also tested in the HRLAF and did not perform satisfactorily. Consequently, work has continued on that separation method, as well as on others, for example, anion exchange from chloride medium, liquid extraction by means of thenoyltrifluoroacetone, and the carrying of plutonium(IV) on lanthanum fluoride and on bismuth phosphate precipitates. Best results have been obtained with the lanthanum fluoride carrying technique. The dissolution of the lanthanum fluoride precipitate in aluminum nitrate solution and subsequent coulometric titration of plutonium resulted in an over-all relative standard deviation of 0.3% with 99.8% recovery when 256 μg of plutonium was determined. The bismuth phosphate carrying technique works but offers no advantage over the lanthanum fluoride method. Extraction into and stripping from thenoyltrifluoroacetone solution was unsatisfactory because no means could be devised to completely destroy the organic material that is introduced into the stripping solution. Similarly, plutonium can be separated very satisfactorily by anion exchange from nitrate or chloride media, but the small amount of organic material that "leaks" from the resin interferes seriously in subsequent coulometric electrolyses. Work is continuing on means to circumvent or eliminate that problem because the ion exchange technique offers greatest utility for this particular application.

Generation and Back-Titration of Intermediate Reagents at Controlled Potential

W. D. Shults

The feasibility of generating and back-titrating intermediate reagents coulometrically at controlled potential rather than at controlled current has been proved by application to the determination of plutonium. This technique has certain advantages over constant-current generation, the most important being that the reagent can be generated in excess and the excess back-titrated electrolytically. Thus, coulometric titrimetry can be applied to reactions that can be driven to completion by an excess of reagent. Other advantages are that specific reagents can be generated, the successive generation of different reagents is possible, and no indicator-electrode system is required. In general, the advantages inherent in the constant-current technique are retained.

Plutonium can be determined by means of the reaction



Plutonium(VI) is prepared with hot concentrated perchloric acid and is then reacted with an excess of iron(II), which is generated at a platinum electrode at controlled potential. When the reaction between PuO₂²⁺ and iron(II) is complete, the excess iron(II) is oxidized electrolytically, also at controlled potential. The weight of plutonium present is then calculated by the difference between the generation and the back-titration electrolysis currents. This procedure was developed for use in the analysis of solutions that contain iron and/or uranium. It is very tolerant to the presence of these ions and also gives good precision; the relative standard deviation is 0.1 to

0.2% when 10 to 50 mg of plutonium is titrated. A paper that describes this method will be published in *Analytical Chemistry*.³⁵

The use of divalent silver as the oxidant for plutonium to the hexavalent state will be studied in order to possibly increase the precision of this method and to extend it to smaller amounts of plutonium. Work has also begun on the application of this technique to the determination of uranium, especially the direct determination of uranium in solutions of stainless steel.

Anion Exchange Separation-Coulometric Titration of Uranium in Reactor Dissolver Solutions

E. L. Blevins

Uranium can be separated from synthetic stainless-steel-type dissolver solutions on an anion exchange resin column and subsequently eluted and titrated coulometrically.³⁶ Initially, the hydrochloric acid system appeared to be the most convenient to use since uranium(VI) is both quantitatively adsorbed from hydrochloric acid solution and easily eluted from the chloride-form resin. However, the work of Kraus and Nelson³⁷ indicated that uranium(VI) and iron(III) cannot be separated by means of anion exchange resin in a hydrochloric acid medium. They can be from sulfuric acid medium; therefore, the uranium is adsorbed on the column as the sulfate, converted to chloride, and eluted. The interference of chromium(VI) is prevented by reduction with hydroxylamine hydrochloride. The accuracy and precision of the method are indicated by the data of Table 4.

Table 4. Accuracy and Precision of Ion Exchange Separation-Coulometric Titration of Uranium

Sample	Uranium (mg)		Number of Titrations	Relative Standard Deviation (%)
	Taken	Found		
Standard solution of uranium	11.93	11.89	9	0.3
	2.65	2.64	7	0.5
Synthetic dissolver solution	8.88	8.92	12	0.2
	0.854	0.855	14	0.7

Coulometric Titration of Uranium in the Presence of Molybdenum

H. E. Zittel E. L. Blevins P. F. Thomason

A coulometric method was developed for the determination of uranium in solutions that contain molybdenum in as high a weight ratio to uranium as 1:10. Heretofore, molybdenum had to be

³⁵W. D. Shultz, "Generation and Back-Titration of Intermediate Reagents at Controlled Potential," a paper accepted for publication in *Anal. Chem.*

³⁶E. L. Blevins, *Anion Exchange Separation of Uranium for Reactor Dissolver Solutions*, ORNL CF-60-4-62 (Apr. 18, 1960).

³⁷K. A. Kraus and F. Nelson, "Metal Separations by Anion Exchange," *Symposium on Ion Exchange and Chromatography in Analytical Chemistry*, Am. Soc. Testing Materials, Spec. Tech. Publ. No. 195 (1958).

separated prior to the coulometric titration of uranium because the reduction potentials of these two elements are nearly the same in acid medium. This interference is avoided by titrating the uranium in a basic solution that contains sodium sulfate and sodium tripolyphosphate. The accuracy and precision of the method are indicated in Table 5.

The possible interferences of Fe, Cu, Cr, Ni, and Ru were investigated. The interference of all these except copper can be avoided by treatment of the sample prior to the titration of the uranium.

Table 5. Accuracy and Precision of the Coulometric Titration of Uranium in Sodium Sulfate-Sodium Polyphosphate Medium

Molybdenum Taken (mg)	Uranium (mg)		Number of Titrations	Relative Standard Deviation (%)
	Taken	Found		
None	2.37	2.37	7	0.6
0.25	2.37	2.37	20	0.7
None	4.73	4.73	8	0.3
0.5	4.73	4.73	16	0.4

Determination of Uranium(VI) in PRFP Type Dissolver Solutions

B. B. Hobbs

Radioactive and nonradioactive solutions of compositions similar to those expected for PRFP type dissolver solutions were analyzed for uranium(VI). The procedure consisted in separation of the uranium(VI) from the solution by extraction into a solution of triisooctylamine in xylene, stripping of the uranium(VI) from the organic layer into an aqueous solution of acid, and quantitative determination of uranium(VI) in the acid solution by use of a controlled-potential coulometer. The results obtained indicate that it should be possible to determine uranium(VI) in PRFP dissolver solutions to within $\pm 1\%$ by this method. The work has been reported.³⁸

Coulometric Determination of Europium in Europium-Activated Lithium Iodide Scintillation Crystals

D. A. Costanzo

A method for the determination of europium(II) and europium(III) by controlled coulometric titration has been developed.³⁹ The method is based on the controlled-potential coulometric oxidation of europium(II) to europium(III) and is similar to the method of Shults.⁴⁰ Total euro-

³⁸B. B. Hobbs, *Coulometric Determination of Uranium in Power-Reactor-Fuel-Dissolver Solutions*, ORNL-2987 (Nov. 18, 1960).

³⁹D. A. Costanzo, "Europium in Scintillation Crystals of Europium-Activated Lithium Iodide, Coulometric Titration Method," Method Nos. 1 212720 and 9 00712720 (5-18-60), *ORNL Master Analytical Manual*; TID-7015, suppl. 3.

⁴⁰W. D. Shults, "Controlled-Potential Coulometric Determination of Europium," *Anal. Chem.* 31, 1095 (1959).

pium, present both as europium(II) and europium(III), in a single-crystal sample is determined on a test portion of the crystal (dissolved in 0.1 M perchloric acid solution) by reducing the europium(III) to europium(II) at a mercury cathode whose potential is controlled at -0.850 v vs the S.C.E. The europium, then present as europium(II), is determined immediately by coulometric oxidation to europium(III) at a platinum anode whose potential is controlled at -0.100 v vs the S.C.E. The oxidation occurs with very nearly 100% current efficiency. The europium(II) originally present is determined separately on another test portion of the crystal, also by oxidation to europium(III) at a platinum anode whose potential is controlled at -0.100 v vs the S.C.E. The titrations are performed under an argon atmosphere and require a total time of 20 to 30 min per analysis. The precision obtained when synthetic standard solutions of europium(III) in aqueous 1.0 M lithium iodide-0.1 M perchloric acid were analyzed by this method is indicated in Table 6.

Table 6. Precision of the Coulometric Determination of Europium

Europium(II) Titrated (mg)	Standard Deviation (mg)	S.E. _R (%) [*]
0.330	0.002	1.0
0.660	0.003	0.3
1.320	0.004	0.2
2.640	0.017	0.4

^{*}S.E._R is the relative standard error of the average at the 95% probability level.

Coulometric Determination of Uranium(IV) and Uranium(VI) in Uranium Tetrafluoride

D. A. Costanzo

The coulometric determination of uranium(IV) and uranium(VI) was investigated in anticipation of the need to determine uranium in fluoride fuels. The sample is dissolved by heating in concentrated phosphoric acid under nitrogen until the removal of fluoride by distillation is complete. The uranium(IV) and uranium(VI) in the residual solution are determined coulometrically in an aqueous medium that contains 6 wt % phosphoric acid and 3 M sulfuric acid; the procedure is described by Stromatt and Connally.⁴¹

Dropping Mercury Electrode for Polarographic Studies in Hydrofluoric Acid Media

H. P. Raen

Some performance data have been obtained for a Teflon D.M.E. capillary tip of physical dimensions not yet perfected to the extent desired. The precision of drop time (t) values for the capillary tip was determined for three media; the data are given in Table 7. These data suggest that

⁴¹R. W. Stromatt and R. E. Connally, "Determination of the Stoichiometry of Uranium Dioxide by Controlled Potential Coulometry," a paper submitted for publication in *Anal. Chem.*

Table 7. Some Performance Data for a Teflon D.M.E. Capillary Tip

Orifice dimensions, $75 \times 85 \mu$
 N , 10 (each an average for 20 drops)
 No applied potential, no grounding

Medium	h (mm)	\bar{t} (sec)	S (%)
Air	320	13.38	0.06
Air	685	6.69	0.07
Distilled H ₂ O	685	6.07	0.10
0.1 M KCl	685	5.63	0.02

the precision of t may be greater for a Teflon than for a glass capillary, for which t values in air and water are reported to be imprecise.⁴²

Applied potential vs t curves were obtained in 0.1 M KCl for this same capillary tip and for a Sargent S-29419 "2-to-5" sec glass capillary; the mercury levels were set so that the t values for the two capillaries were the same at zero applied potential. The two curves were very similar from 0 to -0.8 v; the electrocapillary maximum occurred at the same applied potential for both. At more negative potentials, the data for the Teflon capillary were erratic. It cannot be concluded that the erratic behavior at potentials more negative than -0.8 v is characteristic of the Teflon capillary because the data are limited and especially because the orifice of the Teflon capillary used was not perfectly round and smooth-walled.

Considerable progress has been made, with the help of R. J. Fox⁴³ and V. E. Walker,⁴⁴ on the development of a method of fabricating Teflon capillary tips. Techniques for achieving satisfactory roundness and wall smoothness of the orifice and for producing a smooth face on the capillary about the orifice have been worked out. Ways of making the orifice diameter to specification are now being evolved. Photomicrography (including shadow-casting) has been an excellent tool for comparing the geometric and surface properties of the experimental Teflon capillaries with those of Sargent S-29419 "2-to-5" sec capillaries.

Apparatus for the Automatic Simultaneous Measurement of m , t , w , and Drop Count of a Dropping Mercury Electrode

H. P. Raen

An apparatus is being built that will automatically and simultaneously measure the rate of flow of mercury (m), drop time (t), drop weight (w), and drop count of a dropping mercury electrode (D.M.E.). It will be of general use in polarography; it is needed specifically to facilitate the evaluation of Teflon capillaries. Their characteristics will be established by studying their

⁴²I. M. Kolthoff and J. J. Lingane, *Polarography*, 2d ed., pp 83-84, Interscience, New York, 1952.

⁴³Instrumentation and Controls Division.

⁴⁴Fabrication Shops, Research and Development Group.

behavior in air, water, and solutions of electrolytes; with and without applied potential; and at various heights of mercury column (*b*). The characteristics will be compared with those of a Sargent S-29419 "2-to-5" sec glass capillary. These studies will require a large number of measurements of m , t , w , and drop count, which would be almost prohibitive if done manually.

The design of the apparatus is based on the relationship $k = m/t_{\text{total}}$, where t_{total} is the total time required for the mercury level in the standtube to fall a selected distance, and k is the mass of mercury contained in the segment of standtube corresponding to the distance of fall; k is a constant for the particular standtube. Lingane's device⁴⁵ for the automatic measurement of m is based on this relationship.

The apparatus will consist of a timing device for measuring t_{total} , a drop-counting device, and a special standtube. The circuits for the timing and drop-counting devices were designed by H. C. Jones,⁴⁶ with suggestions from D. J. Fisher⁴⁶ (see "Drop-Counting and Timing Devices for a Polarographic Dropping Mercury Electrode," this report). The timing device is a movable arrangement of two sets (in fixed position with respect to each other) of a light source and a photoconductive cell that will detect the passage of the mercury surface past two points on the standtube. It is similar to a device described by J. Farquharson,^{47,48} who advised regarding the design and functioning of this apparatus. The time of fall of mercury level between the two points (t_{total}) is measured by means of associated circuitry and timer. The standtube is constructed of uniform-diameter tubing so that it is necessary to determine the k value at only one position of the mercury-level-detecting assembly. The standtube is connected to the D.M.E. and mercury reservoir via Teflon-plugged stopcocks and standard-taper joints in order to eliminate the "cushioning" effects and air pockets that are sometimes associated with flexible-tubing connections. A platinum-wire contact is sealed into the standtube to permit grounding of the D.M.E.

A prototype of the timing device and standtube was used to establish the precision of the measurement of t_{total} , a measurement which is critical because it is *the* measurement that determines the reliability of polarographic constants that will be established by means of the apparatus. The precision was established independently of the formation and fall of mercury drops by allowing the mercury to flow freely through a throttling capillary rather than drop from a capillary. Under conditions equivalent to $t \approx 5$ sec, the results of six automatic measurements of t_{total} , each at 25.0°C, were: $\bar{t}_{\text{total}} = 514.4$ sec and standard deviation = 0.26 sec (i.e., 0.05%).

The k value can be determined either by the procedure recommended by Lingane⁴⁵ or by that described by Milner.⁴⁹ It was found experimentally that when t is large (e.g., when the drops are formed in air) the procedure of Lingane gives more accurate results.

⁴⁵J. J. Lingane, "Apparatus for Rapid Polarographic Analysis," *Anal. Chem.* **16**, 329 (1944).

⁴⁶Analytical Instrumentation Group.

⁴⁷ORGDP, Technical Division, Physical Measurements Dept.

⁴⁸J. Farquharson and H. A. Kermicle, "Precise Automatic Manometer Reader," *Rev. Sci. Instr.* **28**, 324 (1957).

⁴⁹G. W. C. Milner, *The Principles and Applications of Polarography and Other Electroanalytical Processes*, p 97, Longmans, Green, New York, 1957.

The apparatus has the following advantages over that of Lingane:⁴⁵ measurements are not limited to one value of b since the mercury-level-detecting device is movable along the standtube; drop count can be measured simultaneously with m , and w can thereby also be measured; the precision of measurements of t_{total} is greater because the clinging of mercury to the wall of the standtube is minimized, that is, the surface condition and smoothness of the wall are not disturbed as they are when tungsten leads have to be sealed into the standtube; the circuitry of the measuring system has no part in common with the polarographic system; and a shock hazard does not exist.

Chemical and Radiolytic Studies of the Simulated Purex Waste Solution–Sodium Chloride System

H. Kubota

The study of the chemical reaction between simulated Purex waste solution and sodium chloride⁵⁰ is being done for the Waste Disposal Section of the Health Physics Division relative to the investigation of the use of salt mines as possible sites for the disposal of waste solutions from nuclear-reactor fuel reprocessing. Two types of reaction can be expected when radioactive waste solutions are in contact with sodium chloride: the direct reaction between the solution and sodium chloride and the radiolytic decomposition resulting from the high activity of the fission products.

It was established⁵¹ that the principal reaction between simulated acid Purex waste solution and sodium chloride is the aqua regia reaction, the rate and extent of which are temperature-dependent. The extent of reaction is also a function of the acidity of the solution. It was found that 60°C and 4 M acidity are the critical solution conditions below which the reaction between simulated acid Purex solution and sodium chloride can be inhibited.

Radiolytic studies were made in order to establish the solution compositions that give the lowest steady-state pressures. The compositions of the simulated Purex solutions tested are given in Table 8. Each type of solution was irradiated "as is." saturated with sodium chloride,

⁵⁰H. Kubota, "Chemical Changes in the Reaction Between Purex Waste Solution and Sodium Chloride," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 11–12.

⁵¹H. Kubota and T. Tamura, *Waste Disposal in Salt: I. The HNO₃-NaCl Reaction*, ORNL-2984 (Sept. 15, 1960).

Table 8. Compositions of Simulated Purex Waste Solutions Investigated for Radiolytic Stability

Treatment	Ionic Concentration (equivalents/liter)				
	Free H ⁺	Fe ³⁺	Ni ²⁺	NO ₃ ⁻	SO ₄ ²⁻
Untreated (7 M acid)	7.0	1.0	0.3	7.3	1.5
Diluted with H ₂ O (3.5 M acid)	3.5	0.5	0.1 ₅	3.6 ₅	0.7 ₅
Semineutralized with NaOH	3.6	0.9	3.2	6.4	1.3
Neutralized with NaOH	1.2	0.8	4.8	5.7	1.2
Formaldehyde-denitrated*	0.5	2.4	0.9	0.5	4.0

*Also contained 0.7 equivalent of Al³⁺.

and saturated with sodium chloride in the presence of excess solid sodium chloride. The solutions being irradiated were contained in tubes provided with mercury columns to indicate the internal pressures. The Co^{60} facility in Building 3029, which provides a dose rate of about 2×10^6 rads/hr, was used. It is thought that irradiation by means of Co^{60} will bring about very nearly the same kind of decomposition that can be expected from the actual Purex waste solutions. The results of the irradiations are shown in Fig. 1. Each type of solution attained a steady-state pressure when the radiation dose approached 10^9 rads. It is not possible to make generalizations about the radiation stability of different solution types; however, the results of the studies to date will be helpful in determining the course of future studies.

Titrimetric Analysis of Mixtures of Monobutyl-, Dibutyl-, and Orthophosphoric Acids

H. Kubota C. C. White

The need for a rapid method for the analysis of mixtures of monobutyl-, dibutyl-, and orthophosphoric acids led to the investigation of a titrimetric procedure in which the first two active hydrogens of all these are titrated in an aqueous medium, and the third hydrogen of orthophosphoric acid is titrated in an essentially nonaqueous (acetone) medium. The similarity in the acid constants of the first two hydrogens makes the titration in aqueous medium possible. Since the small amount of water that is present in the sample behaves in part like an acid in the acetone medium, the amount of water permissible for any given determination is small, and its contribution to the acidity of the system was treated as a reagent blank. The titration was made by means of an automatic titrator; a glass-calomel electrode system was used. Instead of the ordinary fiber-tipped calomel electrode, an electrode was used that had less tendency to clog in the organic medium. It consisted of a calomel microelectrode in contact with a saturated solution of potassium chloride contained in a Vycor tube having an unfired tip. Contact with the solution in the titration vessel was through the porous tip.

The procedure was tested by titrating synthetic mixtures of the acids. When all three are present, each can be determined to within $\pm 8\%$. When only the monobutyl and dibutyl acids are present, the error of the determination of each is less than $\pm 3\%$. When orthophosphoric is present together with either of the other two acids, the error of the determination of any one of the three is $\pm 5\%$. Sodium nitrate in large amounts interferes with the titration in the organic medium. A paper that described the work was presented.⁵²

Spectrophotometric Determination of Technetium(VII) with Thioglycolic Acid

F. J. Miller

A spectrophotometric method of analysis for technetium(VII) has been developed to supplement the radiochemical and polarographic methods that are now used in laboratories of radiochemical

⁵²C. C. White and H. Kubota, "Titrimetric Determination of Mixtures of Monobutyl-, Dibutyl-, and Orthophosphoric Acids," a paper presented at the 138th National Meeting of the American Chemical Society, New York, N.Y., Sept. 11-16, 1960.

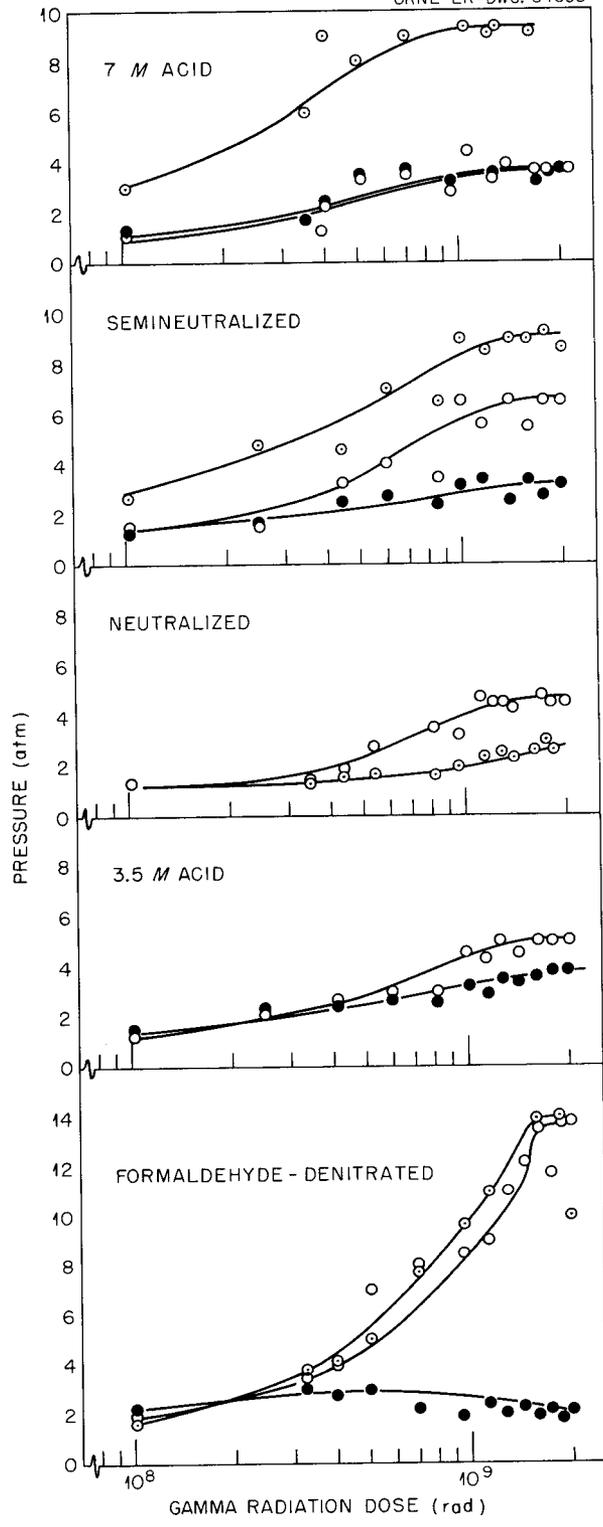


Fig. 1. Effect of Co^{60} Irradiation on Vapor Pressure of Simulated Purex Waste Solutions. ● No NaCl, ○ saturated with NaCl, ⊙ saturated with NaCl plus excess solid NaCl.

processing plants. Technetium is determined as the pertechnetate ion in the concentration range from 2 to 40 $\mu\text{g/ml}$ in the final solution by measuring at 655 $m\mu$ the intensity of the color that is formed at pH 8 with thioglycolic acid. The absorbancy-concentration relationship obeys Beer's law over this range. The molar absorbancy index is estimated to be of the order of 1800. Very few anions interfere. The results of this work have been published.⁵³

Spectrophotometric Determination of Technetium(VII) with Toluene-3,4-dithiol

F. J. Miller

A method has been developed for the spectrophotometric determination of technetium(VII) in the microgram range by reaction with toluene-3,4-dithiol in an aqueous medium that is 2.5 *N* in acid. The colored complex that is formed is extracted into carbon tetrachloride. The intensity of the color of the carbon tetrachloride solution is measured at 450 $m\mu$. The molar absorbancy index is of the order of 15,000. The interference of many metallic cations necessitates the preliminary separation of the technetium(VII). The results of a study of the various factors that influence the formation and extraction of the complex are summarized in a paper that has been accepted for publication in *Analytical Chemistry*.

Revision of Spot Tests and Redesign of Equipment for Use in Hot-Cell Facilities for Isotope Production

F. J. Miller

Revised tests have been suggested as replacements for the spot tests presently in use as quality controls for isotope production. Equipment has been designed and procedures suggested so that all analyses can be performed in hot-cell facilities by means of remotely controlled equipment. The analyses are made at the ppm level. Tests are required for manganese, nitrate-nitrite, heavy metals, and reducing power. The results of the work are described in a paper accepted for publication in *Analytical Chemistry*.

Studies of the Polymerization, Depolymerization, and Hydrolysis of Plutonium in Uranyl Nitrate and Nitric Acid Solutions at Elevated Temperature

R. E. Biggers

D. A. Costanzo

The scope of the study of the rate and extent of polymerization and hydrolysis of plutonium in uranyl nitrate and nitric acid solutions at elevated temperatures has been described;⁵⁴ the study has begun. The experimentation will be similar to that followed at Hanford,⁵⁵ spectrophotometric

⁵³F. J. Miller and P. F. Thomason, "Spectrophotometric Determination of Technetium(VII) with Thioglycolic Acid," *Anal. Chem.* **32**, 1429 (1960).

⁵⁴R. E. Biggers and D. A. Costanzo, *Hazards and Experimental Procedure Evaluation For: "Studies on the Polymerization and Hydrolysis of Plutonium in Uranyl Nitrate and Nitric Acid at Elevated Temperatures,"* ORNL CF-60-5-34 (May 9, 1960).

⁵⁵A. Brunstad, "Polymerization and Precipitation of Plutonium(IV) in Nitric Acid," *Ind. Eng. Chem.* **51**, 38 (1959).

techniques being used. The ranges of other experimental conditions at uranium nitrate concentration (as uranium) of about 350 g/liter will be: plutonium concentration, up to about 100 g/liter; acidity, 0.01 to 1.0 M; and temperature, up to 95°C.

The rate of depolymerization will be studied at various acid concentrations and at various temperatures. The importance of the temperature at which the polymer is formed will be studied with respect to the rate and extent of depolymerization. The effect of sulfate (and perhaps other anions that form strong complexes) on the depolymerization of the polymer in nitric acid and in uranyl nitrate–nitric acid systems will also be studied. In addition, some experiments similar to some that were made by Ockenden and Welch⁵⁶ will be made, particularly with regard to the use of ion exchange methods for the preparation of pure solutions of polymer. High-speed centrifugation (not ultracentrifugation) will be used to fractionate polymers of molecular weights that come within the speed range of the Lourdes model AX high-speed centrifuge (i.e., $36,000 \times G$).

Program for Spectrophotometric Study of Solutions at Elevated Temperatures and Pressures

R. E. Biggers

Purpose and Goals. – Spectrophotometric techniques are being developed for studying the fundamental chemistry of aqueous solutions of uranium, other transuranium elements, some of the lanthanides and fission products, other elements of interest in aqueous solutions at temperatures higher than 100°C, and various mixtures of these elements.⁵⁷ A spectrophotometer that can be operated at temperatures as high as 330°C and at pressures up to at least 3000 psi with highly radioactive (alpha) solutions has been designed for ORNL by the Applied Physics Corporation. It is anticipated that with this instrument it will be possible to make measurements up to near the critical point ($\sim 370^\circ\text{C}$) in both water and deuterium oxide.

An ultimate goal of the program is to study the application of such an instrument suitably modified to provide an in-line analytical system for high-temperature high-pressure fluid streams and for studies of the chemistry of such systems. The technique will eliminate the complexities and uncertainties introduced by withdrawal of a large number of samples. Many of the analytical values determined for the constituents of aqueous solutions at high temperature are questionable if the sample is cooled to room temperature before the determinations are made because solubilities, valence states, adsorption, etc., of ions most often change with temperature.

This instrument will also be used to study high-temperature radioactive systems. Solubilities, reaction rates, and valence-state distributions in such systems will be studied as a function of temperature and other conditions. Fundamental studies of the effects of solution variables and temperature on the parameters of absorption spectra will yield information concerning the role that complex-ion formation, hydrolysis, temperature, etc., play in the chemistry of the systems.

⁵⁶D. W. Ockenden and G. A. Welch, "The Preparation and Properties of Some Plutonium Compounds. Part V. Colloidal Quadrivalent Plutonium," *J. Chem. Soc.* 1956, 3358.

⁵⁷R. E. Biggers and J. M. Chilton, "Program for Spectrophotometric Studies of Aqueous Solutions at Elevated Temperatures," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 13–14.

Subcontract between ORNL and Applied Physics Corporation for the Construction of a High-Temperature High-Pressure Spectrophotometer. – The subcontract work, started last March, between ORNL and the Applied Physics Corporation is proceeding well on schedule. The work consists in the study, development, and detailed designing of a complete spectrophotometric system to be used with highly alpha-radioactive solutions at high temperatures and pressures. The status of the whole program as of July 19, 1960, was summarized recently.⁵⁸ Most of the design aspects of the system have been decided on; the optical design has been completed. Detailed drawings are expected to be finished by February 2, 1961. The drawings for the window and cell have been finished; construction and testing of the most promising window structure will be completed very soon. The design of the entire control system and console is essentially complete. Five different cell and window-closure systems have been investigated and tested. The cell system is unique in many ways and has such design characteristics that little or no trouble is anticipated in reaching the goals of temperature and pressure. The window-cleaning system (for bubble removal) has been re-evaluated, and ultrasonic cleaning methods are being studied. A remote optical inspection system is being designed so that the cell contents can be viewed while the system is operating at high temperature and pressure.

The system will conform to the detailed specifications⁵⁹ drawn up by members of the staff at ORNL and will take advantage of other results and progress made in this field at ORNL in recent years. It will be based on the general characteristics and design features of the Cary model 14PM automatic recording, ultraviolet-visible-near-infrared spectrophotometer. After final agreement is reached concerning the design of the system and the complete drawings are finished, the system will be constructed by an outside subcontractor and then installed at ORNL. Construction should start early in 1961 and will require about eight months, followed by an estimated two or three months for installation and testing. It is hoped that the system will be operating by November 1, 1961, and certainly not later than early in 1962.

If the reliability and adequacy of the characteristics of the high-temperature high-pressure spectrophotometric system are demonstrated successfully with cells operated in the static manner, means for operation in a loop system will be studied. It is expected that the results obtained with the loop described below, when it is operated at moderate pressure and at temperatures not higher than 150°C, will greatly simplify and facilitate the extension of the high-temperature high-pressure system to loop or flowing-stream operation.

Miniature Circulating Loop System. – A miniature circulating loop system was designed and constructed by the Chemical Technology and the Engineering and Mechanical Divisions. The related instrumentation has been developed. This system is designed to be used in conjunction

⁵⁸R. 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).

⁵⁹Specification No. CTD-1 for the Design and Construction of a High Temperature-High Pressure Recording Spectrophotometer, Jan. 19, 1959; revision No. 1, Apr. 6, 1959; revision No. 2, No. CTD-2 (final revision), Dec. 16, 1959. Copies are retained by R. E. Biggers, J. M. Chilton, W. O. Greever, and R. G. Wymer.

with a standard Cary model 14PM recording spectrophotometer without any modification to the instrument. At present, the upper limits of temperature and pressure under which it can be used are not expected to exceed 150°C and 8 atm, respectively, with provision for using gas overpressures. The volume of the loop will be about 500 ml or less, and the liquid will circulate at a rate variable up to about 3 liters/min. The cell-window design is adequate for the maximum temperature and pressure expected. The loop has many useful features which include a filtering system, mechanism for removal of bubbles, sample-container system that makes possible the exposure of corrosion specimens or particulate matter to the circulating liquid, and a means of entry to the loop while it is operating.

The miniature loop will be used primarily⁶⁰ to determine the limitations of absorption spectrophotometry as a method of analysis for many kinds of circulating solutions, including solutions of uranyl sulfate and other materials, especially at elevated temperatures. In particular, the problems associated with gas equilibration and the separation of gas from the liquid phase prior to optical measurement, as well as the means and effect of the removal of suspended solid particles, will be studied carefully. The general types of studies to be carried out with this system have been described.^{58,60} The fundamental chemistry of such systems as mentioned above will be studied. The miniature circulating loop system will make possible the evaluation of some of the proposed design features of the special high-temperature high-pressure spectrophotometer before the construction of it is started.

Mathematical Resolution of Complex Overlapping Absorption Spectra by Digital Computation

R. E. Biggers

A mathematical technique which uses high-speed digital computation has been developed^{58,61} to resolve seriously overlapping spectral bands and fine structure. The visible and near-ultraviolet spectra of uranyl perchlorate and uranyl sulfate have been resolved completely into their individual components. These techniques may enable one to make a quantitative study of complex-ion formation, etc., in solution as a function of temperature and other variables. The results of intensive work, especially on the uranium spectra, show that the least-squares, nonlinear, iterative, matrix programs that have been modified for this use are entirely adequate for the analysis of such spectral systems. It has been demonstrated⁵⁷ that the computer programs can resolve overlapping electronic and vibrational bands and also electronic bands with vibrational fine structure. Correlation of these phenomena with complex-ion formation, etc., is in progress.

It has been found that analysis and interpretation of the systems are possible if high-speed digital computing techniques are used. An iterative, generalized, least-squares-fitting routine

⁶⁰R. E. Biggers and J. M. Chilton, *Proposed Program for Elevated Pressure and Temperature Investigations Using the Cary Spectrophotometer Now Located in Building 3508 at ORNL: February 1, 1959 to July 15, 1960*, ORNL CF-59-2-17 (Feb. 5, 1959).

⁶¹R. E. Biggers and J. M. Chilton, "Mathematical Resolution of UO_2^{2+} Spectral Fine Structure," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 14-16.

that was written for the analysis of x-ray and neutron-diffraction data on the Oracle⁶² (the high-speed digital computer at ORNL) was modified for the purpose of resolving the complex spectra into their components; a similar, though not as versatile, program is available for the IBM 704 and 7090.⁶³ A somewhat more detailed discussion of the routine is available.^{57,58}

A Gaussian type function was found to be the single function that best represents the shape of a single spectral band. A Lorentz type function was evaluated and found not to be as satisfactory. A more nearly theoretically correct model would probably be a function that combines a Gaussian function with a small contribution from a Lorentz function. A more fundamental program of study of the most appropriate functions for representing the shapes of various single spectral bands, of the factors that contribute to the broadening of the spectral "line" into a band in the condensed systems that liquids represent, and of spectral band structure is under way. The application of Voigt function profiles to this problem is being investigated. It is believed that this function will be extremely useful and applicable. These problems were reviewed and discussed in a recent lecture.⁶⁴

Typical least-squares-fitting errors for the parameters of the resolved bands of $\text{UO}_2(\text{ClO}_4)_2$ are as follows: intensity parameter, approximates an experimental error of about ± 0.002 to 0.003 absorbancy unit; half-band-width parameter, about ± 2 to 20 cm^{-1} (400 to 800 cm^{-1} range) depending upon peak sharpness and overlap; position, about ± 1 to 60 cm^{-1} ($30,000$ to $20,000 \text{ cm}^{-1}$ range) depending upon peak position and sharpness. This computing technique is being applied successfully to plutonium and transition-group elements and to mixtures of various elements that exhibit complex spectra. The resolved bands permit one to study various parameters of individual transitions without interference from overlapping nearby bands.

Currently, the least-squares-resolution computer program is being applied to the analysis of the spectrum of Pu^{4+} in perchloric acid from 8000 to $29,000 \text{ cm}^{-1}$; the analysis has almost been completed. Systems of other ions (e.g., PuO_2^{2+} , Pu^{3+} , UO_2^{2+} - Cu^{2+} - Ni^{2+}) and other multicomponent systems are being analyzed.

A new computer program, SPECSYN,⁶⁵ has been completed. This program synthesizes a spectrum, over any given wavelength range, from estimates of the individual band parameters of an experimental spectrum. It then plots the individual bands and the resulting synthesized spectrum on the Oracle Curve Plotter. Finally, it plots the observed spectrum for comparison on the same picture. The program uses the same input-parameter and observation-tape format

⁶²H. A. Levy and W. R. Busing, Chemical Physics Section, Chemistry Division, ORACLE Least Squares II Code, originally written for neutron and x-ray diffraction calculations; modified by W. R. Busing and R. E. Biggers for general applications to resolution of complex overlapping spectra and spectral fine structure.

⁶³P. B. Wood, NLLS: A 704 Program for Fitting Non-Linear Curves by Least Squares, K-1440, p 57 (Jan. 28, 1960).

⁶⁴R. E. Biggers, *Mathematical Resolution of Complex Overlapping Spectra and Spectral Fine Structures by Means of High-Speed Digital Computation and Mathematical Functions for the Representation of Spectral Absorption Bands*, lectures given at ORNL on July 7, 1960, for M. C. R. Symons (Imperial College of Science and Technology, London) and selected members of the ORNL staff.

⁶⁵Codes for Spectrum Calculations and Curve Plotter Output, retained in the files of R. E. Biggers; not yet published because of pending conversion of codes to IBM 7090 operation.

that is used in the least-squares-matrix program. Any plotting interval (either on a cm^{-1} or angstrom basis) can be used. This program enables one to arrive quickly at acceptable estimates of input parameters for the least-squares-matrix program.

Other computer programs have been written⁶⁵ that will take the final parameters calculated for the resolved bands of any spectral system and generate the data according to a given band model. The error for each spectral band at each point and the summation of errors at each point are also generated. These data can then be obtained either in an output form, which when printed yields tabulated data according to any format that is desired, or as a plot on the Oracle Curve Plotter. The x axis may be plotted either as cm^{-1} or wavelength, and the y axis may be either absorbancy or molar absorbancy index. The axes are labeled accordingly, and other information, such as title, date, etc., are put on the Curve Plotter oscilloscope. The resolved bands, the sum of the calculated bands, and the observed spectrum may be plotted in any combination. The summed fitting error (\pm) can then be plotted on a second picture vs either cm^{-1} or wavelength.

Work was begun on the conversion of practically all the computer programs from Oracle to the IBM system so that work can proceed smoothly and rapidly when the IBM 7090 is installed within a few months. This is desirable in view of the forthcoming automatic, digital data-output system that is discussed below. In addition, "Least Squares II" is to be rewritten for the IBM system, and the NLLS code⁶³ (an IBM 704 program for fitting nonlinear curves by least squares) will probably be revised by its author for the IBM 7090 with the incorporation of a number of desired changes and additions. A code will also be written for the IBM 7090 for the spectral analysis of multicomponent systems by use of the least-squares method in matrix form. This differs from the conventional linear simultaneous equation applications, particularly in the possibility for the inclusion of many more analytical wavelengths than components, with attendant increases in precision and accuracy.

Automatic, Digital, Data-Output System for the Cary Spectrophotometer

R. E. Biggers D. Hampel⁶⁶

An automatic, digital, data-readout system has been designed for use with a Cary model 14PM automatic recording ultraviolet-visible-near-infrared spectrophotometer. It should be operating soon. It will feature IBM punched-card output of the spectrophotometric data having the wavelength and absorbancy punched in pairs, in addition to other miscellaneous data. It will be possible to obtain data at wavelength intervals as close as 1 Å. Very ample instrumental resolution is available even for the very fine structure of the lanthanide and actinide elements. At present, the spectra are recorded on a 30-Å-per-inch-of-chart basis (which can be expanded) on a linear

⁶⁶Loan employee from Radio Corporation of America to Computer Development and Engineering Group, Instrumentation and Controls Division.

wavelength scale, and the data for the computer programs are obtained by hand therefrom at 10-A intervals.

The output media for wavelength and absorbancy information will be supplied and installed by the Applied Physics Corporation. A recent study has resulted in a system that eliminates the need for digitizers and permits the data to be put out directly in decimal form on cards via an IBM printing-card punch. The control unit, intermediate memory storage, parameter unit, etc., for a punched-card output system are being designed by the Computer Development and Engineering Group of the Instrumentation and Controls Division. The circuitry is being constructed from ferrite magnetic-core modules insofar as this is possible. It is thought that a packing density of seven data-point pairs per card is feasible for decimal output. It appears that the unit should be capable of an output of ~ 120 points/min.

An automatic digital-output system is also planned for the high-temperature high-pressure spectrophotometer under development by the Applied Physics Corporation. This elevated-temperature spectrophotometric system will feature spectral data output in three forms simultaneously. They are: the spectrum on a strip chart, linear in wavelength; log extinction coefficient (absorptivity) chart record; and digital output of wavelength and of absorbancy-wavelength pairs (together with other scalars and miscellaneous data as may be necessary) on IBM punched cards.

Gas-Solid Chromatography

A. D. Horton

The versatility of a molecular-sieves (Linde Company type 5-A) column is shown by its ability to separate nearly all the inorganic gases and most of the organic gases through the C_3 - group. In this work, the Burrell Instrument Company Kromo-Tog, model K-2, gas chromatograph was used. One of the thermal conductivity cells has been replaced by a Gow-Mac thermistor type cell, which is used for all gas analysis. The 250 cm \times 5 mm diam, wire-wound, glass column is filled with 35-to-60-mesh molecular sieves. When temperatures above 25°C are required to elute the gases, the column is conditioned by preheating to 250°C and is then cooled to 25°C before the sample is admitted.

Samples from the sources and of the compositions indicated in Table 9 have been analyzed.

The mixture of the radioisotopes of krypton and xenon is separated at 25°C, and the fractions are collected in separate charcoal traps immersed in ice water. They are then measured by scintillation counting techniques. This work was done with T. H. Handley of the Radiochemical Group.

Complex samples for which temperature programming is needed in order to elute all the components will require up to 35 min for complete chromatographing. Gases that can be separated at 25°C require a maximum of 12 min. Two of the complex analyses mentioned herein are illustrated in Figs. 2 and 3. A more complete treatment of this subject is being prepared for publication.

Table 9. Samples Analyzed by Gas-Solid Chromatography

Source	Gases Possibly Present in Samples from the Source (in Order of Elution)	
	At 25°C	At 25 to 250°C
Dissolution of UC and UC ₂ in water	H ₂ , O ₂ , N ₂ , CH ₄	CO, C ₂ H ₆ , CO ₂ , C ₂ H ₄ , C ₃ H ₈ , C ₂ H ₂ , C ₄ H ₁₀ *
Dissolution of stainless-steel-clad fuel elements in HNO ₃	H ₂ , N ₂ , NO	CO, N ₂ O, CO ₂
HR off-gas	D ₂ , O ₂ , N ₂	CO, CO ₂
HR shield gas	O ₂ , N ₂	
Catalytic recombination of D ₂ and O ₂ in thoria slurries	D ₂ , O ₂ , N ₂	
Autoclaving of UO ₄ · xH ₂ O in the presence of HNO ₃	O ₂ , N ₂	N ₂ O
Radiolytic decomposition of H ₂ O	H ₂ , O ₂	
Fracture well disposal studies	O ₂ , N ₂ , CH ₄	
Catalytic decomposition of methyl-cyclohexene	H ₂ , O ₂ , N ₂ , CH ₄	C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈
Radiolytic decomposition of fuel elements	Kr, Xe**	

*C₄H₁₀ is not eluted until the temperature is 300°C.

**A mixture of radioisotopes.

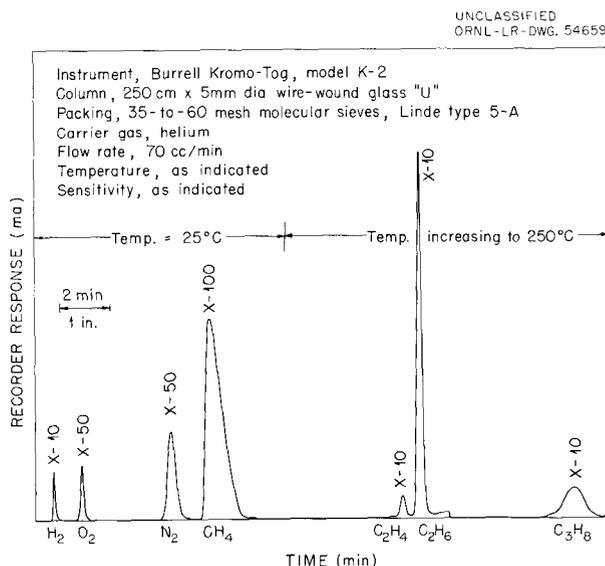


Fig. 2. Chromatogram of Gases from the Dissolution of Uranium Monocarbide in Water.

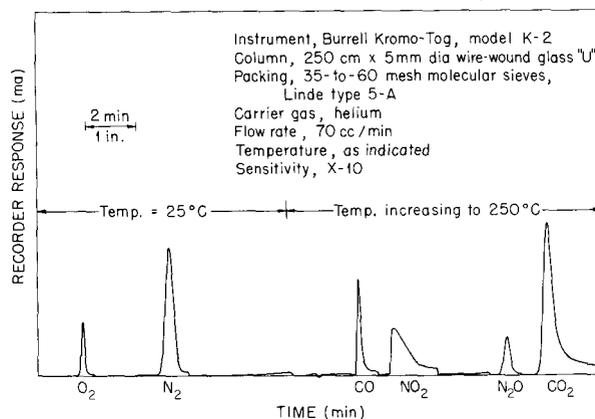


Fig. 3. Chromatogram of Gases from the Dissolution of a Mixture of Uranium Dicarbide, Thorium Carbide, and Graphite in Nitric Acid.

MASS SPECTROMETRY (Y-12)

A. E. Cameron

The relative isotopic abundances of uranium are being determined from less than 10 μg of sample. By the use of isotopic standards obtained from K-25, it has been shown that the accepted values are always within the 95% confidence interval of the data obtained by the Analytical Mass Spectrometry Laboratory; the Laboratory is now doing analyses for uranium inventory.

In order to help clarify the discrepant boron isotopic abundances that are reported in the literature and to furnish analyses for a boron neutron-cross-section experiment at the High Voltage Laboratory,⁶⁷ gravimetrically mixed standards made from isotopically pure materials were studied. One set of mixtures was made at ORNL and another at KAPL. In all cases the mass spectrometric values were within 1% of the gravimetric values. These results confirm work done at KAPL.⁶⁸

The preferred compounds used in analyzing separated stable isotopes vary widely in their performance in the mass spectrometer. Recently, three elements have been run more successfully from stable compounds that undergo thermal decomposition inside the mass spectrometer to much more volatile compounds. Data for germanium are taken on GeF_4 obtained from the thermal decomposition of BaGeF_6 , for silicon on SiF_4 from BaSiF_6 , and for osmium on OsO_4 from OsO_2 .

Several 0.01- μg (2- μc) samples of Sr^{90} have been analyzed isotopically.

A study was made of the differences in the ion fragments from a mixture of U^{235}O_2 and U^{238}C as a function of temperature.

⁶⁷H. W. Schmitt, R. C. Block, and R. L. Bailey, "Total Neutron Cross Section of B^{10} in the Thermal Neutron Energy Range," *Nuclear Phys.* 17, 109 (1960).

⁶⁸W. O. Haas, Jr., et al., *Reliability of Mass Spectrometric Determinations of Boron Isotope Abundance*, KAPL-2062 (Oct. 2, 1959).

Mass Spectrometry Research and Development

J. F. Burns

The retarding-potential-difference method of Fox and co-workers^{69,70} for the study of gaseous ionization has been modified to permit the use of ac signal detection. As a result, the time required to obtain the experimental data has been reduced from hours to minutes; the signal-to-noise ratio has been so greatly improved that greater signal amplification is possible; the upper limit of the electron energy that can be used has been increased, thus permitting study of the excited states of the resulting ions; and finally, through the use of an X-Y recorder, the ionization efficiency curve (number of ions produced as a function of electron energy) can be plotted directly on the recorder chart.

A photograph of the original recorder traces for a series of three measurements of the ionization of krypton near the onset of ionization is shown in Fig. 4. The curves exhibit a clear break about 0.7 ev above onset; the break corresponds to transitions to the $P_{1/2}$ level of the doublet

⁶⁹R. E. Fox *et al.*, "Ionization in a Mass Spectrometer by Monoenergetic Electrons," *Rev. Sci. Instr.* **26**, 1101 (1955).

⁷⁰J. F. Burns, *The Heat of Dissociation of Nitrogen and the Appearance Potential of Some Ions Formed in Fluorine and Hydrogen Fluoride by Electron Impact*, K-1147 (Oct. 8, 1954).

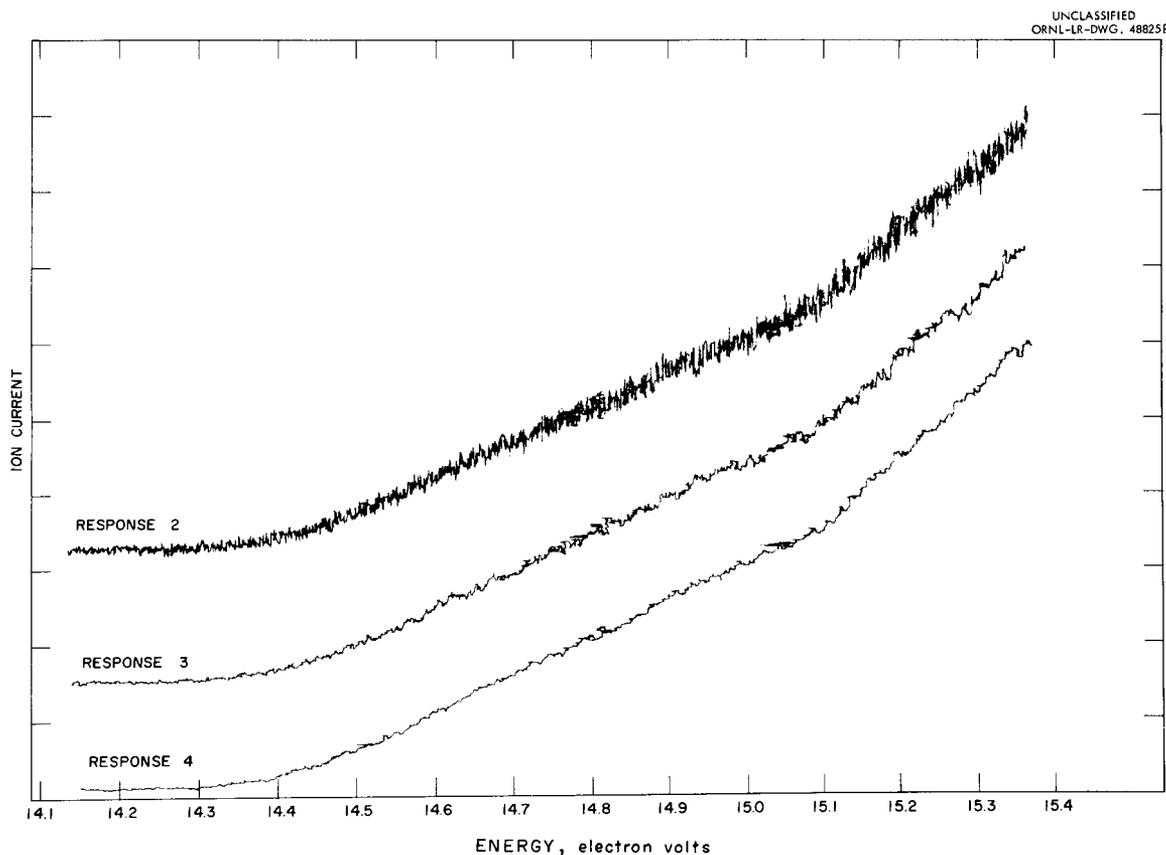


Fig. 4. Appearance Potential Curve for the Kr^+ Ion.

ground state of the Kr^+ ion. The Y-axis zero was displaced between runs to show the reproducibility of the data and to demonstrate that the addition of greater capacitance to the amplifier output in order to reduce the "hash" on the recorder chart did not adversely affect the results, as shown by the curves labeled "Response 3" and "Response 4."

A rather complicated structure, which cannot be explained in terms of the atomic energy levels derived from optical spectra, begins to appear at higher electron energies. This structure may arise from previously unidentified ionization processes⁷¹ or from space-charge-induced plasma oscillations,⁷² or it may be instrumental in origin since the retarding-potential-difference technique, although the best available at the present time, is not universally accepted as completely reliable. A considerable amount of data has been accumulated, and the more obvious instrumental factors have been eliminated from consideration, but it is still too early to make a positive statement concerning the origin of this structure.

NUCLEAR ANALYSES (X-10)

G. W. Leddicotte

Neutron-Activation Analysis

G. W. Leddicotte	J. F. Emery
W. T. Mullins	J. E. Strain
L. C. Bate	F. F. Dyer

Quantitative Applications (G. W. Leddicotte, W. T. Mullins, J. F. Emery, L. C. Bate, J. E. Strain, F. F. Dyer). – Microgram and submicrogram amounts of at least 48 elements have been determined in a variety of materials by means of nondestructive and destructive methods of neutron-activation analysis. In all these analyses, a comparator technique was used. In some instances, the assay was made by measurement of short-lived radionuclides. Typical data are given in Table 10. Some of these applications are discussed separately in other sections of this report.

Neutron-Activation Analysis of Solutions of Radioactive Strontium for Stable Barium (W. T. Mullins). – The neutron reaction $\text{Ba}^{138}(n,\gamma)\text{Ba}^{139}$ has been used to determine stable barium in highly radioactive solutions of Sr^{90} (10^2 mc/ml). In each analysis, the radioactive solution was diluted by some orders of magnitude in order to permit the safe handling of test portions of it during the irradiation and processing. A known amount of barium carrier was added to the irradiated test solution, and the barium carrier and Ba^{139} (84 m) were separated by precipitation from a hydrochloric acid–ether solution.⁷³ Decontamination steps were used to remove the Sr^{90} and any other contaminant radionuclides, and the barium carrier and Ba^{139} were finally precipitated as

⁷¹M. A. Fineman, "Survey of Electron Impact Studies of Argon Done in Several Laboratories," *Bull. Am. Phys. Soc.* **5**, 15 (1960).

⁷²K. G. Emelous and N. R. Daly, "Ion Oscillations in a Cathode Potential Minimum," *Proc. Phys. Soc. (London)* **B69**, 114 (1956).

⁷³G. W. Leddicotte, "Barium, Neutron Activation Analysis (Isotopic Carrier) Method," Method No. 5 11080 (5-3-60), *ORNL Master Analytical Manual*; TID-7015, suppl 3.

Table 10. Quantitative Applications of Neutron-Activation Analysis

Element Determined	Induced Radionuclide	Technique ^a	Material Analyzed	Experimentally Determined Concentration of Element ($\mu\text{g/g}$ or $\mu\text{g/ml}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Al	Al^{28} (2.27 m) ^d	ND	Graphite	≤ 0.1	0.03
			Beryllium oxide	7 to 100	
			Vegetable matter	60 to 300	
			Zirconium	140	
			Soil	100 to 300	
			Reactor water	0.01 to 0.10	
Sb	Sb^{122} (2.80 d) or Sb^{124} (60.9 d)	RC	Meteorites	0.02 to 12	0.005
			Graphite	0.01 to 1.0	
			Copper	0.1 to 0.5	
Ar	Ar^{41} (110 m)	ND	Ammonium nitrate	0.4 to 2.0	0.01
As	As^{76} (26.4 h)	RC	Potassium sulfate	0.02 to 1.0	0.001
			Sodium sulfite	0.005 to 0.02	
			Sodium sulfate	0.005 to 0.02	
			Meteorites	2 to 5	
			Platinum catalysts	4 to 16	
			Graphite	0.09 to 0.15	
			Tobacco	12	
			Aminosol	0.007 to 0.01	
			Soils	10 to 20	
Ba	Ba^{139} (84.0 m)	RC	Sr^{90} solutions	10^1 to 10^4	0.05
			Aminosol	1 to 10	
Br	Br^{82} (35.87 h)	RC	Hydrazine	1 to 20	0.001
			Niobium	2 to 5	
			Copper	2 to 5	
			Vegetable matter	0.5 to 2.6	
Cd	Cd^{115} (53 h) or Cd^{115m} (43 d)	RC	Meteorites	10^1 to 10^3	0.1
			Reactor water	0.1 to 1.0	
Ca	Ca^{45} (164 d)	RC	Beryllium oxide	150	5.0
			Lithium iodide	10	
			Graphite	1	
Ce	Ce^{143} (33 h)	ND	Soils	65 to 400	0.1
Cs	Cs^{134m} (3.2 h) or Cs^{134} (2.07 y)	RC	Uranium-magnesium amalgams	1 to 10	0.1
			Rubidium carbonate	10^3	
			Vegetable matter	0.05 to 1.0	
Cl	Cl^{38} (37.29 m)	RC	Hydrazine	1 to 30	0.05
			Phenol	100 to 150	
			Organic polymers	4 to 35	
			Graphite	2 to 3	

Table 10 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Material Analyzed	Experimentally Determined Concentration of Element ($\mu\text{g/g}$ or $\mu\text{g/ml}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Cr	Cr^{51} (27.8 d)	RC	Feeding materials	0.25 to 1.0	0.10
			Blood plasma	0.10 to 10	
			Sr^{90} solutions	150 to 500	
			Vegetable matter	0.09 to 0.25	
			Tobacco	3 to 11	
Co	Co^{60m} (10.47 m) ^d or Co^{60} (5.24 y)	ND	Inconel	765 to 785	0.05
			Type 304 stainless steel	10^3	
			Type 302 stainless steel	10^2 to 10^3	
			Iron	70 to 90	
			Copper-silicon alloys	4	
			Copper-nickel alloys	4	
			Type 316 stainless steel	10^3	
			Nickel	≤ 0.2	
			Vegetable matter	0.10 to 0.25	
			Tobacco	0.2 to 0.5	
			Soils	5 to 30	
Cu	Cu^{66} (5.10 m) ^d or Cu^{64} (12.80 h)	RC or ND	Cadmium sulfide	≤ 0.02	0.001
			Meteorites	10^1 to 10^3	
			Nickel	1 to 1.5	
			Silicon	0.01 to 0.15	
			Aluminum	20	
			Sea water	≤ 0.02	
			Vegetable matter	0.20 to 1.0	
Au	Au^{198} (2.697 d)	ND	Metal foils	100	0.001
			Copper-silicon alloys	10	
Hf	Hf^{179m} (19 s) ^d or Hf^{181} (44.6 d)	RC or ND	Zirconium	50 to 100	0.05
			Nickel alloys	10 to 10^3	
			Soils	3.5 to 100	
In	In^{116m} (53.99 m) ^d or In^{114m} (50.0 d)	RC	Meteorites	≤ 0.05	0.0001
		ND	Paper fibers	15 to 100	
		ND	Grains and cereals	5 to 12	
I	I^{128} (24.99 m) ^d	ND	Copper	0.1 to 1.0	0.10
Ir	Ir^{192} (74.37 d)	ND	Gold wire	0.5	0.0001
Fe	Fe^{59} (45.1 d)	ND	Tobacco	280 to 1400	2.0
		RC	Graphite	2 to 5	
		ND	Aluminum	10^3	
		RC	Lithium fluoride-beryllium fluoride	10^4	
		RC	Silicon	3	

Table 10 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Material Analyzed	Experimentally Determined Concentration of Element ($\mu\text{g/g}$ or $\mu\text{g/ml}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Fe	Fe^{59} (45.1 d)	RC	Beryllium oxide	8 to 44	2.0
			Titanium	110 to 140	
			Nickel	40	
			Amsco	10 to 20	
			Zirconium	370	
			Soils	10^2 to 10^3	
La	La^{140} (40.22 h)	ND	Vegetable matter	40 to 100	0.01
			Soils	40 to 100	
			Granite	68	
Mg	Mg^{27} (9.45 m) ^d	ND	Vegetable matter	10^3	2.0
			Graphite	≤ 0.25	
			Uranium dioxide	$\leq 10^3$	
			Silicon	1 to 10	
			Beryllium oxide	1 to 10	
Mn	Mn^{56} (2.576 h)	ND	Vegetable matter	≤ 0.1	0.0001
			Graphite	0.003 to 0.005	
			Soils	10^2	
			Aluminum	3	
Hg	Hg^{197m} (24 h)	RC	Uranium-magnesium amalgams	10^{-1} to 10^4	0.1
			Chlorinated compounds	0.10 to 0.26	
			Copper-silicon alloys	6	
Ni	Ni^{65} (2.564 h)	RC	Iron	100 to 160	1.0
			Zirconium	10 to 20	
O	F^{18} (112 m) ^e	RC	Lithium	10^1 to 10^4	1.0
			Beryllium	10^2 to 10^3	
			Aluminum	10^1 to 10^2	
Pd	Pd^{109} (13.5 h)	RC	Ruthenium	10	0.1
			Zirconium	≤ 0.08	
			Thorium oxide	3	
P	P^{32} (14.22 d)	RC	Iron	0.4 to 12	0.04
			Aluminum oxide	200 to 300	
			Aluminum silicate	200 to 300	
			Graphite	0.007 to 0.20	
			Aluminum	10 to 100	
			Vegetable matter	70 to 190	
Pt	Pt^{195m} (3.5 d)	RC	Sea water	≤ 0.01	1.0
K	K^{42} (12.52 h)	ND	Soils	10^1 to 10^4	0.1
			Vegetable matter	190 to 350	
		RC	Stainless steel	10^2 to 10^3	

Table 10 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Material Analyzed	Experimentally Determined Concentration of Element ($\mu\text{g/g}$ or $\mu\text{g/ml}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Rb	Rb ⁸⁶ (18.66 d)	RC	Vegetable matter	2 to 30	0.5
Sm	Sm ¹⁵³ (47.1 h)	RC	Uranium-magnesium amalgams	0.1 to 1.0	0.01
Sc	Sc ⁴⁶ (83.9 d)	ND	Soils	8 to 44	0.01
			Aluminum	0.3	
			Beryllium oxide	0.015 to 0.4	
			Granite	0.7	
			Tobacco	0.05 to 0.30	
Se	Se ⁷⁵ (121 d)	RC	Milk	1 to 2	0.02
			Torula yeast	0.03 to 1.5	
			Dietary supplements	0.1 to 0.2	
			Urine	0.05 to 1.0	
			Germanium	35 to 95	
Si	Si ³¹ (2.62 h)	RC	Bismuth	0.9 to 3.6	1.0
			Niobium	7 to 116	
			Lithium iodide	200 to 400	
			Beryllium oxide	30 to 56	
			Zirconium	10 to 50	
Ag	Ag ¹¹⁰ (24.2 s) ^d or Ag ^{110m} (253 d)	ND	Zinc sulfide	320	0.1
			Gold wire	3 to 167	
			Meteorites	0.01 to 0.1	
			Rain water	≤ 0.1	
Na	Na ²⁴ (14.97 h)	RC	Lithium iodide	10 ³	0.007
			Graphite	0.2 to 0.4	
			Thorium oxide— lithium fluoride— beryllium fluoride	43 to 76	
			Aluminum	10 to 140	
			Sr ⁹⁰ solution	10 ² to 10 ⁴	
			Soil	10 ² to 10 ³	
			Vegetable matter	1 to 5	
			Granite	10 ³	
S	S ³⁵ (87 d)	RC	Graphite	20	1.0
			Niobium	88	
Ta	Ta ¹⁸² (115.1 d)	ND	Zirconium	≤ 0.5	0.002
Te	Te ^{129m} (33.5 d)	RC	Meteorites	≤ 0.05	0.1
Th	Th ²³³ (22.12 m) ^d or Pa ²³³ (27.0 d) ^f	ND	Granite	19 to 100	0.01
			Fused salts	10 ² to 10 ³	
			Beryllium	0.3 to 4	
			Zirconium	≤ 0.08	
			Soils	20 to 66	

Table 10 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Material Analyzed	Experimentally Determined Concentration of Element ($\mu\text{g/g}$ or $\mu\text{g/ml}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Sn	Sn ¹²⁵ (9.4 d)	RC	Meteorites	≤ 1.0	1.0
Ti	Ti ⁵¹ (5.79 m) ^d	ND	Zirconium Organic fibers Graphite	10^1 to 10^3 10^3 0.05 to 0.2	5.0
W	W ¹⁸⁷ (24.0 h)	RC	Zirconium-gallium alloys Zirconium	3 to 13 0.001 to 0.09	0.001
U	U ²³⁹ (23.5 m) ^d or Np ²³⁹ (2.346 d) ^g or Ba ¹⁴⁰ (12.80 d) ^b	RC	Fused salts Aluminum Graphite Reactor water Thorium oxide Beryllium	10^0 to 10^3 0.1 to 200 ≤ 0.1 ≤ 0.001 10^3 0.01 to 10	0.001
V	V ⁵² (3.76 m) ^d	ND	Graphite	≤ 0.07	0.001
Zn	Zn ^{69m} (13.8 h) or Zn ⁶⁵ (245 d)	RC	Meteorites Aluminum Vegetable matter Tobacco Granite	46 to 550 5 to 14 10 to 25 35 to 110 10^3	0.02
Zr	Zr ⁹⁷ (17.0 h) or Zr ⁹⁵ (65 d)	ND	Soils	10^2 to 10^3	0.2

^aND = nondestructive assay; RC = radiochemical separations.

^bThe number of determinations varied; therefore a range is given for the element concentration. Also, observed concentrations for liquid samples are expressed as micrograms per milliliter.

^cBased on the conditions of irradiation and method of analysis used. Value will vary with the duration of the irradiation, neutron flux, the method of processing the sample after irradiation, and the efficiency of the counter used in the radioactivity measurement.

^dAnalyses made in the Short-Half-Life Neutron-Activation Products Analyses Laboratory.

^eProduced by the reactions (1) $\text{Li}^6(n,\alpha)\text{H}^3$ and (2) $\text{O}^{16}(\text{H}^3,n)\text{F}^{18}$.

^fProduced by the reaction $\text{Th}^{232}(n,\gamma)\text{Th}^{233} \xrightarrow{\beta^-, \gamma} \text{Pa}^{233}$,
(23.5 m)

^gProduced by the reaction $\text{U}^{238}(n,\gamma)\text{U}^{239} \xrightarrow{\beta^-, \gamma} \text{Np}^{239}$,
(23.4 m)

^hProduced by the reaction $\text{U}^{235}(n,f)$ fission products, i.e., Ba¹⁴⁰, etc.

BaCl₂·H₂O for the radioactivity measurements. Solutions of radioactive strontium that contained Ba¹³⁸ in concentrations ranging from 10² to 10⁴ μg/ml have been analyzed by this method.

Use of Short-Lived Radionuclides in Neutron-Activation Analysis (J. F. Emery, G. W. Leddicotte). – The operability of the Short-Half-Life Neutron-Activation Products Analysis Laboratory in the Oak Ridge Research Reactor building⁷⁴ has made possible many analyses by a rather simple analytical procedure. Table 10 lists these applications. Each one has been accomplished by irradiating the test sample for a very short time (usually 1 min or less) and then assaying the irradiated material by means of gamma scintillation spectrometry. The previously described complement-subtraction technique of gamma spectrometry⁷⁵ has been used in many of these analyses; in others a simple decay measurement is made. The use of short-lived radionuclides in analysis is unique in that most frequently nondestructive assays are used and the time required to complete an analysis is very short. Studies on the use of these short-lived radionuclides are being extended, and it is expected that radionuclides with half lives even as short as 10 s or less can be used readily in many other applications.

Determination of U²³⁵, U²³⁸, and Th²³² in Beryllium Metal by Neutron Activation (W. T. Mullins, G. W. Leddicotte). – Microgram and submicrogram amounts of U²³⁵, U²³⁸, and Th²³² are now being determined routinely in beryllium metal by neutron-activation analysis. The beryllium metal and the comparator standard are irradiated and then dissolved in acid. The radionuclides Ba¹⁴⁰ (12.8 d), Np²³⁹ (2.346 d), and Pa²³³ (27.0 d) are then isolated by means of radiochemical procedures^{76,77} and are measured by gamma scintillation spectrometry. Amounts of U²³⁵, U²³⁸, and Th²³² as small as 0.0007, 0.10, and 0.10 μg, respectively, can be determined by this method.

Nondestructive Activation Analyses (L. C. Bate, J. F. Emery, W. T. Mullins, G. W. Leddicotte). – Use of the nondestructive technique in activation analysis is increasing. The technique is simple; it consists in irradiation of the test sample followed by gamma spectrometry of the induced radionuclides. Complement subtraction is usually the means of resolving the gamma spectrum.⁷⁵ In order to obtain quantitative results for stable isotopes being determined by a nondestructive activation-analysis technique, the gamma-spectral data are converted to disintegration-rate data, which are then quantized by means of an absolute method of calculation.⁷⁸ Recently, this method of calculation has been used extensively in obtaining activation-analysis results on "pure" metals, vegetable matter, waters, soils, materials of construction, etc. Typical data are given in Table 11.

⁷⁴G. W. Leddicotte, "Short-Half-Life Neutron-Activation Products Analysis Laboratory," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 22.

⁷⁵L. 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.

⁷⁶H. A. Mahlman and G. W. Leddicotte, "Determinations of Microgram and Submicrogram Quantities of Uranium by Neutron Activation Analysis," *Anal. Chem.* **27**, 823 (1955).

⁷⁷G. W. Leddicotte and H. A. Mahlman, "Determination of Microgram and Submicrogram Quantities of Thorium by Neutron Activation Analysis," *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955* **8**, 250 (1955).

⁷⁸G. E. Boyd, "Methods of Activation Analysis," *Anal. Chem.* **21**, 335 (1949).

Table 11. Quantized Data from Complement-Subtraction Gamma Spectrometry:
The Analysis of Construction Materials

Element Determined	Element Concentration ($\mu\text{g/g}$)		
	Cement	Limestone	Sand
Cr	5570	432	11,500
Co	4.6	0.2	4.5
Mn	380	38	164
K	2390 2600	266 225	43,000
Sc	3.7	0.24	5.1
Na	776	128	6,000
Th	3.3 2.0	0.20 0.25	3.7 2.8
U	32.0 30.0	2.6 2.6	2.2 2.4

Radiochemical Separations Used in Neutron-Activation Analysis (W. T. Mullins, G. W. Leddicotte). – *New Radiochemical Separation Method for Silicon*. – In the neutron-activation determination of silicon, the initial radiochemical separation of silicon carrier and Si^{31} (2.62 h) as SiO_2 (ref 79) has usually not removed completely the contaminant radionuclides. A more rapid and efficient separation (except from radioactive tantalum) is achieved by dissolving the irradiated specimen (usually a metal or alloy) in the presence of silicon carrier and distilling the silicon carrier, together with the Si^{31} , from the mixture as SiF_4 (ref 80). The silicon and Si^{31} are removed from the distillate by precipitation as SiO_2 .

Evaluation of Radiochemical Separation Procedures. – The radiochemical separation procedures now used in a number of neutron-activation-analysis methods have been evaluated with respect to ease of decontaminating the desired radionuclide from contaminant radionuclides. A summary of this evaluation is given in Table 12. The improved radiochemical procedures that have resulted from these studies now appear or will appear in nuclear analyses methods in the *ORNL Master Analytical Manual*.

Particle-Size-Distribution Analysis (L. C. Bate, G. W. Leddicotte). – The methods for determining particle-size distribution previously described^{81,82} continue to be used for samples of

⁷⁹G. W. Leddicotte, "Silicon, Neutron Activation Analysis (Isotopic Carrier) Method," Method No. 5 11770 (3-11-60), *ORNL Master Analytical Manual*; TID-7015, suppl 3.

⁸⁰W. F. Hillebrand *et al.*, *Applied Inorganic Analysis*, 2d ed., p 672, Wiley, New York, 1953.

⁸¹G. W. Leddicotte and H. H. Miller, "Particle-Size Distribution," *Anal. Chem. Div. Semiann. Progr. Rept.* Oct. 20, 1954, ORNL-1788, pp 21-23.

⁸²L. C. Bate and G. W. Leddicotte, *Determination of Submicrogram Particle Sizes by an Activation Analysis—Centrifugation Method*, ORNL CF-57-1-116 (Jan. 29, 1957).

Table 12. Summary of Typical Evaluations of Decontaminations in Radiochemical Separation Procedures

Element Determined	Induced Radionuclide Measured	Material Analyzed	Interfering Radionuclides	Method of Isolating Induced Radionuclide	Decontamination Factor
Fe	Fe ⁵⁹ (45.1 d)	Zirconium	Co ⁶⁰	One isopropyl ether extraction of Fe	150
			Zr ⁹⁵ -Nb ⁹⁵		1000
			Ta ¹⁸²		350
Se	Se ⁷⁵ (121 d)	Biological materials	Na ²⁴	Wet digestion; distillation of Se with HBr; pptn. with NH ₂ OH·HCl	10 ⁶
			As ⁷⁶		10 ⁵
			Te ¹³¹		10 ⁵
Si	Si ³¹ (2.62 h)	Zirconium	Mn ⁵⁶	Initial separation of Si as SiO ₂	10 ⁷
			Ta ¹⁸²		10 ⁶
		Indium	In ¹¹⁴	Initial separation of Si as SiO ₂	10 ⁷
Cu	Cu ⁶⁴ (12.80 h)	Aluminum alloys	Na ²⁴	Initial separation of Cu as CuS	10 ⁶
			Zn ⁶⁵		10 ⁵
			Zn ^{69m}		10 ⁵
		Zirconium	Zr ⁹⁵ -Nb ⁹⁵ Zr ⁹⁷	Initial separation of Cu as CuS	10 ⁶ 10 ⁶
Ni	Ni ⁶⁵ (2.564 h)	Zirconium	Si ³¹	Pptn. of Ni with nickel dimethylglyoxime	10 ⁴
			Mn ⁵⁶		10 ⁶
			Zr ⁹⁷		10 ⁶
Co	Co ⁶⁰ (5.24 y)	Metals and alloys	Na ²⁴ , K ⁴² , Cr ⁵¹ , Mn ⁵⁶ , Fe ⁵⁹ , Cu ⁶⁴ , Ni ⁶⁵ , As ⁷⁶ , Sr as Sr ⁸⁵ , rare-earth-element radionuclides, Rb ⁸⁶ , Zr ⁹⁵ , Cs ¹³⁴ , Ba as Ba ¹⁴⁰ , Ta ¹⁸²	Anion exchange, HCl complexation on Dowex 2	10 ³ to 10 ⁶ for all radionuclides

Table 12 (continued)

Element Determined	Induced Radionuclide Measured	Material Analyzed	Interfering Radionuclides	Method of Isolating Induced Radionuclide	Decontamination Factor
Co	Co ⁶⁰ (5.24 y)	Biological materials	Mn ⁵⁶ , Cu ⁶⁴ , Zn ⁶⁵ , Mo ⁹⁹	Solvent extraction of Co from HCl soln. with MDOA*-trichloroethylene	10 ⁶ for all radionuclides
Zn	Zn ^{69m} (13.8 h) or Zn ⁶⁵ (245 d)	Biological materials, metals, alloys	Mn ⁵⁶ Co ⁶⁰ Ni ⁶⁵	Solvent extraction of Zn from HCl soln. with MDOA*-trichloroethylene	10 ⁷ 10 ⁶ 10 ⁶
Mo	Mo ⁹⁹ (66.0 h)	Metals	Mn ⁵⁶ Cu ⁶⁴ Zr ⁹⁵ W ¹⁸⁷	Pptn. of Mo with α -benzoinoxime	10 ⁶ 10 ⁶ 10 ⁶ 450
U	Np ²³⁹ (2.346 d)	Ores	Th (as Pa ²³³)	Solvent extraction of Pa ²³³ with diisobutylcarbinol from an HCl-H ₂ C ₂ O ₄ solution	10 ⁶
Rb	Rb ⁸⁶ (18.66 d)	Alkali metals	Na ²⁴ K ⁴² Cs ¹³⁴	Ion exchange; elution with HCl (Na ²⁴ > K ⁴² > Rb ⁸⁶ > Ca ¹³⁴)	10 ⁶ 10 ⁶ 10 ⁶
Sr	Sr ^{87m} (2.80 h)	Aluminum, water	Na ²⁴ Ba ¹³⁹ K ⁴² , Cr ⁵¹ , Mn ⁵⁶ , Fe ⁵⁹ , Cu ⁶⁴ , Zn ⁶⁵ , Zn ^{69m} , Ga ⁷²	Pptn. of Sr with fuming HNO ₃ ; BaCrO ₄ separation of Ba ¹³⁹	10 ⁶ 10 ⁶ 10 ⁵ to 10 ⁶

*MDOA = methyl dioctylamine.

Table 12 (continued)

Element Determined	Induced Radionuclide Measured	Material Analyzed	Interfering Radionuclides	Method of Isolating Induced Radionuclide	Decontamination Factor
Ba	Ba ¹³⁹ (84.0 m)	Aluminum, water	Na ²⁴	Pptn. of Ba with fuming HNO ₃ ; BaCrO ₄ separation from Sr ^{87m}	10 ⁶
			Sr ^{87m} K ⁴² , Cr ⁵¹ , Mn ⁵⁶ , Fe ⁵⁹ , Cu ⁶⁴ , Zn ⁶⁵ , Zn ^{69m} , Ga ⁷²		10 ⁶ 10 ⁵ to 10 ⁶
K	K ⁴² (12.52 h)	Alkali metals, aluminum, other metals	Na ²⁴	Perchlorate pptn. of K with alcoholic leach	10 ⁶
P	P ³² (14.22 d)	Arsenic, aluminum, sodium fluoride, zirconium fluoride, magnesium, other metals	Na ²⁴	Pptn. of P with molybdate; Fe(OH) ₃ scavenging	10 ⁷
			Fe ⁵⁹		10 ⁶
			As ⁷⁶		10 ⁶
			Zr ⁹⁵		10 ⁶
Ag	Ag ^{110m} (253 d)	Copper	Cu ⁶⁴	Pptn. of Ag as AgCl; repptn.	10 ⁶
O	F ¹⁸ (112 m)	Metals	Na ²⁴	Pptn. of Cu as CuS; pptn. of F as PbClF; Na ²⁴ in soln.	10 ⁶
			Cu ⁶⁴		10 ⁵

thorium oxide, thorium oxide-uranium oxide, glass beads, etc. Samples of particulate thorium oxide-uranium oxide from in-pile loop studies have been analyzed recently. Definite interference from Cs^{137} , produced as a product of the fission of U^{235} , has been observed. Ways of minimizing this interference are being investigated.

Analytical Applications of Neutron Absorptiometry and Neutron Transmission

J. E. Strain G. W. Leddicotte

The Am^{241} -Be neutron sources previously described⁸³ have been used to determine B, Cd, Li, Hg, Ag, and Cl in materials contained in static systems and to determine the isotopic ratios in B, Li, and U. Similar techniques can be readily adapted to continuous type (in-stream) analyses. Neutron sources of this same type have already been used in the nondestructive analysis of plastics and stainless steel for boron by neutron transmission.⁸³ This method is now being used to analyze other materials. A report of the work will be made soon.

Am^{241} as a Gamma Source for Gamma Radiography

J. E. Strain G. W. Leddicotte

The 0.05957-Mev gamma radiations from Am^{241} (458 y) appear to be usable in gamma radiography. Use of the method to detect voids in dense materials and small objects in mockups has shown that it is practicable. A quantity of Am^{241} as small as 20 mg is satisfactory as a gamma source, and, in some instances, very short exposure of a photographic plate or film can be used to produce the image.

Applications of Radioactive Tracers

Recovery of Uranium and Protactinium from Molten Fluorides (J. E. Strain). – Recent small-scale experiments with radioactive Pa^{233} and U^{237} have shown that protactinium and uranium can be removed from molten fluorides by a process that appears to be surface precipitation of protactinium on particles of beryllium oxide or thorium oxide. This work was done in conjunction with the Reactor Chemistry Division; the results will appear in a formal report from that division.

Measurement of Surface Area of Uranium Oxide by Use of U^{237} Tracer (F. F. Dyer, G. W. Leddicotte). – The work previously described⁸⁴ has been extended to include the use of an exchange solution of very dilute nitric acid (pH \sim 5) with the U^{237} tracer. Although only a few measurements have been made with the acid-containing exchange solution, the results indicate that the exchange is much more easily reproduced than it had been in the case of 10^{-3} M sodium

⁸³J. E. Strain, J. H. Oliver, and G. W. Leddicotte, "Preparation and Uses of Alpha, Gamma, and Neutron Sources from Am^{241} ," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 32.

⁸⁴R. L. Ferguson and G. W. Leddicotte, *Surface-Exchange Method for Determination of Surface Area of UO_2 Powder*, ORNL CF-59-8-62 (Aug. 6, 1959).

pyrophosphate. These studies are being furthered in order to relate these results to those obtained by a gas-adsorption method that is based on the theory of Brunauer, Emmett, and Teller.⁸⁵ In one test, a surface-area value of 4.4 m²/g was obtained; this is in reasonable agreement with the value 5.6 m²/g obtained by means of the gas-adsorption method.

Analytical Applications of Delayed-Neutron Counting

F. F. Dyer G. W. Leddicotte

Delayed-neutron counting has been investigated as a method for the determination of U²³⁵. Samples are irradiated in a pneumatic tube of the Oak Ridge Research Reactor for short periods and are then analyzed in a neutron-counting assembly (Fig. 5). Uranium-235 has been determined

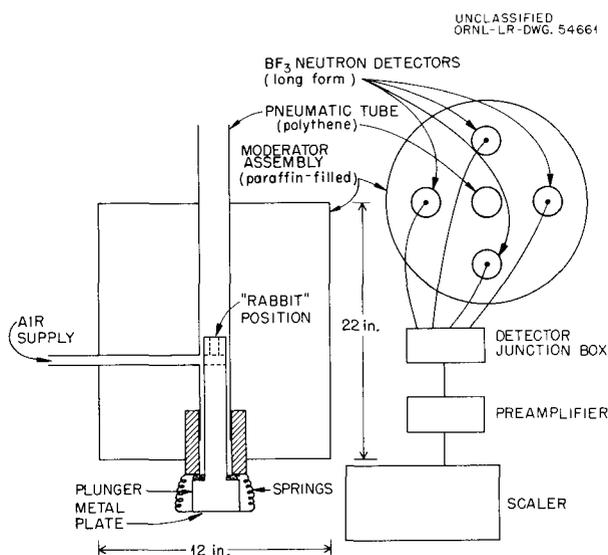


Fig. 5. Schematic Diagram of Delayed-Neutron-Moderator Assembly and Counter.

with a sensitivity of 2.0×10^5 total neutrons counted per μg of U²³⁵. Results of the analysis by this method of uranium ore samples for total uranium are given in Table 13. The data obtained in the analysis of samples of various U²³⁵ concentrations used to determine the sensitivity of the method are shown graphically in Fig. 6. Other radionuclides fissionable by thermal neutrons (e.g., Pu²³⁹ and U²³⁸) are also being studied.

Radioactivity Measurements

Mathematical Resolution of Radionuclide Spectral Data (G. W. Leddicotte). — A computer program designed to resolve and reduce gamma spectral data obtained by a 200-channel pulse-height analyzer in the assay of radionuclide mixtures⁷⁵ is now under investigation. The proposed

⁸⁵S. Brunauer, P. H. Emmett, and E. Teller, "The Adsorption of Gases in Multimolecular Layers," *J. Am. Chem. Soc.* 60, 309 (1938).

Table 13. Precision of Delayed-Neutron-Counting Method for Determining Total Uranium in Uranium Ore

Sample	Method of Analysis	Total Uranium Concentration (wt %)		Standard Deviation of ORNL Results	
		Supplier	ORNL	Absolute (wt %)	Relative (%)
1	Delayed-neutron counting		3.04	0.10	3.5
	Gamma spectrometry		2.84	0.04	1.4
	Mass spectrometry	2.85			
2	Delayed-neutron counting		0.19	0.02	10
	Gamma spectrometry		0.19	0.01	5
	Mass spectrometry	0.15			
3	Delayed-neutron counting		0.100	0.006	6.0
	Beta counting		0.098	0.007	7.2
	Mass spectrometry	0.09			

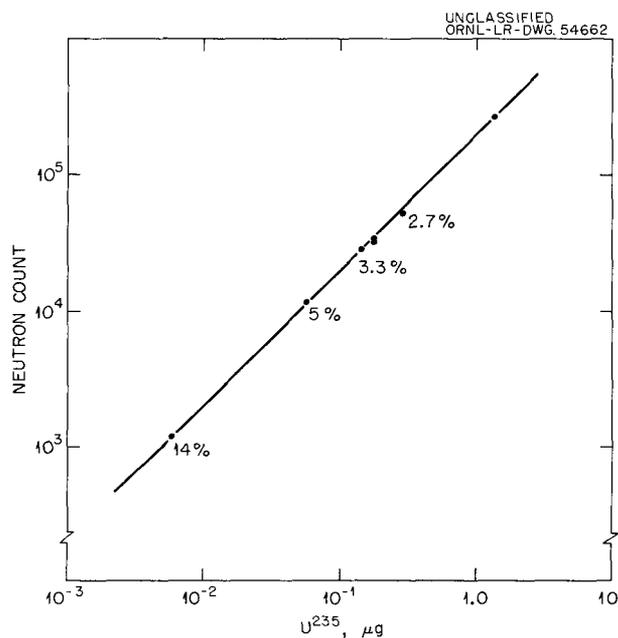


Fig. 6. Plot of Micrograms of U^{235} vs Neutron Count. Relative standard deviations of the average values plotted are indicated.

program has already been used to analyze two-, five-, and eight-component mixtures of radionuclides. Very little difficulty was encountered in analyzing a spectrum in which 15 different photo-peaks were displayed. A high-speed digital computer (IBM 704) was used in this preliminary investigation. A report of this work is now being written.

Low-Level Gamma Counting (J. F. Emery, L. C. Bate, G. W. Leddicotte). — The low-level gamma radioactivities in a number of materials have been counted. The counting room of the laboratory in the Oak Ridge Research Reactor⁷⁴ affords an unusual low-level environment and has been used as the area for these measurements. The low-level gamma spectrometer used in this work consists of a 3 × 3 in. thallium-activated sodium iodide crystal mounted in a shield of the type shown in Figs. 7 and 8. The radioactivity is measured by means of a gamma spectrometer equipped with a 200-channel pulse-height analyzer. A typical background spectrum for this counting arrangement is shown in Fig. 9. Samples are mounted directly on the crystal. A modification of the equipment for use with samples of large volume or mass is shown in Fig. 10. Experimental results indicate that such counting equipment makes it possible to extend the identification and determination of many radionuclides to very low levels. Data obtained by use of this equipment will be given in a formal report.



Fig. 7. Shield for Low-Level Gamma Counting. View of exterior.

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PHOTO 52012



Fig. 8. Shield for Low-Level Gamma Counting. View of interior.

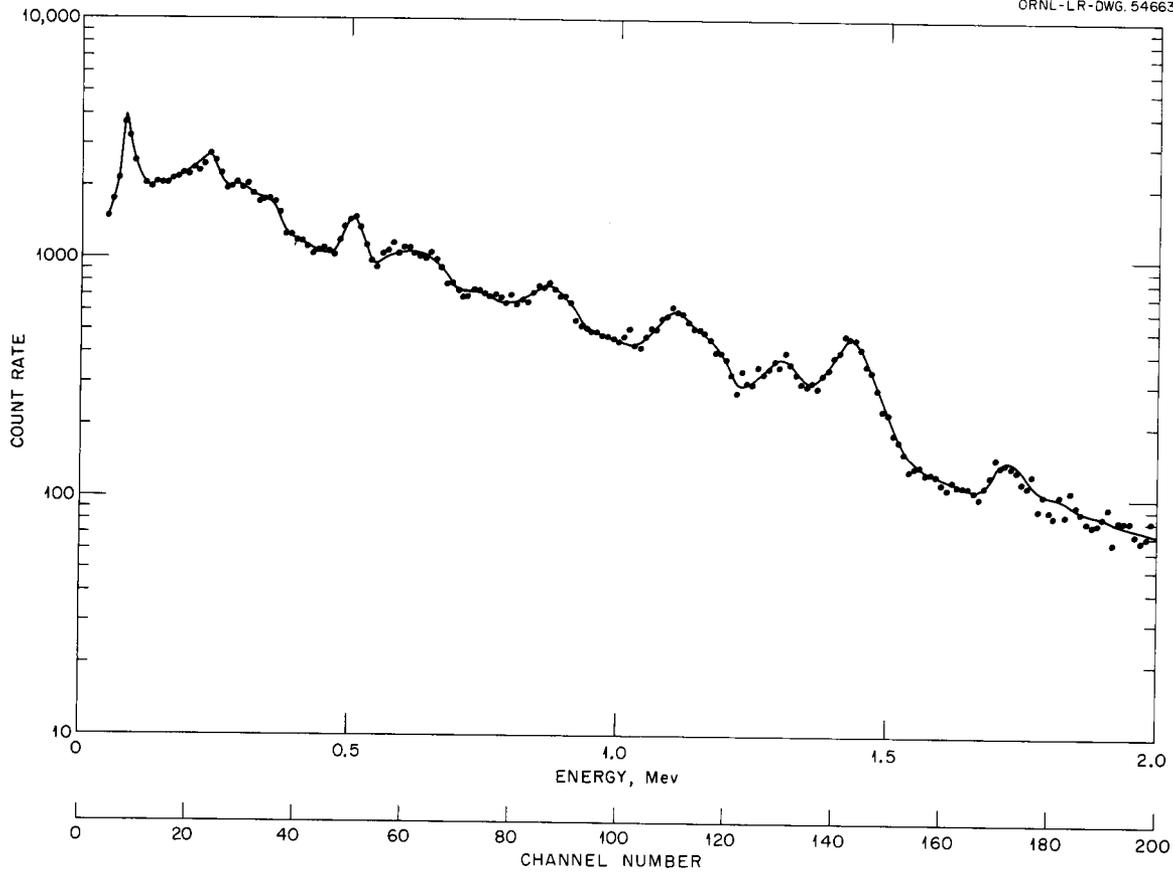


Fig. 9. Background Gamma Spectrum. Total background = 170 counts/min for energy interval from 0.04 to 2 Mev.

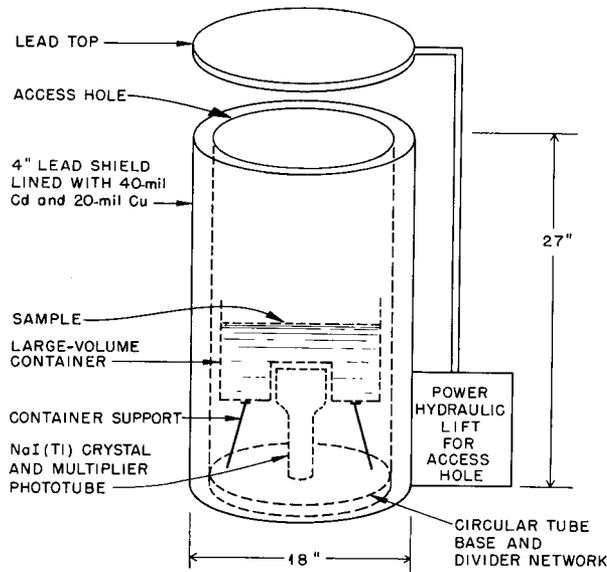


Fig. 10. Lead Pig for Crystal Shielding, Showing Large-Volume Container.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods (X-10 and Y-12)

H. P. Raaen (X-10)

H. P. House (Y-12)

Two supplements have been issued to the reprinted form of the *ORNL Master Analytical Manual* and are available from the Office of Technical Services, Department of Commerce, Washington 25, D.C., as follows:

Designation	Methods	Price
TID-7015 (suppl 1)	New and revised methods issued in 1958	\$5.75
TID-7015 (suppl 2)	New and revised methods issued in 1959	6.75

The methods contained in Subsection 9 09, "Aircraft Nuclear Propulsion (ANP) Project Methods," were declassified and relocated as a subsection in the unclassified part of Sec 9, "Process Methods."

Forty-six new methods were added to the *Manual* (see "Presentations of Research Results"); of these, four were for the purpose of record only. Twelve revised methods were issued. The Table of Contents for Sec 5, "Nuclear Analyses Methods," was revised to bring it up to date. The *Manual* was issued to two new custodians.

OPTICAL AND ELECTRON MICROSCOPY (X-10)

T. E. Willmarth

H. W. Wright

T. G. Harmon

The Optical and Electron Microscopy Group has continued to assist ORNL staff members on those research problems in which microscopy or electron diffraction has been necessary, especially when direct electron microscopy has been essential to the observation of surface structures and particles beyond the resolving power of the optical microscope. Electron diffraction has been used as an aid in the interpretation of electron micrographs and as a direct approach in the study of thin films and single crystals. The types of new methods and techniques developed in the fields of microscopy and electron diffraction have been governed by the nature and scope of the problems. A wide variety of materials have been examined; the results are reported directly to the person or group requesting the study. Such results usually become a part of the complete report made on a research project or experiment.

Studies of Particle Size and Shape. – Studies were made of the size and shape of particles of the following materials: UO_2 , $\text{UO}_2\text{-SeO}_2$, $\text{UO}_2\text{-Al}_2\text{O}_3$, $\text{UO}_2\text{-ThO}_2\text{-SeO}_2$, $\text{UO}_2\text{-BeO}$, UO_3 , U_3O_8 , ThO_2 , $\text{ThO}_2\text{-BeO}$, ThO_3 , $\text{ThO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-Fe}$, $\text{SiO}_2\text{-Fe-UO}_2$, ZrO_2 , $\text{ZrO}_2\text{-U}$, ZrCl_4 , CeO , SrTiO_3 , RuO_2 , Fe_2O_3 , $\text{FeF}_3\text{-UO}_2$, S , MgO , TeO_2 , Al_2O_3 , WO_3 , Gd_2O_3 , PbO , SnO , Ag_2O , graphite, graphite-dextrin, metallic tungsten powders, and various clays. The surfaces of many of these materials were studied by carbon replication and shadow-casting.

At the request of the Reactor Division, the feasibility of using electron microscopy and diffraction to investigate radioactive particulate matter is being determined. Study is being made of methods whereby certain radioactive materials not exceeding the median activity range may be handled safely, dispersed, entrapped in thin plastic films, held on electron microscope grids, and introduced into the sample chamber of the microscope without endangering the operator or contaminating the instrument.

Examination of Thin Films, Bulk Oxide Coatings, Corrosion Products, and Surface Structures. – Corrosion test specimens, metallic elements, and ceramic bodies derived from studies of reactor test loops and from metallurgical experiments were examined. The experimental variables in these studies were time, temperature, and environment. Replication techniques and transmission and reflection electron diffraction were used to study the surface layers. The materials studied were types 304, 347, and 430 stainless steel; types T-1, A-212, and INOR-8 steel; Croloy-2 $\frac{1}{4}$, -5, and -6; aluminum-titanium steel; beryllium; beryllium oxide; reactor-grade graphite; zirconium; molybdenum; tantalum; and platinum.

Thin films of gold, silver, platinum, and iron were studied. The surface structures of cast iron and electrodeposited iron were examined. The interesting surface of electrodeposited iron that had been etched in hydrochloric acid–hydrogen peroxide is shown in Fig. 11. The nature of the surface was revealed from surface replicas by the electron microscope.

Single-Crystal, Surface-Barrier Type of Alpha Counters. – The experimental solid state radiation detectors that were fabricated from silicon and germanium by the Physics and Chemistry Divisions have been studied. This work has led to improved techniques for producing a proper crystal face and for controlling the nature of the thin film of gold that is vaporized onto it. Reflection electron diffraction indicated whether the etching step had removed successfully the polycrystalline layers produced by cold working and any surface contaminants. This technique also revealed the nature, extent of continuity, and range of thickness of the gold-film surface covering. The electron-diffraction pattern from the surface of a single polished and etched crystal of silicon is shown in Fig. 12. Somewhat weakened Kikuchi lines indicate plastic deformation at the surface; the diffuse rings show the presence of surface contaminants.

Biological Studies. – Assistance was given to the Biology Division in their studies of radiation effects on the glomerulus coils, liver, and intestines of mice and rats.

Instrumentation. – The proposed changes to the General Electric diffractograph⁸⁶ have been made. Power is now available to provide a range of accelerating voltage from 40 to 100 kv for both transmission and reflection electron diffraction. The diffractograph now has a highly stabilized lens system consisting of a Philips condenser lens, an objective lens, and a General Electric diffraction lens. Each lens can be focused individually; this individual focusing produces a final, small-diameter, monochromatic beam of electrons. One-inch-thick lead-glass windows have

⁸⁶T. E. Willmarth, H. W. Wright, and T. G. Harmon, "Instrumentation," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 36–41.



Fig. 11. Electron Micrograph of Surface of Electrodeposited Iron Etched in Hydrochloric Acid-Hydrogen Peroxide. Faxfilm-carbon replica; chromium shadow-cast. 24,000X. Reduced 16%.



Fig. 12. Reflection Electron-Diffraction Pattern from the Surface of a Polished and Etched Single Crystal of Silicon.

been installed to protect the operator from x rays scattered during reflection-diffraction examinations. By means of the modified instrument, measurable patterns have been obtained for crystalline material (e.g., bulk oxides) that heretofore could not be examined by reflection-diffraction techniques with the original instrument.

An adjustable, motor-driven, traveling-stage densitometer for $3\frac{1}{4} \times 4$ in. high-contrast photography plates has been designed and is now being fabricated. It will be used in the measurement and interpretation of diffraction patterns photographed on the diffractograph.

A method of producing improved filaments of a design described by Fernandez-Moran⁸⁷ (see Fig. 13) for use in the electron microscope and electron diffractograph is being studied. Such filaments greatly increase resolution at high magnifications without loss of screen intensity.⁸⁷

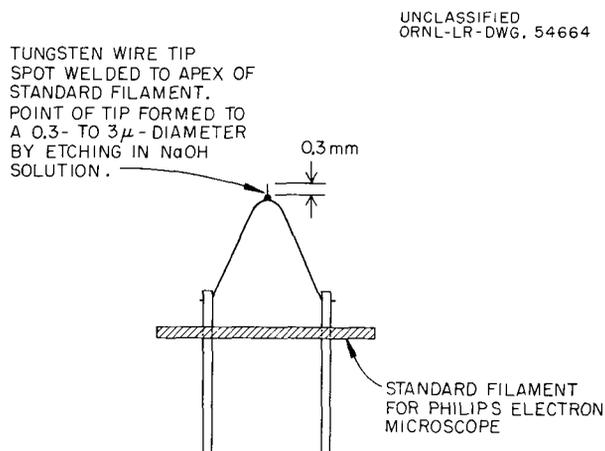


Fig. 13. Detail of Improved Filament for Philips Electron Microscope.

RADIOCHEMICAL ANALYSES (X-10)

S. A. Reynolds

Nuclear Properties

Gamma-Ray Branching in Kr⁸⁵ (W. S. Lyon). – The gamma-ray branching in 10-y Kr⁸⁵ has been determined by measuring the intensity of the 0.51-Mev gamma ray by use of a gamma-ray spectrometer provided with a thallium-activated sodium iodide crystal and the beta disintegration rate by absolute beta counting. The gamma ray was found to accompany 0.38% of the beta decays. A paper on this subject has been accepted for publication in *Nuclear Science and Engineering*.

Radiations from Pm¹⁴⁸ (J. S. Eldridge, W. S. Lyon). – The study of the radiations from Pm¹⁴⁸ (ref 88) was completed. An account of the complete work will be published elsewhere. The decay scheme of the 42-d isomer of Pm¹⁴⁸ that was proposed by Bhattacharjee and co-workers⁸⁹ was essentially confirmed; the proposed decay scheme for the 5.4-d isomer is given in Fig. 14.

Reactor-Neutron-Capture Cross Sections for Production of Os¹⁸⁵ and Cd¹⁰⁹ (W. S. Lyon). – The abundance of Os¹⁸⁴ in natural osmium is 0.018%; that of Cd¹⁰⁸ in natural cadmium is 0.88%. Previously reported neutron-capture cross sections reflect great uncertainty:⁹⁰ that for Os¹⁸⁴

⁸⁷H. Fernandez-Moran, *Improved Pointed Filaments of Tungsten, Rhenium, and Tantalum for High-Resolution Electron Microscopy and Electron Diffraction*, paper No. A25 presented at the Eighteenth Annual Meeting of the Electron Microscope Society of America, Marquette University, Milwaukee, Wis., Aug. 29–31, 1960.

⁸⁸J. S. Eldridge and W. S. Lyon, "Radiations from Pm¹⁴⁸," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 42–45.

⁸⁹S. K. Bhattacharjee, B. Sahai, and C. V. K. Baba, "Decay of Pm¹⁴⁸," *Nuclear Phys.* 12, 356 (1959).

⁹⁰D. J. Hughes and R. B. Schwartz, *Neutron Cross Sections*, 2d ed., BNL-325, p 21 (July 1, 1958).

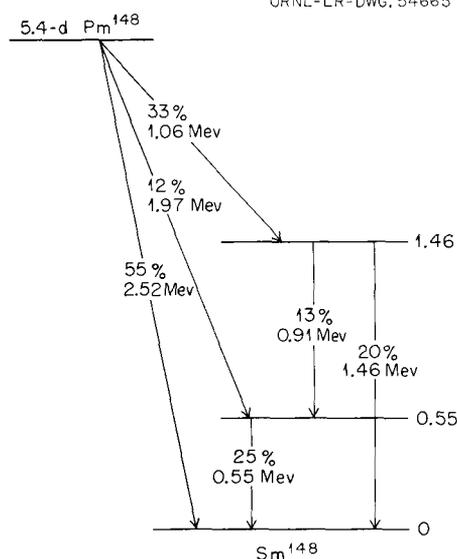


Fig. 14. Proposed Decay Scheme for the 5.4-d Isomer of Pm^{148} .

is given as <200 barns, whereas no value is listed for Cd^{108} . With the high neutron fluxes now available for radioisotope production, detectable quantities of many radionuclides produced from low-abundance stable nuclides are formed and in some instances have been mistaken for impurities. By measurement of the absolute amount of the minor radioactive component, as well as the absolute disintegration rate of the major radioisotope product, it is possible (with knowledge of the irradiation time and decay constants of the radionuclides) to obtain a number equal to the ratio of the reactor-neutron-capture cross sections. For Os^{185} and Os^{191} , for example,

$$\frac{A_{185}}{A_{191}} = \left(\frac{F_{184}}{F_{190}} \right) \left(\frac{\sigma_{184}}{\sigma_{190}} \right) \left(\frac{1 - e^{-\lambda_{185}t}}{1 - e^{-\lambda_{191}t}} \right),$$

where

A = absolute activity of radionuclide at end of irradiation time t ,

F = abundance of stable isotope,

σ = neutron-capture cross section of stable isotope,

λ = decay constant of radionuclide.

The capture cross sections for Os^{190} and Cd^{114} are listed as 8 ± 3 barns⁹⁰ and 1.1 ± 0.3 barns,⁹¹ respectively. When these numbers are used, the cross sections obtained for production of Os^{185} and Cd^{109} are:

$$\begin{aligned} \sigma_{184} &= 1500 \pm 400 \text{ barns} , \\ \sigma_{108} &= 100 \pm 30 \text{ barns, respectively} . \end{aligned}$$

⁹¹*Ibid.*, p 13.

It is planned to determine cross sections for other low-abundance stable isotopes as radionuclides produced from them are detected in radioisotope products.

Neutron-Capture Cross Section of Gold at 29 kev and 63 kev (W. S. Lyon, L. W. Weston⁹²). – The value for the neutron-capture cross section of gold obtained both by shell transmission⁹³ and by capture gamma-ray tank measurements⁹⁴ is 0.6 barn at 25 kev; the values obtained by Sb-Be source activation measurements (at 25 kev) were 0.9 barn⁹⁵ and 1.1 barns.⁹⁶ Because these values differ significantly, experiments were undertaken to measure this cross section by use of kinematically collimated neutrons from the $\text{Li}^7(p,n)\text{Be}^7$ and $\text{T}(p,n)\text{He}^3$ reactions.

The ORNL 5-Mev Van de Graaff generator was used as a source of protons. The neutron flux was monitored by means of a 1.5-m-diam, graphite-sphere neutron counter and also by means of indium foil activation. The radioactivity of the induced Au^{198} was measured by use of gamma-ray spectrometry. The cross sections at 28.8 and 63 kev were found to be 0.767 ± 0.060 and 0.456 ± 0.040 barn, respectively. The value obtained at 29 kev thus is not in agreement with either previously reported value.

Measurement of Radioactivity

Disintegration Rates of Radioisotopes (W. S. Lyon, S. A. Reynolds, H. A. Parker,⁹⁷ E. I. Wyatt⁹⁷). – The methods used in the Analytical Chemistry Division for measurement of the disintegration rates of radioisotopes have been summarized.⁹⁸

Standard solutions of radioisotopes have been procured from a commercial supplier, and measurements of disintegration rates of the radioisotopes in the solutions have been made by established methods. The results are summarized in Table 14, the last column of which shows the deviations of the ORNL values from the means. All deviations are considered to be within the combined experimental errors of the three establishments.

Applications of Liquid Scintillation Counting (J. S. Eldridge). – The applications of liquid scintillation counting⁹⁹ have increased considerably. A scintillator solution useful for the determination of radionuclides in aqueous samples has been tested. It is similar to

⁹²Neutron Physics Division.

⁹³H. W. Schmitt and C. W. Cook, "Absolute Neutron Adsorption Cross Sections for Sb-Be Photoneutrons," *Nuclear Phys.* **20**, 202 (1960).

⁹⁴J. H. Gibbons *et al.*, "Neutron Radiative Capture Cross Sections from 10 to 150 kev," *Bull. Am. Phys. Soc.* **4**, 385 (1959).

⁹⁵R. L. Macklin, N. H. Lazar, and W. S. Lyon, "Neutron Activation Cross Sections with Sb-Be Neutrons," *Phys. Rev.* **107**, 504 (1957).

⁹⁶E. G. Bilpoch, L. W. Weston, and H. W. Newson, "Neutron Capture Cross Sections in the Kev Region. Part I. Methods of Measurement and Analysis," *Ann. Phys. (N.Y.)* **10**, 455 (1960).

⁹⁷Radioisotopes-Radiochemistry Group.

⁹⁸E. I. Wyatt *et al.*, *Assay Methods Used in the ORNL Radioisotope Program*, ORNL CF-60-2-39 (Feb. 1, 1960).

⁹⁹J. S. Eldridge, "Liquid Scintillation Counting," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 46.

Table 14. Disintegration Rates of Radioisotopes

Radioisotope	Date of Supplier's Measurement	Half-Life Used	Disintegration Rate (dis/sec $\times 10^{-3}$ to 10^{-6})			Deviation of ORNL Result (%)
			Supplier	NBS	ORNL	
Na ²⁴	4/60	15.0 h	6.75	<i>a</i>	6.70	-0.4
	10/60	15.0 h	4.66	4.72	4.69	0
P ³²	3/60	14.3 d	1.04 ^b	1.09	1.09	0
S ³⁵	9/59	87 d	7.50	7.50	7.33	-1.5
K ⁴²	8/60	12.47 h	3.37	3.48	3.56	+2.6
Fe ⁵⁹	10/59	45 d	6.86 ^c	6.70 ^c	7.03 ^c	+2.5
Co ⁶⁰	10/53	5.27 y	6.85 ^d	6.85	6.85	0
Sr ⁹⁰ -Y ⁹⁰	4/57	28 y	9.63 ^d	9.63	9.95	+1.6
I ¹³¹	1/60	8.08 d	1.36	1.32	1.37	+1.5
	6/60	8.08 d	9.45	9.50	9.56	+0.6
Cs ¹³⁷	1/60	30 y	1.04 ^c	1.027 ^c	1.00 ^c	-2.2
Ta ¹⁸²	6/59	115 d	3.34	3.41	3.48	+2.1
Au ¹⁹⁸	5/60	2.69 d	2.27	2.30	2.28	-0.1
	11/60	2.69 d	6.86	6.82	6.84	0
Tl ²⁰⁴	6/57	3.56 y	1.91 ^d	1.91	1.90	-0.3

^aNot available.^bWithdrawn. Not averaged.^cMeasured as gammas/sec.^dUsed NBS value.

that proposed by Kinard¹⁰⁰ and has the following composition:

Constituent	Amount
Solvent, parts by volume	
1,4-Dioxane	5
Xylene	5
Ethyl alcohol	3
Solute, grams per liter	
Naphthalene	80
2,5-Diphenyloxazole	5.0
<i>p</i> -Bis[2-(5-phenyloxazolyl)]-benzene	0.05

This solution will retain 7 v/v % water without phase separation. The efficiency for determining tritium by means of this scintillator is about 10%; the solution (aqueous or organic) of the radionuclide is added to the scintillator solution.

¹⁰⁰F. E. Kinard, "Liquid Scintillator for the Analysis of Tritium in Water," *Rev. Sci. Instr.* **28**, 293 (1957).

Radionuclides that have been determined by means of the liquid scintillation technique are: Pu²⁴¹ (0.02 Mev) in aqueous solution; Ni⁶³ (0.067 Mev) in aqueous solution and as a complex with di-2-ethylhexylphosphoric acid in benzene; C¹⁴ (0.155 Mev) as organic acids and in aqueous solutions of smear samples from the Health Physics Division; S³⁵ (0.167 Mev) in aqueous solution and as triisooctylamine sulfate in benzene; Pm¹⁴⁷ (0.223 Mev) in aqueous solution and as a complex with di-2-ethylhexylphosphoric acid in benzene; P³³ (0.249 Mev) in aqueous solution in the presence of P³² (1.71 Mev); P³² as tri- and dibutyl phosphate in xylene; and H³ (0.018 Mev), Ca⁴⁵ (0.254 Mev), Cl³⁶ (0.714 Mev), Tl²⁰⁴ (0.764 Mev), and Sr⁸⁹ (1.46 Mev) each in aqueous solution.

Preparation of Large Liquid Scintillators (W. S. Lyon, G. DeSaussure,⁹² J. D. Kington,⁹² L. W. Weston⁹²). – A program was begun to measure the average number of neutrons per fission ($\bar{\nu}$) for several isotopes of uranium and of plutonium, the capture-to-fission ratio, and the probability of the emission of 1, 2, etc., neutrons per fission. Prompt gamma rays arising from neutron capture by the isotope under study and delayed gamma rays occurring when the fission neutrons produced are captured by a high-cross-section “poison” present will be detected by use of a large (~300-gal) liquid scintillator equipped with many multiplier phototubes.

A small test unit has been made; it consists of an ~30-ml aluminum test vessel that is coated on the inside with reflecting Al₂O₃. The solution to be tested is added to the vessel, dry nitrogen is passed through it for 15 min in order to remove dissolved oxygen, and a multiplier phototube (RCA 6810) is immersed in the solution. The assembly is made light-tight, and the pulse-height spectrum is obtained by use of an external Zn⁶⁵ source displayed on a 256-channel analyzer. Some of the best data obtained for various scintillators are given in Table 15. Results obtained when the “poison” gadolinium 2-ethylhexanoate is added to the standard solution are shown in Table 16. On the basis of these data, a 27-liter test vessel provided with three multiplier phototubes has been fabricated, and a solution consisting of *p*-terphenyl (4 g/liter), *p*-bis[2-(5-phenyloxazolyl)]-benzene (0.3 g/liter), 1% gadolinium 2-ethylhexanoate (1% Gd by weight), and C₂H₅OH (1 vol %) in xylene has been chosen for use in the further evaluation of the technique.

Instrumental Methods

Applications of Gamma Spectrometry (J. S. Eldridge, T. H. Handley, W. S. Lyon, S. A. Reynolds). – Gamma scintillation spectrometry continues to be a very useful method for the analysis of many different materials. Techniques that have been adequately described in the literature¹⁰¹ are used. Typical of the applications in reactor and cyclotron work are: the analyses of a cyclotron target for induced impurity activity, identification of contamination in water from a fuel-transfer case, and analysis of a section of the HRT core vessel. The

¹⁰¹R. L. Heath, *Scintillation Spectrometry – Gamma-Ray Spectrum Catalogue*, IDO-16408 (July 1, 1957).

Table 15. Comparison of Some Organic Scintillator Solutions

Primary Solute*		Secondary Solute*		Solvent*	Relative Pulse Height
Identity	Concentration (g/liter)	Identity	Concentration (g/liter)		
<i>p</i> -Terphenyl	4	POPOP	0.3	Xylene	1.00
				TEB (technical)	0.68
				TEB (double-distilled)	0.75
PPO	4	POPOP	0.3	α NPO	0.90
				Xylene	0.90
				TEB (technical)	0.71
				TEB (double-distilled)	0.80
				TS28M + 15 g/liter naphthaline	0.81
PBD	4	POPOP	0.3	Xylene	1.01

*The identities of the initial components are:

- α NPO = α -naphthylphenyloxazole,
- PBD = 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole,
- POPOP = *p*-bis[2-(5-phenyloxazolyl)]-benzene,
- PPO = 2,5-diphenyloxazole,
- TEB = triethylbenzene,
- TS28M = Shell solvent of hydrocarbons (60% aromatic and 40% aliphatic; boiling range 160 to 194°C).

Table 16. Reduction in Pulse Height of Xylene-*p*-Terphenyl (4 g/liter)-POPOP (0.3 g/liter) Solution with Addition of "Poisons"

Material Added ("Poison")	Relative Pulse Height
1% gadolinium 2-ethylhexanoate + 1% 2-ethylhexanoic acid	0.88
Commercial preparation NE313*	0.56
1% gadolinium 2-ethylhexanoate + 1% C ₂ H ₅ OH	0.94

*NE313 = 1% gadolinium 2-ethylhexanoate.

analysis of corrosion coupons for the purpose of determining neutron flux in in-pile loops was continued.

Applications related to radiological safety included the analysis of various special samples derived from several accidental releases of radioactivity at ORNL. In particular, nondestructive gamma scintillation spectrometry was used to help establish the type and extent of radioactive contamination in Building 3025 following the spread of contamination on April 26, 1960. These examinations established that the radioactivity (Ru¹⁰⁶-Rh¹⁰⁶) found on the roof of the building did not arise from the release of radioactivity in the cell area.

Radioactive contamination found in ruthenium metal was identified as Ru^{106} , and the concentration ($\text{dis min}^{-1} \text{g}^{-1}$) was measured. The Health Physics Division program of sampling the effluent from several ORNL stacks¹⁰² was completed. Many analyses of filters and charcoal traps were made in support of their program.

Determination of Traces of U^{232} (S. A. Reynolds, F. L. Moore). – Alpha spectrometry has been used to measure quantities of U^{232} (5.3-Mev alpha) ranging from <0.2 to 46 dis/min on plates that contained 2000 to 11,000 dis/min of electrodeposited U^{233} , U^{234} , U^{235} , U^{236} , and U^{238} . A Frisch-grid ionization chamber was used in this work; data were taken by M. Davis of the ORNL Instrumentation and Controls Division.

Fission Products

Fission Gas Analysis (T. H. Handley). – Numerous samples of fission gases have been analyzed for radioactive components by gamma scintillation spectrometry. Through the assistance of A. D. Horton,¹⁰³ the fission gases xenon and krypton were separated by means of gas chromatography. A molecular-sieve column was used. The method is similar to those already reported;^{104,105} however, the techniques used were somewhat different. Separation of the gases makes it possible to obtain more reliable results faster because the counting techniques are simplified and it is not necessary to wait for certain radionuclides to decay before others can be measured. This technique has been used on only a few special samples; however, it may have broad application in the future.

Natural Radionuclides

Radiolead (S. A. Reynolds, T. H. Handley). – Natural radiolead, Pb^{210} , has been determined in compounds of radiogenic lead isolated from uranium- and thorium-bearing minerals. The method used was the direct counting of the beta radiation from Bi^{210} , the daughter of Pb^{210} .

At the request of the Health Physics Division, Pb^{210} has been measured recently in samples from six springs in the Oak Ridge area. The method used is based on one reported previously,¹⁰⁶ and consists in precipitation of lead sulfide from 700- to 1000-ml samples of water, with subsequent beta counting of Bi^{210} in the precipitate. Concentrations of Pb^{210} found in the various spring waters ranged from 3 to 16 pc/liter.¹⁰⁷

¹⁰²T. H. Handley *et al.*, "Gamma Scintillation Spectrometry," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 46–47.

¹⁰³Ionic Analyses Group.

¹⁰⁴R. C. Koch and G. L. Grandy, "Xenon-Krypton Separation by Gas Chromatography," *Nucleonics* **18**, 76 (1960).

¹⁰⁵W. R. Kritz, *Chromatographic Analysis of Radioactive Gases*, a paper presented at the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12–14, 1960.

¹⁰⁶J. Fresco, E. Hardy, and J. Harley, *A Method for the Determination of Radon in Water*, NYO-4664 (November 1955).

¹⁰⁷The unit *picocurie*, abbreviated *pc*, is the same as the *micromicrocurie*; it is 10^{-12} curie.

Radon (S. A. Reynolds, L. C. Bate¹⁰⁸). – Radon-222 in the six spring-water samples mentioned above was determined by gamma spectrometry. One-liter samples were placed in containers having a re-entrant well in the bottom (see "Nuclear Analyses," this report), and the intensity of the 0.61-Mev gamma radiation from Bi²¹⁴ was measured as an index of Rn²²² concentration. Cesium-137 was used as a standard, with suitable correction for relative spectrometer efficiency being made. Measured Rn²²² concentrations ranged from 300 to 640 pc/liter. One of these results was confirmed by the radiochemical method mentioned above;¹⁰⁶ alpha and beta activities of Pb²¹⁴, Bi²¹⁴, and Po²¹⁴ were measured.

Radium (T. H. Handley, S. A. Reynolds). – The U.S. Public Health Service method¹⁰⁹ for Ra²²⁶ was tested and was subsequently recommended to the Low-Level Radiochemical Laboratory for use on spring-water samples. No significant activity of Ra²²⁶ has been found in these samples.

Uranium Ore Program (S. A. Reynolds). – The Health Physics Division is planning a program of study of the uptake of radioactive constituents from uranium ore in the lungs of experimental animals. Analyses for uranium, Th²³⁰, and Ra²²⁶ will be required. Three samples of ore were examined by gamma spectrometry to determine whether radioactive equilibrium existed. The intensity of the 1.76-Mev gamma radiation from Bi²¹⁴ furnishes a direct measurement of uranium concentration if all members of the uranium series are in equilibrium. For two of the three samples, adequate agreement existed among the results of (1) the supplier's chemical analysis, (2) delayed-neutron counting (see "Nuclear Analyses," this report), and (3) gamma spectrometry. The gamma spectrometric result for the third sample was lower than the results by methods (1) and (2). It was found subsequently by means of beta counting that the uranium content of the third sample was as high as the results of methods (1) and (2), above, indicated. Therefore, equilibrium did not exist, and the gamma spectrometric result was rejected. In beta counting, an absorber was used to minimize the contribution of beta radiation other than that of Pa²³⁴, the second daughter of U²³⁸. Beta counting is thus a more nearly direct measure of uranium content than is gamma spectrometry, although it is inherently a less precise technique. From the results of the analyses described, the concentrations of uranium, Th²³⁰, and Ra²²⁶ were readily deduced. It is anticipated that the following methods will be used in the analysis of the samples resulting from the animal experiments: delayed-neutron counting for uranium determination, the U.S. Public Health Service method¹⁰⁹ for radium, and an adaptation of an existing method¹¹⁰ for Th²³⁰.

¹⁰⁸Nuclear Analyses Group.

¹⁰⁹P. F. Hallbach, editor, *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).

¹¹⁰F. L. Moore, "Radiochemical Determination of Ionium in Uranium Fluorination Ash," *Anal. Chem.* 30, 1020 (1958).

Thorium in Rock Samples (S. A. Reynolds). – Gamma spectrometry has been shown to be feasible for the direct measurement of thorium in samples of granite and other rocks. The intensity of the 2.6-Mev gamma radiation from Tl^{208} in samples is compared with that in a rock of known thorium content. Details of the method have been reported.¹¹¹

Cyclotron Research

T. H. Handley

Studies of Neutron-Deficient Radionuclides. – In cooperation with members of the Electronuclear Research Division, the investigation of neutron-deficient radionuclides is continuing. Two papers that report the work have been published.^{112,113} Future results will be submitted for publication in the open literature also.

Solvent-Extraction Methods

New Technique for the Separation of Trivalent Actinide Elements from Trivalent Lanthanide Elements (F. L. Moore). – A new liquid-liquid extraction technique for the rapid separation of the trivalent actinide elements from the trivalent lanthanide elements has been developed. The method is based on the preferential extraction of the trivalent actinide elements from dilute hydrochloric acid-concentrated lithium chloride solution into a solution of triisooctylamine in xylene or other solvents. The order of decreasing extractibility is: americium, curium > thorium > europium, promethium > cerium > yttrium, thulium. Favorable extractions of anionic chloro complexes of the lanthanide elements and of thorium are also possible under certain other conditions, for example, if another organic diluent is used. Interestingly, the lanthanide elements and thorium always previously have been reported as not forming anionic chloro species. These new findings suggest useful applications of the technique. The most useful current application is a new and more efficient separation of promethium from americium. A paper that describes the method in detail has been submitted for publication in *Analytical Chemistry*.

Triphenyl Phosphite, a Selective Extractant for Copper (T. H. Handley, J. A. Dean¹¹⁴). – Continued investigation of the extraction of elements by means of organophosphorus compounds has revealed another unique member of this promising family. Triphenyl phosphite, a neutral ester of phosphorous acid, reacts readily with copper(I) halides to yield addition-type compounds, which are extractable into carbon tetrachloride. Optimum distribution coefficients are obtained when the aqueous phase is a 0.15 M solution of either a hydrogen or an alkali-metal halide. The numerical values of the distribution coefficients exceed 100 when a 5 w/v % solution of triphenyl phosphite in carbon tetrachloride is used. Ascorbic acid and stannous chloride have each proved satisfactory

¹¹¹S. A. Reynolds, *Determination of Thorium in Rock Samples by Gamma Spectrometry*, ORNL CF-60-6-37 (June 7, 1960).

¹¹²K. P. Jacob *et al.*, "Electron Capture Decay of Tm^{168} and Tm^{166} ," *Phys. Rev.* 117, 1102 (1960).

¹¹³B. Harmatz, T. H. Handley, and J. W. Mihelich, "Nuclear Spectroscopy of Neutron-Deficient Lu, Ta, and Re Isotopes," *Phys. Rev.* 119, 1345 (1960).

¹¹⁴University of Tennessee.

as a reductant for copper(II). The reduction rate increases with increasing temperature; however, the optimum distribution coefficients are obtained at room temperature. Of the anions investigated, thiosulfate and cyanide completely inhibit the extraction, perchlorate and thiocyanate decrease the extractability, whereas the other common anions aid the extraction. Of the 30 elements tested, only Th, Pb, Au, and Ag showed appreciable distributions. Copper in concentrations in the aqueous phase as high as 2000 ppm is completely extracted with a single 2-min equilibration. The specificity of the method for copper rivals that of the well-known procedure in which steric-hindered compounds of 1,10-phenanthroline are used; triphenyl phosphite, by contrast, is inexpensive and readily available.

Monograph on Extractions with Amines (F. L. Moore). – A monograph, "Liquid-Liquid Extraction with High-Molecular-Weight Amines," is being prepared for the Subcommittee on Radiochemistry of the National Research Council. The manuscript is nearly completed and will be issued soon.

Foreign Guest Program

W. S. Lyon S. A. Reynolds

Visitors from Argentina, Indonesia, Greece (two), Thailand, and India have studied radioactive measurements and standardizations for periods ranging from two weeks to four months. These guests have been interested primarily in absolute beta- and gamma-ray measurements. Among the subjects in which they gained information and laboratory experience were 4π -beta and 4π -beta-gamma coincidence counting, qualitative and quantitative gamma-ray spectrometry, gamma-gamma coincidence counting, measurement of half-lives of nuclides in metastable states in the 0.1- to 25- μ sec range, and calibration of commonly used gamma-ray-measuring devices. This program is continuing.

Participation in National Organizations

ASTM Committee E-10, Radioactive Isotopes. – *Subcommittee II (Dosimetry, Fuel Burnup)* (W. S. Lyon). – Some sections of the dosimetry handbook have been completed. A method for determining fuel burnup that requires an analysis for Cs^{137} has been drafted. In addition, methods other than chemical methods are being evaluated for solution to the problem of burnup determination.

Subcommittee III (Task Group on Radioisotope Methods and Specifications) (W. S. Lyon). – Two methods, a general radiochemical procedure and a radiochemical method for P^{32} , have been written by this task group and are now to be voted upon by Subcommittee III.

American Standards Association Committee N 5.4 (Use and Handling of Radioisotopes and High-Energy Radiations) (W. S. Lyon). – Work has continued on standard procedures for handling, packaging, shipping, and measuring unsealed sources of radiation. W. S. Lyon was a delegate to the meeting of the International Standards Organization in Geneva in May 1960, where standards and standardization problems at the international level were studied.

ASTM Committee D-19 (Industrial Water) (S. A. Reynolds). – S. A. Reynolds is chairman of a task group of ASTM Committee D-19, "Industrial Water." The task group is concerned with the

preparation of methods for the radiochemical determination of radiostrontium in water. He is also a member of three other task groups that are concerned with writing methods for sampling radioactive water, for determining radionuclides in reactor-cooling water, and for determining gross radioactivity in water and of a fourth group whose function is to prepare and maintain a bibliography on radioactivity in water.

REACTOR PROJECTS LABORATORY (Y-12)

J. C. White

A portion of the research and development work of this group is reported in the progress reports of the Gas-Cooled Reactor Project and the Aircraft Nuclear Propulsion Project.¹¹⁵⁻¹²³

Spectrophotometric Studies of Molten Salts

J. P. Young

The study of the absorption spectra of various molten-salt systems was continued. The finding of analytical applications for spectra derived from salts dissolved in molten-fluoride salts has been of primary interest. The usefulness of the pendent-drop technique for confining liquids for spectrophotometric study has been evaluated further. Some of the more interesting investigations are described below.

Spectrophotometric Studies in Molten Lithium Fluoride. – Spectrophotometric studies have been conducted at temperatures as high as 950°C with pendent drops of molten lithium fluoride by increasing the electrical power supplied to the high-temperature cell assembly.¹²⁴ Molten lithium fluoride is apparently very transparent, in terms of Kirchhoff's law of radiation,¹²⁵ which relates absorptive and emissive properties of materials as a function of temperature, since no black-body

¹¹⁵“Determination of Impurities in Helium,” *GCR Project Quart. Progr. Rept. Mar. 31, 1960*, ORNL-2929, pp 223–26.

¹¹⁶“Determination of Oxygen-to-Uranium Ratios in UO₂ Pellets,” *GCR Project Quart. Progr. Rept. Mar. 31, 1960*, ORNL-2929, pp 226–27.

¹¹⁷“Analysis of Mixtures of Helium and Argon,” *GCR Project Quart. Progr. Rept. June 30, 1960*, ORNL-2964, pp 212–15.

¹¹⁸“Preparation of Synthetic Gas Mixtures,” *GCR Project Quart. Progr. Rept. June 30, 1960*, ORNL-2964, pp 215–16.

¹¹⁹“Sequential Plan for Sampling and Testing Batches of UO₂ Pellets,” *GCR Project Quart. Progr. Rept. June 30, 1960*, ORNL-2964, pp 216–19.

¹²⁰“Automatic Continuous Analysis of Helium,” *GCR Project Quart. Progr. Rept. Sept. 30, 1960*, ORNL-3015, pp 143–45.

¹²¹“Determination of Helium in Air,” *GCR Project Quart. Progr. Rept. Sept. 30, 1960*, ORNL-3015, pp 145–47.

¹²²*ANP Project Semiann. Progr. Rept. Apr. 30, 1960*, ORNL-2942, pp 50–52 (classified).

¹²³*ANP Project Semiann. Progr. Rept. Oct. 31, 1960*, ORNL-3029, pp 72–73 (classified).

¹²⁴J. P. Young and J. C. White, “A High-Temperature Cell Assembly for Spectrophotometric Studies of Molten Fluoride Salts,” *Anal. Chem.* **31**, 1892 (1959).

¹²⁵R. W. Wood, *Physical Optics*, 3d ed., chap. 23, “Thermal Radiation,” Macmillan, New York, 1934.

radiation was observed to emanate from the molten drop. The spectra of the fluorides of praseodymium, neodymium, and samarium dissolved in molten lithium fluoride have been obtained¹²⁶ and compared with their spectra in aqueous and nonaqueous solvents.

At the request of the Reactor Chemistry Division, spectral studies of the 3d transition-element fluorides in pure alkali-metal fluorides are being undertaken. The spectrum of 0.25 mole % cobalt(II) fluoride in molten lithium fluoride has been obtained; it shows absorption maxima at 495 and 572 m μ and a shoulder at 615 m μ . Cobalt(II) fluoride in LiF-NaF-KF exhibited peaks at 510 and 580 m μ . It has not been possible to obtain the spectra of nickel(II) fluoride in molten lithium fluoride because of difficulties in dissolving the nickel fluoride. Work on this problem is continuing.

Modifications of the High-Temperature Cell Assembly. – The ability to routinely perform spectral studies at 900°C makes possible spectral investigations in a wide variety of molten salts. Consideration has been given to studies with higher melting salts, particularly sodium fluoride (mp, 998°C). One of the better methods of obtaining temperatures in the range from 1000 to 2000°C is to use a graphite resistance heater. Such a heater was designed and fabricated. The heater assembly alone has been operated successfully. A temperature of 1400°C was registered within 15 min by a Chromel-Alumel thermocouple placed within, but not touching, the graphite tube. In order to attain this temperature, a current of 45 amp was required at 25 v. This graphite heater not only should make it possible to attain temperatures well above 1000°C with the high-temperature cell assembly but also to provide more uniform heat at temperatures below 1000°C.

During the studies with molten lithium fluoride, etching of the fused silica windows in the cell assembly by hydrogen fluoride gas became a serious problem. The problem was solved temporarily by placing Mylar film between the windows and the furnace heaters. The quartz windows have now been replaced by synthetic sapphire (Al₂O₃) windows, which are not attacked by gaseous hydrogen fluoride.

A pendent-drop container of new design was made. It has excellent mechanical rigidity and stability and is also useful at temperatures above 1000°C since gold is no longer used as a brazing metal. A platinum tube fits snugly in a 1/4-in.-diam platinum tube in a direction parallel to the circular end of the larger tube. The larger tube is bonded to a 1/8-in.-diam ceramic rod by alundum cement (Norton RA 1139, Norton Abrasive Company). This pendent-drop assembly has undergone repeated thermal cycling up to temperatures as high as 1300°C without any apparent loss of rigidity.

Pendent-Drop Techniques. – Three methods are now available for obtaining pendent drops of salts for spectrophotometric study. The original method of immersing the platinum tube in a molten salt and withdrawing a sample has been discussed.¹²⁷

¹²⁶ 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).

¹²⁷ 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).

A new method for filling the platinum tube at room temperature has been evaluated in which a solid, finely ground sample is placed in the pendent-drop container and then is firmly tamped so that the sample holder can be transferred to the high-temperature cell assembly without loss of sample. This method offers the following advantages: (1) The salt can be manipulated as a solid at room temperature, (2) the exact weight of the contents of the tube can be determined easily since none of the salt is on the outside of the tube as is the case in the immersion method of filling, and (3) only a small amount of sample (about 100 to 200 mg) is required for spectral study. One disadvantage of the tamped sample is that if a clear melt is not obtained there is no way to eliminate suspended material; the immersion method does not have this disadvantage. Quantitative spectral data have demonstrated that a tamped sample can be loaded into a pendent-drop container and melted with no loss of material; also, useful spectra can be obtained.

The third method involves placing only the platinum tube of the new platinum-tube assembly in a melt. On cooling, the main body of the solidified salt is broken away from the tube, and the tube is inserted into the platinum-tube assembly for subsequent remelting.

Spectra of Borax Solutions. – In connection with the study of analytical possibilities of spectrophotometry of molten salts, borax has been considered because of the solubility of many metal salts and oxides in molten borax. A spectral study of M_xO_y borax beads, both molten and at room temperature, was reported in 1924;¹²⁸ however, much experimental detail is lacking in the account, and the resolution of the various spectra that were discussed seemed relatively poor by present standards. The pendent-drop technique offers an excellent means for confining molten borax for spectral study. It is especially useful since the materials used for cell windows, that is, fused silica, crystalline magnesium oxide, and synthetic sapphire, all react rapidly with molten borax. The results of spectral studies with borax systems are summarized in Table 17.

According to the results given in Table 17, the absorbance of these metal ions is more intense at room temperature than at 900°C. The absorption maxima of nickel fluoride are practically identical with those of nickel chloride, considering the experimental error involved in the estimated molar absorbance indexes. The absorption maxima of the cobalt salts are not identical, however. It was not possible to calculate the molar absorbance indexes for cobalt fluoride; however, the ratio of the peak intensity at 900°C to that at 25°C for this salt compared closely with a similar ratio for cobalt chloride. The sensitivity of absorbance spectra in borax is indicated by the fact that 40 ppm (w/w) of $CoCl_2$ in a borax bead of 1-cm light path, at room temperature, will give an absorbance of 0.10 based on the molar absorbance index of 110.

Chromogenic Reagents in Molten-Salt Systems. – The investigation and evaluation of possible chromogenic reagents for use in molten-salt media¹²⁹ have continued. Both phthalocyanine and its sulfonate derivative were found here to be insoluble in molten alkali-metal halide eutectics and

¹²⁸K. Schaum and M. Funck, "Photometrische und spektral photometrische Studien. IV. Über den Einfluss der Temperatur auf die Absorptionsspektren der Borax- und Phosphorsalzperlen," *Z. wiss. Phot.* 23, 73 (1924).

¹²⁹J. P. Young, "Spectrophotometric Studies of Molten-Fluoride-Salt Systems," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959, ORNL-2866*, pp 52-54.

Table 17. Absorption-Spectra Maxima of Cobalt and Nickel in Sodium Borate Solution

Solute	Temperature (°C)	Absorption Maxima (m μ)	Estimated Molar Absorbance Index*
NiF ₂	25	444	55
	900	468	30
NiCl ₂	25	442	60
	900	462	40
CoF ₂	25	640**	
		595	
		518	
	900	640**	
		595	
		518	
CoCl ₂	25	630**	110
		588	
		522	
	900	658**	
		605	
		510	

*Error in this calculation is approximately $\pm 10\%$.

**Shoulder.

in molten potassium pyrosulfate. It was found here that phthalocyanine is soluble in *m*-diphenoxybenzene (mp, 60 to 62°C), an experimental high-temperature lubricant (Eastman Kodak Company). When a solution of phthalocyanine in *m*-diphenoxybenzene was contacted with metallic copper in molten potassium pyrosulfate, copper-phthalocyanine was formed in the organic phase, as evidenced by the change in spectrum of the solution of phthalocyanine after the contact. Further work will be necessary to elucidate the nature of this reaction, but these results do indicate that phthalocyanine may be a useful chromogenic reagent, and apparently an extractant, at temperatures below its decomposition temperature ($\sim 400^\circ\text{C}$).

The possibility of using heteropoly salts as chromophores in molten-salt media has been considered. The facts that heteropoly compounds exist with much water of hydration and that these compounds decompose in basic solution provide a rather firm basis for doubting that heteropoly compounds exist as such in molten halide salts. It has been found here that phosphotungstic acid is insoluble in molten LiCl-KCl and that phosphomolybdic acid does dissolve in LiCl-KCl to yield a faint yellow solution. This yellow solution cannot be formed, however, if a phosphate salt is added to molybdate ion in LiCl-KCl.

Solvent Extraction with Organophosphorus Compounds

W. J. Ross

The extraction characteristics of tracer quantities of thorium and zirconium have been investigated further with cyclohexane solutions of organophosphorus extractants.

Thorium. – Thorium-234 tracer (10^{-8} M) exhibits erratic extraction behavior unless accompanied by a carrier. When 20 μ g or more of thorium carrier is present, the extraction of the tracer from acid chloride, nitrate, and sulfate solutions with tri-*n*-octylphosphine oxide and tris(2-ethylhexyl)phosphine oxide essentially duplicates that observed in systems that contain macro amounts of thorium.¹³⁰⁻³²

Zirconium. – Zirconium-95 tracer and zirconium carrier (20 μ g) are extracted completely from 5.0 to 10 M HCl or 0.5 to 10 M HNO₃ into 0.1 M solutions of tri-*n*-octylphosphine oxide. Almost complete extraction of zirconium is also achieved from 0.2 to 7 M H₂SO₄ into 0.1 M tri-*n*-octylphosphine oxide in a single 30-min extraction. The extraction previously reported¹³³ for macro amounts of zirconium in sulfate-tri-*n*-octylphosphine oxide systems has been found to be affected by the presence of nitrate in such systems, the concentration of which was then unknown. In the complete absence of nitrate, as much as 5 mg of zirconium is extracted completely from 5 ml of 3 to 5 M H₂SO₄, and 1 mg of zirconium is extracted completely from 5 ml of 0.2 to 7 M H₂SO₄ into 5 ml of 0.1 M tri-*n*-octylphosphine oxide. Some zirconium is extracted from < 1 M H₂SO₄, but apparently the amount of acid that accompanies the zirconium is not enough to prevent hydrolysis. After a short time, the organic phase becomes turbid because of the hydrolysis of the zirconium-tri-*n*-octylphosphine oxide adduct. Chloride has no effect on the extraction; however, sulfate and, to a much greater extent, nitrates and nitric acid seriously depress the extraction.

Carrier-level zirconium is extracted completely from 0.5 to 10 M HCl into 0.1 M solutions of tris(2-ethylhexyl)phosphine oxide in cyclohexane. Complete extraction is also achieved from 5 ml of 0.2 to 3 M H₂SO₄ into 5 ml of 0.1 M di(2-ethylhexyl)phosphoric acid, whereas the degree of extraction is diminished at higher sulfuric acid concentrations.

Antagonistic rather than synergistic effects were observed in the extraction of zirconium, at carrier and macro levels, into solutions of mixtures of tri-*n*-octylphosphine oxide and di(2-ethylhexyl)phosphoric acid. The degree of extraction is dependent on the concentration of di(2-ethylhexyl)phosphoric acid in 0.2 to 2 M H₂SO₄ and on the concentration of tri-*n*-octylphosphine oxide in more acid systems. Complete extraction is achieved from 0.2 to 8 M H₂SO₄ when the concentration of tri-*n*-octylphosphine oxide is at least twice that of di(2-ethylhexyl)phosphoric acid.

¹³⁰W. J. Ross and J. C. White, *The Use of Tri-*n*-octylphosphine Oxide in the Solvent Extraction of Thorium from Acidic Solutions*, ORNL-2627 (Nov. 20, 1958).

¹³¹W. J. Ross and J. C. White, "Extraction and Determination of Thorium from Sulfate and Phosphate Solutions with Tri-*n*-octylphosphine Oxide," *Anal. Chem.* 31, 1847 (1959).

¹³²W. J. Ross, "Solvent Extraction with Organophosphorus Compounds," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 54.

¹³³J. C. White and W. J. Ross, *The Use of Tri-*n*-octylphosphine Oxide in the Solvent Extraction of Zirconium*, ORNL-2498, p 5 (Apr. 10, 1958).

Application of Pyrocatechol Violet as a Spectrophotometric Reagent for Tin

W. J. Ross

Pyrocatechol violet was used as a sensitive reagent for the spectrophotometric determination of tin. This reagent forms a red complex with tin(IV) in aqueous solutions buffered to pH 2.5 by potassium acid phthalate. The complex has a mole ratio of reagent/tin of 2 and a molar absorptivity index of 65,000 at 555 $m\mu$. The absorptivity-concentration relationship obeys Beer's law over the range of tin concentration from 0.1 to 0.6 $\mu\text{g/ml}$. A colored species is not formed between pyrocatechol violet and tin(II); however, microgram quantities of tin(II) are completely oxidized to tin(IV) under the conditions used. The tin complex is sensitive to high ionic strength but is readily formed in dilute solutions that contain less than 0.17 meq/ml of acid and/or salt. Those metals interfere that form colored species with the reagent in solutions when the pH is less than 5; they include Zr, Ti, Bi, Sb, Ga, and Mo. Copper, uranium, lead, zinc, arsenic, and nickel have not been observed to interfere. Small amounts of chloride, sulfate, nitrate, and bromide do not interfere; however, fluoride, tartrate, and ethylenediaminetetraacetate reduce the intensity of the color of the tin-pyrocatechol violet complex.

An almost specific spectrophotometric method has been developed for the determination of tin in lead-, zinc-, copper-, iron-, and zirconium-base alloys. The tin is extracted from acid chloride or chloride-sulfate solutions into a cyclohexane solution of tris(2-ethylhexyl)phosphine oxide, $[\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2]_3\text{PO}$. The extracted species is $\text{SnCl}_4 \cdot 2\{[\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2]_3\text{PO}\}$, regardless of the original oxidation state of tin in the aqueous solution. As much as 20 mg of tin is extracted completely from 5 ml of solution in a single 10-min equilibration with 5 ml of 0.1 M tris(2-ethylhexyl)phosphine oxide in cyclohexane; 100 μg of tin is completely extracted under the same conditions into 0.01 M solution. Of 50 elements tested, only Sb, Ga, Fe, and Mo are coextracted with tin into 0.01 M tris(2-ethylhexyl)phosphine oxide from solutions that are 1 M in HCl and 2 M in H_2SO_4 . These potential interferences are readily backwashed from the organic phase into a fresh solution of the mineral acids. Tin is determined spectrophotometrically in ethyl alcohol-pyridine solutions of the organic phase as the red complex of pyrocatechol violet. This species has a mole ratio of reagent/tin of 2 and exhibits a molar absorptivity index of 43,000 at 575 $m\mu$. The recommended concentration range of tin in the final solution is 2 to 20 $\mu\text{g/ml}$. The method has been applied successfully to the determination of tin in a number of alloys that have been dissolved according to ASTM procedures.

Determination of Molybdenum in Cyclohexane Solutions of Tri-*n*-octylphosphine Oxide

W. J. Ross

A method was developed for the determination of molybdenum in cyclohexane solution of tri-*n*-octylphosphine oxide. The method is based on the spectrophotometric measurement of the yellow complex formed between molybdenum and thioglycolic acid in ethyl alcohol-pyridine dilutions of the cyclohexane solution. The absorptivity-concentration relationship obeys Beer's law at 353 $m\mu$ for molybdenum concentrations of 2 to 20 $\mu\text{g/ml}$ in the final solution; the molar absorptivity index

is 4500. As much as 25 mg of molybdenum is extracted completely from 5 ml of 3 M HCl into 5 ml of 0.1 M tri-*n*-octylphosphine oxide in cyclohexane. The desired range of concentration of molybdenum is achieved by diluting the organic phase with ethyl alcohol. Titanium(IV), chromium(VI), iron(III), and bismuth cannot be tolerated in the cyclohexane solution.

Determination of Uranium and Thorium in Granite

W. J. Ross

As a part of a program to establish the feasibility of separating uranium and thorium from granite and other siliceous rocks, a method was developed for the determination of these elements in pulverized samples of the rocks before and after leach with mineral acids.

Rock samples are decomposed with hydrofluoric and nitric acids.¹³⁴ The resulting fluorides are dissolved by repeated digestion with nitric acid; persistent residues are rendered soluble by fusion with potassium pyrosulfate. Thorium and uranium are then extracted from 1 M HNO₃ solutions of the sample into 0.1 M tri-*n*-octylphosphine oxide in cyclohexane. Uranium is determined fluorometrically in an aliquot of the organic phase; thorium is back-extracted into 0.3 M H₂SO₄ and is determined by the spectrophotometric Thoron method. Each of the separations involved has been checked by tracer techniques and found to be better than 99% complete. The over-all accuracy and precision are comparable with those achieved by gamma spectrometry¹³⁵ or by more lengthy and tedious chemical methods.

This method has been used routinely for six months to analyze rocks and acid-leach residues that contained 1 to 10 ppm of uranium and 5 to 10 ppm of thorium.

Determination of Oxygen by the Potassium Tetrafluorobromide Fluorination Method

A. S. Meyer, Jr. G. Goldberg

The apparatus for the determination of oxygen in metal oxides and fluoride salts by fluorination with molten potassium tetrafluorobromide, KBrF₄,^{136,137} has been adapted to permit the determination of both oxygen and nitrogen. In the modified procedure the volume of the mixture of nitrogen and oxygen, which are evolved quantitatively, is first measured; then the oxygen is removed by pumping the gases through a tube packed with copper turnings at about 500°C until the volume of the gas becomes constant. The residual gas is reported as nitrogen. This method eliminates the transfer of gas that is required if the evolved mixture of gases is analyzed by gas chromatography or mass spectrography and thereby eliminates the possibility of contamination.

¹³⁴H. Levine and F. S. Grimaldi, "Determination of Thorium in the Parts per Million Range in Rocks," *Geochim. et Cosmochim. Acta* **14**, 93 (1958).

¹³⁵S. A. Reynolds, *Determination of Thorium in Rock Samples by Gamma Spectrometry*, ORNL CF-60-6-37 (June 7, 1960).

¹³⁶A. S. Meyer, Jr., and G. Goldberg, "Direct Determination of Total Oxygen in Uranium Oxide," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 50-51.

¹³⁷A. S. Meyer, Jr., and G. Goldberg, "Determination of Oxides in Fluoride Salts," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1958*, ORNL-2662, pp 68-70.

The method has also been applied extensively to the determination of oxygen in beryllium, a determination that is difficult to perform by vacuum-fusion techniques because of the "gettering" action of beryllium vapor. Beryllium reacts vigorously with KBrF_4 to evolve powdery beryllium fluoride, which tends to plug reactor connections. It is therefore necessary to limit the size of test portions to 25 to 50 mg. This size is usually adequate since the concentration of oxygen is ordinarily in the percentage range. Because of the hazard of inhalation of the powdery beryllium fluoride, special precautions are required. In the analysis of finely divided beryllium metal, the KBrF_4 method offers the particular advantage that oxygen present as recent surface oxidation is recovered and measured. Surface oxide is not determined quantitatively by the bromine-methanol¹³⁸ method in use in the Y-12 laboratories.

This fluorination method has also been used to determine oxygen in Dy, Si, Nb, Mo, erbium phosphide, europium oxide-stainless steel mixtures, and magnetite ore.

Gas-Chromatographic Determination of Oxygen from Irradiated Alkali-Metal Bromates

A. S. Meyer, Jr. I. B. Rubin

A gas chromatographic method for the determination of oxygen released from irradiated alkali-metal bromates was developed relative to the Chemistry Division's study of the effects of radiation on alkali-metal bromates. It is postulated that the bromates are degraded to bromites and, on continued irradiation, to bromine salts in which the anions are in even lower oxidation states. Upon dissolution of the irradiated materials, any oxygen that was released by the irradiation but trapped in the crystal lattice is liberated together with oxygen that is liberated by the decomposition of unstable salts such as bromites. The measurement of this liberated oxygen is thus of value in estimating the degree of degradation of the bromate radical.

Only minor changes in present apparatus were required since, in the analysis of gases evolved from graphite,¹³⁹ a method for the transfer of gases under low pressure (<5 mm Hg) to the gas chromatograph had been developed. The chromatographic separation and determination of the oxygen are performed with a Perkin-Elmer model 154-C chromatograph; an 8-ft column of Linde type 5A molecular sieves at 100°C is used.

Samples of the bromates of Li, Na, K, and Rb have been analyzed. Recoveries of oxygen range from 450 to 6800 $\mu\text{l/g}$ in samples that have received Co^{60} irradiations of the order of 10 to 100 megarep. In comparison, only 19 $\mu\text{l/g}$ was recovered from an unirradiated sample of potassium bromate. The relative standard deviation of the determination is about 3%.

¹³⁸A. R. Eberle and M. W. Lerner, "The Rapid Determination of Beryllium Oxide in Beryllium Metal," *Metallurgia* **59**, 49 (1959).

¹³⁹A. S. Meyer, Jr., and I. B. Rubin, "Gas Chromatographic Analysis of Helium," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 49-50.

Infrared Spectral Study of Irradiated Potassium Bromate

C. A. Horton

A preliminary study was undertaken of the possibility of detecting and determining by infrared spectroscopy the chemical changes induced in potassium bromate by gamma irradiation. Infrared spectra were recorded from about 660 to 1700 cm^{-1} for the following: KBr pellets that contained unirradiated potassium bromate, KBr pellets that contained irradiated potassium bromate, and KBr pellets that contained unirradiated potassium bromate and that were irradiated after they were formed. Since irradiation damage increased the general visual and infrared opacity of those pellets that were irradiated after they were prepared, recordings were also made after re-pressing the pellets and sometimes after repolishing the pellet surfaces. A significant decrease in the absorption intensity of bromate at 795 cm^{-1} was observed for the irradiated pellets and those containing the irradiated potassium bromate. Bands not previously observed were obtained for the pellets that contained irradiated potassium bromate or that were themselves irradiated. Two of the bands are probably attributable to nitrate, formed from trapped oxides of nitrogen as a result of the irradiation, on the surface of the pellets. The other new bands are as yet unidentified.

Improved Rapid Determination of Microgram Quantities of Sulfur

J. E. Attrill

A rapid accurate method, compatible with present equipment and procedures, was desired for the determination of microgram quantities of sulfur. Excellent results¹⁴⁰ had been obtained in the range of 50 to 500 μg of sulfur by means of the Leco induction furnace and automatic titrator. In the lower range (0 to 10 μg), however, both the accuracy and precision were unsatisfactory.

According to Larsen, Ross, and Ingber¹⁴¹ sulfur dioxide in *p*-rosaniline-formaldehyde solution forms a faint red complex that can be used in an analytical method. The optimum range of sulfur for a test portion analyzed by this method is reported to be 0.5 to 10 μg . Since sulfur is released by combustion in the Leco equipment as sulfur dioxide, this gas was absorbed in *p*-rosaniline-formaldehyde reagent, and the absorbancy of the solution was measured at 560 $\text{m}\mu$. A straight-line absorbancy-concentration relationship was obtained. For the limited number of samples analyzed, the relative standard deviation is indicated to be somewhat better than 10%. The change in absorbancy per microgram of sulfur is small. Attempts are being made to increase the sensitivity of the method.

¹⁴⁰J. E. Attrill, "Determination of Sulfur with a Leco Automatic Sulfur Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 51-52.

¹⁴¹R. P. Larsen, L. E. Ross, and N. M. Ingber, "Separation and Determination of Microgram Amounts of Sulfur," *Anal. Chem.* **31**, 1596 (1959).

Methods for Determining Oil in Perclene

C. A. Horton

Several methods for determining residual cutting oil in Perclene, a chlorinated solvent, were investigated. Measurements were made of: the weight of the residue remaining after the evaporation of the Perclene, the fluorescence of a carbon tetrachloride solution of the mixture, the ultraviolet absorbancy, and the near-infrared absorbancy. In each case, a linear relationship between a function of the property measured and the concentration of the oil was obtained. None of these methods was as satisfactory as measurement of the absorbancy of the carbon-hydrogen stretching frequency at 3.4μ ; a carbon tetrachloride solution of the mixture was used for the measurement.

Special Infrared Spectral Studies

C. A. Horton

The infrared spectra of several types of samples were obtained in order to identify functional groups, study purity, detect changes during other experiments, or determine band-pass regions. The samples included several types of plastic films, massive plastics, organophosphorus extractants, oils, a carbon-chlorine polymer, ethylene dibromide, commercial fatty acids, and ion exchange resins. Spectra were recorded with either an Infracord or a Beckman IR-7 spectrophotometer.

Determination of Tin in Chromic Fluoride

R. F. Apple

A method for the determination of trace quantities of tin in chromic fluoride was developed. One gram of the salt is dissolved in 5 ml of concentrated H_2SO_4 . If the temperature is slightly less than $160^\circ C$ during the dissolution, the fluoride is quantitatively evolved as hydrofluoric acid, and $Cr_2(SO_4)_3 \cdot xH_2O$ remains completely in solution. The solution is diluted, and the tin is then extracted from it into a 0.1 M solution of tri-*n*-octylphosphine oxide in cyclohexane and is determined by the spectrophotometric pyrocatechol violet method.¹⁴²

Chemical Analysis of Beryllium and Its Oxide

R. F. Apple

A program was initiated in regard to beryllium metal and its oxide to determine whether present methods of analysis are sufficiently precise for the determination and control of the variables encountered in research studies. Little or no improvement of the present methods has been deemed necessary for the determination of trace quantities of Fe, Cr, Ni, Al, and fluoride in beryllium

¹⁴²W. J. Ross and J. C. White, "Extraction of Tin with Tris-2-ethylhexylphosphine Oxide and Its Determination in Non-Aqueous Medium with Pyrocatechol Violet," a paper accepted for publication in *Anal. Chem.*

metal and its oxide. New methods for silicon, magnesium, and lithium in beryllium oxide have been developed and described.¹⁴³⁻⁴⁵

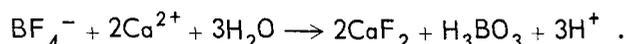
Determination of Boron Trifluoride in Helium

R. F. Apple

A simple rapid method was required for the determination of boron trifluoride, BF_3 , in helium. This need resulted from the investigation of the solubility of BF_3 in $\text{LiF}\text{-BeF}_2\text{-ZrF}_4\text{-UF}_4\text{-ThF}_4$ (70-23-5-1-1 mole %), the fuel chosen for the Molten Salt Reactor Experiment.

The BF_3 is introduced into the fluoride mixture at various temperatures and pressures. The dissolved BF_3 is then stripped from the salt with helium. The off-gas, which carries the BF_3 , is passed through a series of three Pyrex columns, filled with glass beads, in each of which 150 ml of a saline-saturated absorbing solution is contained. After approximately 100 liters of gas has passed through the columns, each absorbing solution is drained into a 1-liter volumetric flask. The column is washed with successive portions of water until the combined absorbing solution and washings equal 1 liter.

The BF_3 reacts with the saline solution to form the BF_4^- anion. Since the conversion reaction is rather slow, a 2 M solution of calcium chloride is added to an aliquot from the column washings, and the temperature of the solution is held at 90°C for 1 hr on a steam bath. The reaction is as follows:¹⁴⁶



The resultant acid is then titrated with base to the methyl orange end point. The method is in routine use and has a standard deviation of 1%.

Determination of Low Concentrations of Carbon in Electron-Beam-Melted Niobium

J. E. Attrill

In general, little difficulty has been encountered in the determination of >200 ppm of carbon in niobium by use of the Leco induction furnace and conductometric carbon analyzer. Deviation between different laboratories on standard samples is usually about $\pm 10\%$. Considerable disagreement was observed, however, when carbon in a control sample of electron-beam-melted niobium was determined. The carbon content is considered to be of the order of 50 ppm in the electron-beam-melted metal. Despite the satisfactory precision of the results from each of the laboratories, the

¹⁴³R. F. Apple, "Silicon in Beryllium Oxide, Spectrophotometric Molybdenum Blue Method," Method Nos. 1 217712 and 9 00717712 (10-3-60), ORNL Master Analytical Manual; TID-7015, suppl 3.

¹⁴⁴R. F. Apple and J. C. White, *Separation and Colorimetric Determination of Trace Quantities of Mg in High-Purity BeO*, a paper presented at the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960.

¹⁴⁵R. F. Apple and J. C. White, "Separation and Colorimetric Determination of Trace Quantities of Lithium in High Purity Beryllium Oxide," to be submitted for publication in *Talanta*.

¹⁴⁶H. S. Booth and D. R. Martin, *Boron Trifluoride and Its Derivatives*, p 228, Wiley, New York, 1949.

carbon values reported from all the laboratories ranged from 25 to 100 ppm. The main differences in the procedures were the size of the test portion taken and the temperature at which it was burned. It was found that for lower temperatures the larger the test portion, the lower the carbon result. When an induction furnace is used, it is necessary to increase the amount of accelerator in order to increase the temperature. This in turn often increases unreasonably the blank of the determination (sometimes greater than the amount of carbon found in the sample itself).

In an attempt to overcome these difficulties, a method was developed by which a larger amount of accelerator (2 to 3 g) is burned until it is practically free of carbon. The molten mass is then cooled to about 300°C, and the test portion together with a small amount of accelerator is added to it. On reheating, the carbon in the test portion plus a small blank is obtained. The results of a number of analyses on 0.1- to 2.0-g test portions of the control sample were between 20 and 30 ppm of carbon. The cooling of the melt to room temperature before reheating it was useless because of the large amounts of oxides in the slag, which do not couple with an induction furnace and do not heat easily.

Work on the procedure is not yet complete. The Metallurgy Division is presently attempting to prepare pure niobium metal that contains a trace of carbon only, all present as C¹⁴, in order to study the concentration and distribution of carbon in such material.

Preparation of Organic Compounds

J. C. White H. L. Holsopple

Organic compounds were prepared and purified on request from the various research divisions, primarily the Chemistry and Chemical Technology Divisions. The compounds were either not readily available from commercial sources or available in impure form only and therefore required purification. A summary of this program follows.

Organophosphorus Compounds. – Several organophosphorus compounds were prepared and purified for use in extraction studies by the Chemical Development C Section of the Chemical Technology Division.

More than 4 kg of di(*sec*-butyl)phenylphosphonate was synthesized by reacting *sec*-butyl alcohol with benzene phosphorus oxydichloride in the presence of pyridine, according to the method reported by Kosolapoff.¹⁴⁷

A 262-g batch of monododecyl phosphoric acid was prepared from Dowsol-12 (a hydrolytic product of a 12-carbon alcohol–P₂O₅ reaction mixture) by converting a quantity of Dowsol-12 to its sodium salt, refluxing the salt with 6 M HCl, and then extracting the mixture with petroleum ether. Following several washes with phosphoric acid–water and 1:1 hydrochloric acid to remove all demonstrable iron, the material was partitioned with propylene glycol from which the monododecyl phosphoric acid was extracted into petroleum ether. The yield was 44%.

In addition, 133 g of *sec*-butyl phenylphosphonic acid and 280 g of capryl phenylphosphonic acid were purified by hydrolysis with ethanolamine followed by extraction into petroleum ether.

¹⁴⁷G. M. Kosolapoff, *Organophosphorus Compounds*, p 182, Wiley, New York, 1950.

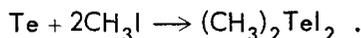
Nitrooctane, Decyl Nitrite, and Octyl Nitrate. – Three nitrogen-containing aliphatic hydrocarbons were synthesized at the request of the Chemical Development C Section of the Chemical Technology Division to compare their effects on the extraction performance of tributyl phosphate–Amsco 125-82 solutions with their effects on that of chemically degraded Amsco 125-82. Adaptations of standard methods were used to prepare nitrooctane, $C_8H_{17}NO_2$; ¹⁴⁸ decyl nitrite, $C_{10}H_{21}ONO$; ¹⁴⁹ and octyl nitrate, $C_8H_{17}ONO_2$. ¹⁵⁰ Although the purity of the compounds has not been established, the presence of major amounts of the groups characteristic of each of the three compounds named, with little or no cross-contamination, was shown by infrared spectroscopy.

Quaternary Ammonium Salts. – Small quantities (10 to 25 g) of each of the following quaternary ammonium salts were prepared: trimethylbenzylammonium chloride, trimethylbenzylammonium bromide, dimethylethanolbenzylammonium chloride, and dimethylethanolbenzylammonium bromide. The procedure, which is described elsewhere, ¹⁵¹ consists in reacting equivalent quantities of the appropriate tertiary amine with the required alkyl halide. The resulting salts were purified by crystallization from suitable solvents. The quaternary ammonium chlorides were a great deal more hygroscopic than the corresponding bromides.

Dimethyl Selenide. – At the request of the Chemical Separation of Isotopes Group of the Chemistry Division, 500 g of dimethyl selenide was prepared for use in the separation of the isotopes of boron. The procedure, described elsewhere, ¹⁵² consists in forming sodium selenide by the reaction of metallic selenium with sodium formaldehyde sulfoxylate in an aqueous solution of sodium hydroxide, after which dimethyl selenide is produced by reacting the sodium selenide with methyl iodide. A practically pure product was obtained which, after double distillation, had the analysis:

	Theoretical	Found
Carbon, %	22.0	21.9
Hydrogen, %	5.55	5.50
Selenium, %	72.4	72.6

Dimethyl Telluride. – At the request of the Chemical Separation of Isotopes Group of the Chemistry Division, 220 g of dimethyl telluride was synthesized for use in the separation of isotopes of boron. The procedure, to be described in detail in a formal report, consists in first forming dimethyltelluronium diiodide by the reaction of metallic tellurium with methyl iodide in a sealed container for 48 hr at 80°C:



¹⁴⁸N. Kornblum, B. Taub, and H. E. Ungnade, "The Reaction of Silver Nitrite with Primary Alkyl Halides," *J. Am. Chem. Soc.* **76**, 3209 (1954).

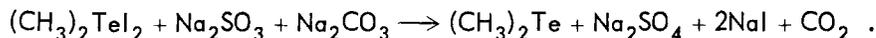
¹⁴⁹H. J. Lucas and D. Pressman, *Principles and Practice in Organic Chemistry*, Wiley, New York, 1949.

¹⁵⁰A. F. Ferris *et al.*, "Metathetical Reactions of Silver Salts in Solution. III. The Synthesis of Nitrate Esters," *J. Am. Chem. Soc.* **75**, 4078 (1953).

¹⁵¹H. L. Holsopple and J. C. White, *Synthesis of Some Quaternary Ammonium Salts*, ORNL CF-60-5-134 (May 27, 1960).

¹⁵²H. L. Holsopple and J. C. White, *Synthesis of Dimethyl Selenide*, ORNL CF-60-10-26 (Oct. 7, 1960).

The diiodide is extracted into chloroform and crystallized from this solvent, after which it is re-acted in an aqueous solution that contains stoichiometric quantities of sodium carbonate and hydrated sodium sulfite:



A brown oil was distilled from the mixture at 75°C. On redistillation of the brown oil, a yellow-orange oil was recovered as the distillate at 92 to 93°C. It had the obnoxious and persistent odor characteristic of tellurium compounds. The yield, based on the dimethyltelluronium diiodide used in the reaction, was 59%.

SPECTROCHEMICAL AND X-RAY ANALYSES (X-10 AND Y-12)

C. Feldman (X-10)

J. A. Norris (Y-12)

Chemical Preparation of Samples (X-10)

C. Feldman

P. V. Hoffman

C. A. Pritchard

M. Murray

W. R. Musick

Beryllium Oxide. – It was found that high-fired beryllium oxide, which is very difficult to dissolve, can be rendered soluble by fusion for 1 to 2 hr in ammonium fluoride at ~250°C.

Isolation of Rare-Earth Elements. – Microgram quantities of the rare-earth elements can be isolated from most other metals (e.g., from HRT fuel solutions) by coprecipitation on thorium oxalate in acid solution.¹⁵³ If the oxalate precipitate is then dissolved in 8 M nitric acid and the solution is passed through an anion exchange column, the thorium remains on the column and the rare-earth elements are eluted in carrier-free form.

Silicon in Copper. – The following procedure was developed for isolating traces of silicon from copper. The copper was dissolved in nitric acid. Excess perchloric acid was added, and the solution was evaporated to strong fumes of perchloric acid in order to dehydrate the silica. The solution was then filtered through a Millipore filter. The residue was fused with sodium carbonate, and the melt was dissolved in dilute phosphoric acid to convert the silica to silicophosphate. This solution was analyzed by the porous-cup method; synthetic solutions prepared similarly were used for comparison.

Spark Solution Analysis (X-10)

C. Feldman

The precision obtained with graphite porous-cup electrodes varies among lots of electrodes, occasional lots being unacceptable. Porous cups made of carbon gave excellent precision ($\sigma = 1.86\%$) in one case,¹⁵⁴ but no general study of their behavior had been made. Such a study was

¹⁵³M. W. Lerner and L. J. Pinto, "Separation of Rare Earths from Beryllium, Magnesium, Zirconium, Titanium, Uranium, and Stainless Steel," *Anal. Chem.* 31, 549 (1959).

¹⁵⁴R. O. Scott and A. M. Ure, "The Determination of Magnesium in Solution by Direct Photometry," *Analyst* 83, 561 (1958).

therefore undertaken along two lines. First, the results obtained from electrodes fabricated by several shops from different lots of carbon were compared. The spectral line pair used for comparison (B 2497.73/Co 2582.24) was chosen because it constitutes a rather poor match with regard to spectral excitation behavior and because it could be expected to show no better reproducibility than the line pairs usually selected for use in analysis. The results reported in Table 18 were obtained with an Applied Research Laboratories (ARL) Industrial Research Quantometer. Each reading was corrected for dark current but not for spectral background. The approximate line/background ratio was 12/1 for both lines. The weighted average deviation for NCC (National Carbon Company) electrodes is 2.2%; the corresponding figure for UCP (United Carbon Products Company) electrodes is 4.3%. Two successive exposures were made with each electrode, and the ratios were calculated separately. The figures given in Table 18 include both types of figures. In all cases, however, the intensity ratios obtained from the second exposures showed better interelectrode agreement than did those obtained from the first exposure; therefore, the use of a 60-sec pre-spark could be expected to give precision better than that listed.

Table 18. Precision of Line-Intensity Ratios Obtained with Carbon Porous-Cup Electrodes

An arc/spark line pair was used

Manufacturer*	Manufacturer's Lot No.	Fabricator	Number of Exposures	Average Deviation of Ratio
				$\frac{\text{B 2497.73} + \text{background}}{\text{Co 2582.24} + \text{background}}$ (%)
NCC	48	ORNL-Shop 1	18	1.8
UCP	3909	UCP	26	4.1
UCP	3926	UCP	16	6.8
UCP	0218	UCP	16	2.2
NCC	48	ORNL-Shop 2	63	2.3
NCC	41A	NCC	22	2.3

*NCC = National Carbon Co.; UCP = United Carbon Products Co.

Since the NCC carbon porous-cup electrodes appeared to give more reproducible results than the UCP electrodes, additional tests were made with NCC electrodes. In these tests, the lines used were all arc lines having similar excitation potentials. Line/background ratios were approximately 5/1. The average deviations for 18 exposures when the ratio of the intensity of each line to the intensity of each of the others was measured are given in Table 19. The mean average deviation for all arc/arc line pairs in this experiment was 1.5%.

Table 19. Precision of Line-Intensity Ratios Obtained with Carbon Porous-Cup Electrodes

Various arc/arc line pairs used

Lines*	Fe 3021 (4.09)	Cu 3274 (3.78)	Ni 3415 (3.65)	V 3184 (3.90)	Al 3082 (4.02)
	Average Deviation (%)				
Fe 3021 (4.09)		2.4	0.9	1.1	1.4
Cu 3274 (3.78)	2.4		1.2	1.8	2.2
Ni 3415 (3.65)	0.9	1.2		1.4	1.8
V 3184 (3.90)	1.1	1.8	1.4		1.2
Al 3082 (4.02)	1.4	2.2	1.8	1.2	

*Figure in parentheses is excitation potential of line in volts.

Retention of Boron During Evaporation of Acid Solutions (X-10)

C. Feldman

Preliminary experiments¹⁵⁵ have shown that 100 μg of boron (as borate) in hydrochloric or hydrochloric-hydrofluoric acid can be retained quantitatively during the evaporation of the solution provided a substantial excess of mannitol is present. This work has now been extended to include the range from 50 to 1000 μg of boron and the range of mannitol/boron mole ratios from 0 to 39.

Table 20 shows the per cent recovery of boron after the evaporation on a steam bath of 100 ml of 30 vol % hydrochloric acid solutions that had the indicated composition. Recoveries were

¹⁵⁵C. Feldman and P. F. Hoffman, *Retention of Boron with Mannitol During the Evaporation of Acid and Acid-Fluoride Solutions*, ORNL CF-59-11-87 (Nov. 17, 1959).

Table 20. Recovery of Boron from Steam-Bath Evaporation of 1:2 HCl-Mannitol-H₃BO₃ Solutions

Volume = 100 ml

Mole Ratio, Mannitol/Boron	Boron Taken (mg)	Mannitol Present (mg)	Boron Recovered (%)*
0	0.500	0	1.2 ₀
0.6	0.500	5.0	72
1.2	0.500	10.0	82
2.4	0.500	20.0	91
3.0	1.000	50.0	94
4.8	0.500	40.0	95
6.0	0.500	50.0	95
14.9	0.200	40.0	99

*Average deviation of measurement: $\pm 2.3\%$ of amount present.

measured by emission spectrochemical methods (carbon porous-cup electrodes); an ARL Industrial Research Quantometer was used. These results indicate that loss of boron from hydrochloric acid solutions can be prevented by the addition of a 10 to 15 molar excess of mannitol.

In preliminary experiments with 0.5 and 10.0 vol % nitric acid solutions that contained 0.500 mg of boron at a mannitol/boron mole ratio of 9.6, the boron was recovered completely.

X-Ray Absorption-Edge Analysis (X-10)

H. W. Dunn

The stability of the instrumentation used in the x-ray absorption-edge method has been improved by the installation of a cooling system in which water recirculates through copper tubing. Procedures essentially similar to those used for zirconium¹⁵⁶ were developed for molybdenum, hafnium, and tin.

The hypothesis that the x-ray absorption-edge method is independent of matrix effects rests on the assumption that the slope of the mass absorption vs wavelength curve of a given element at a given wavelength does not depend on the atomic number of the element. This assumption has been found valid at the wavelength of the K_{α} absorption edge of zirconium for matrix elements between nickel ($Z = 28$) and tin ($Z = 50$). Some variation of the slope with Z at this wavelength has been found beyond these limits.

In determining chemical concentrations by the x-ray absorption-edge method, the sample characteristic that is sought is the vertical height of the edge at the critical absorption wavelength (i.e., I_{eU}/I_{eL} in Fig. 15). This height cannot be measured directly, however, because two independent intensity measurements cannot be made at the same wavelength and because the observed edge, in any case, is broadened by instrumental characteristics. It is therefore necessary to take intensity readings, I_{λ_1} and I_{λ_2} , at adjacent wavelengths, λ_1 and λ_2 , and to extrapolate these readings to the absorption edge to give I_{eU} and I_{eL} . The extrapolation functions that have been found best for this purpose are

$$\log I_{eU} = m_1 \log I_{\lambda_1} + b_1$$

and

$$\log I_{eL} = m_2 \log I_{\lambda_2} + b_2$$

where I_{eU} and I_{eL} are the intensities at the upper and lower extremes of the absorption edge (see Fig. 15), I_{λ_1} and I_{λ_2} are the intensities observed at the wavelengths indicated, and m_1 , m_2 , b_1 , and b_2 are empirical constants.

Once the parameters m_1 , m_2 , b_1 , and b_2 have been measured for a given system, observed values of I_{λ_1} and I_{λ_2} can be extrapolated to give I_{eU} and I_{eL} . The chemical concentration curve

¹⁵⁶H. W. Dunn, "X-Ray Absorption-Edge Analysis," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 63-65.

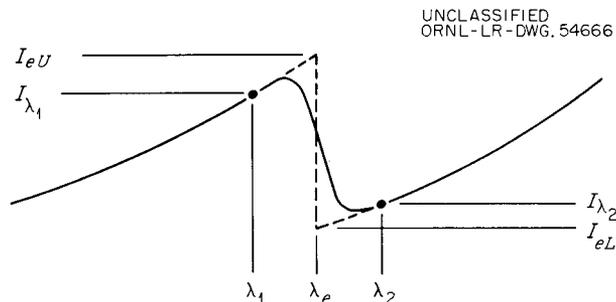


Fig. 15. Schematic Diagram of Variation of Transmitted X-Ray Intensity Near an Absorption Edge. Solid curve = observed variation; dashed curve = theoretical variation; λ_e = theoretical wavelength of edge.

is then expressed in the form

$$C \approx \frac{2.303}{l \Delta \mu_m} \left(\log \frac{I_{eU}}{I_{eL}} \right),$$

where C is the concentration of the element having an absorption edge between λ_1 and λ_2 , l is the thickness of the absorption cell, and $\Delta \mu_m$ is the increase in the bulk absorption coefficient at the absorption edge.

Preliminary results indicate that this method of calculation will permit greater sensitivity than does the previous procedure¹⁵⁶ and will be equally precise.

Tissue Analysis (X-10)

S. R. Koirtiyohann C. Feldman

A new laboratory has been established in which the drying, ashing, and preparation of human-tissue specimens for spectrographic analysis are done. All tissue preparation for the ORNL Health Physics Division's "Trace Elements in Human Tissue" program is now done in this laboratory. An inventory of ~5400 samples on hand has been completed.

Development work has continued along several lines as follows.

Reduction of Test-Portion Size. – In order to obtain maximum efficiency in ashing, the test portion of tissue sample actually ignited should be as small as is consistent with adequate sampling. Attempts to use an Osterizer blender to pulverize dried tissue were unsuccessful with some tissues, and an impact shaker (Spex Mixer Mill) is now being used. In this device, as adapted, the dried tissue is placed in the inner chamber of a double-walled polyethylene container, along with a $\frac{1}{4}$ -in.-diam tungsten ball. The chamber has linen-base laminated Bakelite end plates. As the tissue is pulverized, the pulverized material sifts through the holes in the inner wall, thus exposing the remaining tissue to the full impact of the tungsten ball. This pulverizing procedure appears to give a material satisfactory for ashing.

Cross-Contamination. – A test was made to determine whether the routine dishwashing procedure is adequate to prevent cross-contamination of samples. A normal liver sample was ashed in a silica dish. The ash was removed mechanically, and the dish was washed by the usual procedure (i.e., live-steam dishwasher, 2 hr in 15 vol % concd HNO_3 –85 vol % concd H_2SO_4 , overnight in Versene solution, rinsing). Ten grams of ammonium bisulfate was then fused in the dish (covered tightly with a watch glass) for 1 hr at 330°C . The watch glass was then removed, the ammonium bisulfate was evaporated away, and any residue present was dissolved in dilute acid. Spectrographic analysis of the solution of the residue showed no evidence of major or minor components of liver ash above blank levels. It thus appears that if any trace of the previous sample does continue to adhere to the vessel after it has been washed, it adheres too tightly to be removed by ammonium bisulfate fusion. The danger of cross-contamination via ignition dishes at levels of interest in this program is therefore considered to be small.

Sensitivity and Precision. – In direct spectrometric analysis, both sensitivity and precision are limited by the variation of the background from one exposure to the next. Considerable effort was therefore devoted to controlling this factor. Variation in matrix composition from one type of tissue to the next has been minimized by diluting samples with a buffer mixture. Variation due to arc turbulence has been minimized by use of the Stallwood jet (with helium and oxygen) and carbon electrodes and by undercutting the lower electrode (anode) immediately below the lip of the crater. The relative standard deviations for the determinations of 20 elements ranged from 2 to 8%; the mean relative standard deviation is 4.8%.

The temperature of the spectrometer also varies; this variation causes the spectral lines to move with respect to the receiving slits. Comparatively wide receiving slits therefore must be used. Unwanted background is thereby admitted to the detector, thus lowering the signal-to-noise ratio. The less the temperature fluctuation, the narrower the receiving slits can be made, and the greater the line-to-background ratio (and thus the real sensitivity limit) will be. The spectrometer shell was lined with a $\frac{1}{2}$ -in.-thick layer of polyurethane foam. This thermal insulation has reduced the apparent wandering of line positions by a factor of 5 to 10, thus making it possible to use narrower receiving slits. A set of $38\text{-}\mu$ -width slits will be installed in the near future; this installation is expected to improve line/background ratio and sensitivity by a factor of 2 to 3.

Analog Computer for Direct-Reading Spectrometer (Y-12)

R. E. Weekley J. A. Norris

An analog computer has been designed and constructed; it will eliminate the tedious and time-consuming process of manual data reduction. This computer accepts the independent-variable input information in parallel from 16 Baird Direct Reader channels, sequentially solves the equation that relates condenser discharge time to element concentration for each channel, and logs both channel identification and corresponding element concentration for all 16 channels in less than 1 min. All

operations are carried out automatically on command from the pre-existing Baird readout instrumentation.

With the advent of the automatic spectral-background-compensation system described previously,¹⁵⁷ it has become possible to achieve analytical working curves that are linear, in semi-logarithmic coordinates, over the entire working range of interest. Linearizing the analytical working curve makes it fully practicable to automate the entire data logging and reduction process. Thus it becomes possible, with relatively simple and economical instrumentation, to provide for any desired value of the parameters in the linear equation that relates condenser discharge time to element concentration, to make easily and rapidly any desired changes in these parameter values, to solve sequentially the resulting equations if values for the independent variable are available, and to print out on paper tape the resulting element-concentration values together with suitable identification. All operations are carried out automatically and rapidly.

The computer described herein accepts input information in the form of a voltage pulse on each Baird channel whose width is equal to the condenser discharge time. These pulses are used to gate linear-voltage ramp-function generators whose stored voltage outputs are numerically equal to the corresponding condenser-discharge time in seconds. These ramp outputs, which are independent variables, are then introduced sequentially into the computing section, in which the proper values of line slope and intercept for each channel have been preset. The computer outputs are fed sequentially to a digital voltmeter and printer, which automatically records directly both channel identification and corresponding element concentration.

This computer is now in the final stages of completion and checkout. By eliminating economically all manual data logging and reduction, this computer will greatly expedite both the routine service functions of the Paschen-Runge spectrograph and the extensive research programs being carried on in conjunction with this instrument.

STATISTICAL DEVELOPMENT (Y-12)

H. P. House R. L. McCutchen

Nearly 200 requests for assistance with individual statistical problems were received from this and other ORNL divisions. A sequential-sampling and -testing plan¹⁵⁸ for evaluating the oxygen-to-uranium ratio in batches of UO₂ pellets was designed. Specifications for the UO₂ pellets were reviewed, and changes were suggested as a means of decreasing the unit cost of this material. The computing and data-handling requirements for Department 4270 were estimated, and the results were reported¹⁵⁹ for inclusion in the summary of the plant-wide survey that was being made. Additional experiments were designed in connection with the investigation of sources of variability

¹⁵⁷J. A. Norris and O. B. Rudolph, "Electronic Background-Compensating System for Photoelectric Spectrometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 65-66.

¹⁵⁸"Sequential Plan for Sampling and Testing Batches of UO₂ Pellets," *GCR Project Quart. Progr. Rept. June 30, 1960*, ORNL-2964, pp 216-19.

¹⁵⁹R. L. McCutchen, *Computing and Data Handling Survey*, memorandum to R. J. Klein (Mar. 8, 1960).

in spectrographic analysis.¹⁶⁰ Youden's Graphical Procedure¹⁶¹ was explained in several cases and was specifically recommended for use in evaluating the results obtained in the cooperative analysis of BeO samples¹⁶² in different laboratories. A simple but tentative method was devised for locating the best-fitting straight line when calibration data are arranged in class intervals (i.e., cells) and the relationship between the two parameters is known to be linear.¹⁶³ In this particular problem, the data were plotted with the cell midpoints as ordinates and the normal deviates (i.e., percentage of values over a given cell midpoint) as abscissas. In addition, general information about the use of established statistical techniques was supplied in connection with a variety of individual problems.

The following proposed ASTM methods were reviewed for ASTM Subcommittee II of E-2: "Suggested Practices for the Use of Statistical Methods in Spectrochemical Methods," "Suggested Practices for Establishing and Controlling Spectrochemical Analytical Curves," and "Suggested Practices for Flame Photometric Methods of Spectrochemical Analysis." Recommendations for revising the methods were sent to Subcommittee II for consideration.

THERMAL BREEDER REACTOR PROJECTS ANALYTICAL CHEMISTRY LABORATORY (Y-12)

H. E. Zittel

Conductometric Titration of Free Acid in Solutions of Uranyl Sulfate

G. Goldstein D. L. Manning

Free acid in impure solutions of uranyl sulfate under test as simulated fuels for the HRT cannot be titrated by conventional means because of the interference of uranyl and other easily hydrolyzable cations. A modification of a conductometric method suggested by Pepkowitz, Sabol, and Dutina¹⁶⁴ has been used successfully. The sulfuric acid is titrated conductometrically with sodium hydroxide solution after the addition of sodium fluoride to form slightly dissociated fluoride salts (or complexes) with uranyl and other hydrolyzable cations. Sodium fluoride in excess over that required to react with the hydrolyzable ions is avoided because it reacts with sulfuric acid to form weakly ionized hydrofluoric acid, which obscures the end point. By the use of electrodes of large surface area, the end point can be determined readily with a conventional conductance bridge. The precision of this method was determined by titrating a series of simulated HRT fuel solutions that contained 0.04 meq of sulfuric acid and also 6 mg of uranium, 800 μ g of copper, and

¹⁶⁰J. A. Norris and R. L. McCutchen, *Investigation of Spectrochemical Solution - Methods of Analysis*, ORNL-2927 (Apr. 25, 1960).

¹⁶¹R. L. McCutchen, *Statistics for Spectrographers*, a paper presented at 8th Annual Spectroscopy Seminar, University of Florida, Gainesville, Jan. 6-8, 1960.

¹⁶²J. C. White and J. A. Norris, *Report of Trip to Atlantic City, N.J., June 29, 1960*, ORNL CF-60-8-137 (Aug. 31, 1960).

¹⁶³R. L. McCutchen, letter to E. F. Taylor, The Martin Co., Baltimore, Md. (Oct. 10, 1960).

¹⁶⁴L. P. Pepkowitz, W. W. Sabol, and D. Dutina, "Determination of Free Acid in the Presence of Hydrolyzable Ions," *Anal. Chem.* 24, 1956 (1952).

400 μg of nickel (each as the sulfate) per milliliter; the relative standard deviation was less than 1%. The method is easily adaptable to remotely controlled operations.

Indirect Determination of Sulfate in Solutions of Uranyl Sulfate by Nonaqueous Titrimetry

G. Goldstein D. L. Manning

A nonaqueous titrimetric method was developed for the rapid determination of 1 to 6 mg of sulfate in the presence of such substances as UO_2^{2+} , Fe^{3+} , and Zr^{4+} , which interfere in conventional methods for sulfate. The sulfate is precipitated in an acetic acid solution by the addition of a known amount (excess) of barium acetate. Since barium acetate is a moderately strong base in an acetic acid medium, the excess is titrated either potentiometrically or conductometrically with a strong acid, such as perchloric acid. Sulfate is then computed from the difference between the amount of barium acetate added and that found by titration. Most monovalent and divalent cations except UO_2^{2+} and Cu^{2+} interfere. Tri- and tetravalent cations do not interfere. Of the anions, nitrate, phosphate, and fluoride may interfere, depending upon the associated cation.

The method was applied specifically to the determination of total sulfate in solutions of reactor fuels that contained uranyl and copper sulfates, sulfuric acid, and also corrosion products of stainless steel as minor components. A relative standard deviation better than 1% was obtained in replicate titrations. The results were in good agreement with known values for synthetic samples and with values obtained by an independent method for actual samples.

A paper that describes the method has been accepted for publication in *Analytical Chemistry*.

Indirect Polarographic Determination of Thorium

D. L. Manning

An indirect polarographic method for the determination of microgram quantities of thorium was studied by means of the ORNL model Q-1673 derivative polarograph. The method is based on the reaction of thorium with lead ethylenediaminetetraacetate at a pH of 3.5 and the determination of the liberated lead(II) polarographically at a half-wave potential of -0.45 v vs the S.C.E. Thorium in the concentration range from 2 to 16 $\mu\text{g}/\text{ml}$ can be determined by this method with a relative standard deviation of about 6%. Flaschka, Khalafalla, and Sadek¹⁶⁵ determined milligram quantities of thorium by a similar technique. However, they presented no data relative to possible interferences.

The following possible interferences were tested: uranium(VI), nickel(II), copper(II), chromium(VI), iron(III), and molybdenum(VI). Copper(II), nickel(II), and iron(III) must be absent because they appear to displace lead from its ethylenediaminetetraacetate complex in the same manner as does thorium. Uranium(VI), chromium(VI), and molybdenum(VI) constitute a second type of interference; these elements are reduced polarographically prior to lead. Consequently, the lead wave must be measured on top of a diffusion-current wave recorded prior to the lead wave.

¹⁶⁵H. Flaschka, S. Khalafalla, and F. Sadek, "Über die Verwendung komplexchemischer Verdrängungsreaktionen bei polarographischen Analysen," *Z. anal. Chem.* 156, 169 (1957).

The tolerance level therefore depends largely on the ability of the instrument to resolve the polarographic wave of lead under these conditions. With the ORNL model Q-1673 polarograph, 270, 80, and 10 μg of uranium(VI), chromium(VI), and molybdenum(VI), respectively, can be present without interfering with the indirect measurement of 20 μg of thorium.

Amperometric Titration of Thorium

G. Goldstein D. L. Manning

A method was developed for the determination of thorium in molten-salt reactor fuels, which consist of the fluorides of lithium, beryllium, thorium, uranium, and zirconium. It is applicable to remotely controlled operations. Thorium is titrated amperometrically with disodium ethylenediaminetetraacetate in a deaerated acetate-buffered medium at pH 4.5. Iron(II) is used as the indicator ion. The indicator electrode is platinum foil to which is applied a potential of +0.4 v vs the S.C.E. Iron(II) is not oxidized at this potential; however, ferrous ethylenediaminetetraacetate, which forms after the titration of thorium is complete, is oxidized, and the resulting current is measured. A graph is constructed of current vs the volume of titrant, and the end point is established by extrapolating the two lines of different slopes to a point of intersection. In this manner, milligram quantities of thorium can be titrated over the pH range from 2.5 to 4.5 with a relative standard deviation of less than 1%. At pH values below 2.5, the ferrous ethylenediaminetetraacetate complex apparently does not form since no change in current is observed beyond the thorium equivalence point. At pH values greater than 4.5, thorium tends to hydrolyze.

Zinc(II), Ni^{2+} , Cu^{2+} , Fe^{3+} , Co^{2+} , and VO^{2+} in concentrations equimolar to that of thorium interfere in the determination of thorium. Cerium(III), Cr^{3+} , and Al^{3+} interfere at pH 4.5 but not at pH 2.5. Zirconium interferes at pH 2.5 by forming a precipitate when disodium ethylenediaminetetraacetate is added but not at pH 4.5. Lithium(I), UO_2^{2+} , Mn^{2+} , and Mg^{2+} do not interfere at either pH. A mole ratio of uranium and/or zirconium to thorium of at least 5:1 can be tolerated at pH 4.5. Chloride, nitrate, and sulfate in molar concentrations ten times that of thorium do not interfere. At pH 4.5, fluoride in concentration equimolar to that of thorium can be tolerated. Phosphate interferes seriously.

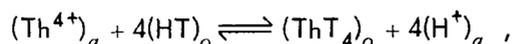
Separation of Macro Quantities of Thorium with 2-Thenoyltrifluoroacetone

T. C. Rains N. M. Ferguson

Of methods reported for the separation of thorium from the rare-earth¹⁶⁶ and alkaline-earth elements, extraction with 2-thenoyltrifluoroacetone in organic solvents is satisfactory for micro quantities of thorium. Extraction of macro quantities is extremely slow, and difficulty is encountered because of the formation of basic precipitates of 2-thenoyltrifluoroacetone when attempts are made to control the pH. These difficulties have been overcome by use of an acetate-buffered solution to control the acidity during the extraction.

¹⁶⁶H. J. Bronaugh and J. F. Suttle, *Chelation of the Rare Earth Elements as a Function of pH Using Thenoyltrifluoroacetone*, LA-1561 (June 1953).

For test portions that contain 1 to 5 g of thorium, the thorium is extracted into a 0.5 or 1 M solution of 2-thenoyltrifluoroacetone in chloroform at pH 1.2. Since hydrogen ions are released during the extraction, the pH must be controlled for the extraction to be efficient. The over-all reaction is:



where HT refers to 2-thenoyltrifluoroacetone and the subscripts *a* and *o* refer to the aqueous and organic phase, respectively. By the addition of an ammonium acetate solution (pH 4.3 ± 0.2) during the extraction, the pH can be controlled without localized hydrolysis of the 2-thenoyltrifluoroacetone, and the acetate enhances the extraction of the thorium. By the use of this procedure, 5 g of thorium was extracted within 30 min; three 40-ml portions of the reagent were used.

After the extraction of the thorium into the organic phase, the aqueous phase can be used directly without further treatment for the flame photometric determination of the alkaline-earth metals. If the acetate interferes in any subsequent determination, it can be removed by adding aqua regia and heating the solution.

Determination of Osmium in Molybdenite

G. Goldstein D. L. Manning

Osmium may be present in molybdenite ores as a result of the beta decay of Re^{187} , which is present in natural molybdenite. Since the half-life of Re^{187} is known, the age of a molybdenite deposit can be calculated from the concentrations of rhenium and osmium in the ore. In conjunction with a study of the age of molybdenite ores, a procedure was developed for the determination of osmium. The molybdenite is decomposed by heating the sample in a 50 vol % concd HNO_3 -10 vol % concd H_2SO_4 solution. The osmium is oxidized to the tetroxide, which is distilled into 1 M H_2SO_4 . After the oxidation with potassium permanganate of the lower oxides of nitrogen (NO , NO_2 , etc.), which accompany the osmium tetroxide in the distillation, the osmium tetroxide is extracted into chloroform and is determined by the spectrophotometric diphenylcarbazide method.¹⁶⁷ By means of Os^{191} tracer, it was established that approximately 90% of the osmium in the trap was subsequently extracted, giving an over-all recovery of approximately 85%.

Five molybdenite concentrates were analyzed. In each case the osmium concentration was found to be less than 5 ppm. Two samples of flue dust that contained a relatively high concentration of rhenium were found to contain 6 and 10 ppm of osmium.

¹⁶⁷G. Goldstein and O. Menis, *Spectrophotometric Determination of Microgram Quantities of Osmium with Diphenylcarbazide*, ORNL CF-59-7-16 (June 2, 1959).

Spectrophotometric Titration of Samarium and Neodymium

F. L. Layton D. L. Manning

For the purpose of determining both samarium and neodymium in their mixtures by means of simultaneous equations based on extraction data,¹⁶⁸ it is essential that an accurate and precise method be used for the determination of the total of these rare-earth elements that remains in the aqueous phase. The method of chelometric titration as suggested from the work of Fritz, Oliver, and Pietrzyk¹⁶⁹ was used successfully. The rare-earth elements are titrated at pH 5.5 to 6.0 with a solution of disodium ethylenediaminetetraacetate. The end point is detected spectrophotometrically at 570 m μ by means of trisodium 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid (Arsenazo or Neothorin) as the indicator. In this respect, the method differs from that of Fritz, Oliver, and Pietrzyk, who established the end points visually. Two to ten milligrams of either samarium or neodymium, or of both, in a titration volume of approximately 60 ml can be determined with a relative standard deviation of 0.5%. For smaller quantities (0.5 to 1 mg), however, the relative standard deviation is about 1.5%.

Coulometry of Molybdenum in Nitrilotriacetic Acid

D. L. Manning

The derivative polarographic method for the determination of molybdenum¹⁷⁰ was studied further. Emphasis was placed on elucidating the oxidation states of molybdenum responsible for the various polarographic waves in nitrilotriacetic acid. On the basis of data obtained by coulometric measurements at a controlled potential in conjunction with absorbancy measurements of the molybdenum(V)-nitrilotriacetic acid species at 297 m μ , it is postulated that the polarographic waves which occur at half-wave potentials of -0.22, -0.33, and -0.48 v vs the S.C.E. are due to the reduction of molybdenum(VI)-nitrilotriacetic acid species, whereas the wave at -0.64 v is due to the reduction of molybdenum(V) at the D.M.E. It is presumed that molybdenum(V) is reduced to molybdenum(III).

Flame Photometric Determination of Rare-Earth Elements

T. C. Rains

The study was continued on the extraction and flame photometric determination of the rare-earth elements.¹⁷¹ Optimum conditions were established for the extraction of several of these elements into a 0.1 M solution of thenoyltrifluoroacetone in a mixture of 4-methyl-2-pentanone and

¹⁶⁸H. R. Hunt and O. Menis, "Simultaneous Extraction and Determination of Neodymium and Samarium," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 73-74.

¹⁶⁹J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, "Chelometric Titrations Using an Azoarsonic Acid Indicator," *Anal. Chem.* **30**, 1111 (1958).

¹⁷⁰R. G. Ball and D. L. Manning, "Polarographic Determination of Molybdenum," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 71.

¹⁷¹T. C. Rains, "Evaluation of Flame Photometry for the Determination of Rare-Earth Elements," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, pp 69-70.

cyclohexane and their subsequent flame photometric determination in the extract. Mutual effects of flame interferences were evaluated. Extraction difficulties encountered with 4-methyl-2-pentanone as a result of emulsification were eliminated by the use of a 3:1 volume mixture of 4-methyl-2-pentanone and cyclohexane. This solvent gives the same distribution ratio reported previously¹⁷² without loss of radiant intensity.

Effect of Anions on the Flame Radiant Intensity of Calcium

T. C. Rains

The relative effects of various anions on the radiant intensity of calcium were studied; both oxyacetylene and oxyhydrogen flames were used. It was established that interferences of the anions tested are less with an oxyacetylene than with an oxyhydrogen flame (see Fig. 16A and B). When the oxyacetylene flame is used, nitrate has no significant effect on the radiant intensity of calcium, whereas perchlorate at concentrations up to approximately 1 M enhances the radiant intensity. The effect of phosphate depends on the type of fuel used and on the phosphate concentration. Phosphoric acid at the higher concentrations enhances the radiant intensity of calcium in an oxyacetylene flame, whereas, if phosphate is added as diammonium hydrogen phosphate, the usual suppression of radiant intensity is observed. The suppression is far greater if an oxyhydrogen flame is used because of the low temperature of the flame.

Several methods proposed for preventing the interference of many anions in the flame photometric determination of calcium¹⁷³⁻⁷⁵ were studied. It was established that if the mole ratio of phosphate to calcium is less than 4:1, phosphate has no effect on the radiant intensity of calcium. Further, if a 20% ethylene glycol-water medium is used, 1 M phosphate (as phosphoric acid) does not interfere. If, however, the phosphate is added as the diammonium hydrogen salt, the radiant intensity is suppressed approximately 20%. The interference can be largely eliminated by adding nitric acid until the pH is within the range from 0.5 to 1 (see Fig. 16C). Addition of ethylene glycol was observed not only to eliminate the effect of phosphate on the radiant intensity of calcium but to exert a similar effect on several other cations.

Apparatus for Differential Thermal Analysis

C. M. Boyd

An apparatus for differential thermal analysis has been assembled. This apparatus consists of an electric furnace that can be heated to 1000°C, a "stepless" furnace controller for achieving

¹⁷²T. C. Rains, "Separation of Aluminum and Lanthanum from Interferences," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1958*, ORNL-2662, pp 24-26.

¹⁷³M. J. Pro and A. P. Mathers, "Metallic Elements in Wine by Flame Photometry," *J. Assoc. Offic. Agr. Chemists* **37**, 945 (1954).

¹⁷⁴A. C. West and W. D. Cooke, "Elimination of Anion Interferences in Flame Spectroscopy. Use of (Ethylenedinitrilo)tetraacetic Acid," *Anal. Chem.* **32**, 1471 (1960).

¹⁷⁵J. I. Dinnin, "Releasing Effects in Flame Photometry. Determination of Calcium," *Anal. Chem.* **32**, 1475 (1960).

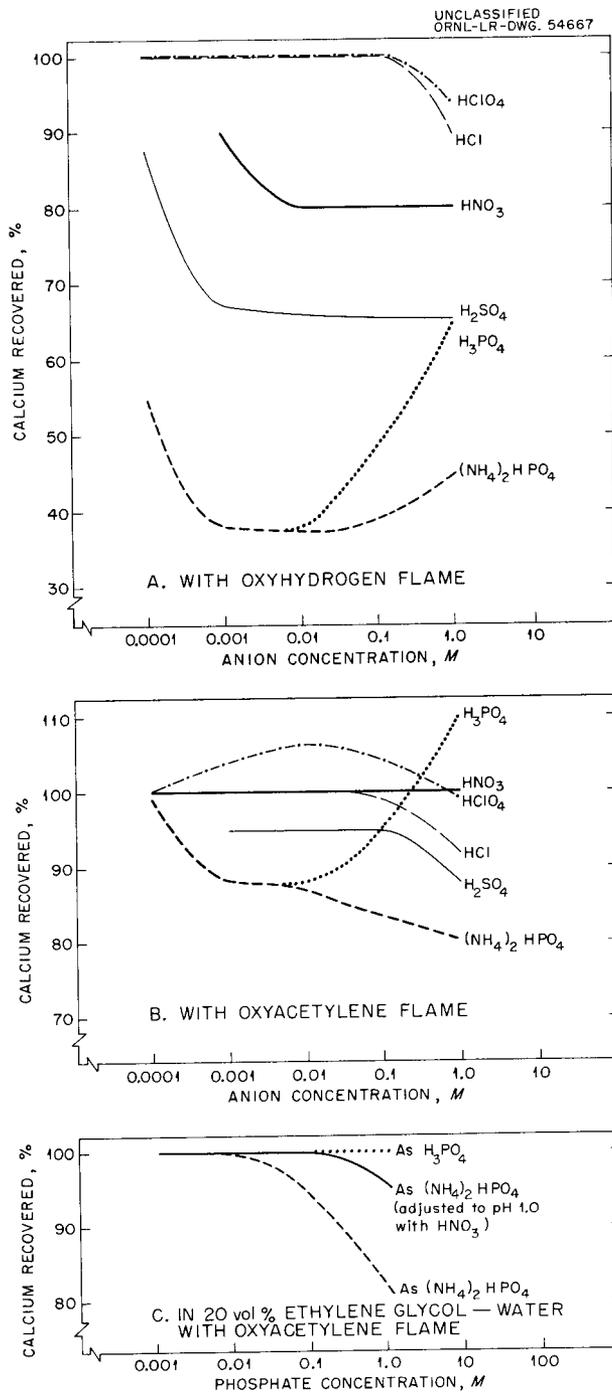


Fig. 16. Effects of Various Anions on the Flame Photometric Determination of Calcium. Calcium concentration, 10 $\mu\text{g}/\text{ml}$; wavelength, 422.7 $\text{m}\mu$; flame photometer, modified Beckman model DU.

linear increase in temperature, sample blocks of nickel and stainless steel, thermocouples, a voltage amplifier for the differential thermocouple, and an X-Y recorder. The response of the apparatus to changes in temperature that result from endothermic and exothermic processes was determined by use of silicon dioxide and sodium nitrate as standards and aluminum oxide as the reference material. The differential thermal analysis technique, together with thermogravimetric methods of analysis, was used to detect various effects of gamma radiation on the alkali-metal bromates. In general, the irradiated samples exhibited lower melting points and more rapid decomposition rates than did the corresponding nonirradiated compounds.

SERVICE ANALYSES

A summary of the service analyses made by the laboratories of the Analytical Chemistry Division is given in Table 21.

QUALITY CONTROL (X-10 AND Y-12)

R. L. McCutchen (Y-12) B. J. Ginocchio (X-10)

The 85 Statistical Quality Control (SQC) programs, operative in nine service laboratories of the Analytical Chemistry Division, were curtailed ~50% in order to compensate for revisions in the projects of other ORNL divisions and for the subsequent reduction in the analytical services required by those divisions. About 4300 results were obtained for control purposes in 1960, as compared with some 8300 in 1959.^{1,2} The distribution of the ~4300 control results, by laboratory, is shown in Table 22; a similar compilation, by analysis, is presented in Table 23.

With one exception, the quality of the work of these laboratories equaled or exceeded that attained in 1959 (see Table 22). However, a new quality level of 95% was achieved for the Division; in Table 22 this is designated as the average quality level.

GENERAL SERVICES (Y-12)

L. J. Brady

Counting Laboratory

J. M. Peele

The Counting Laboratory processed about 3800 samples and reported 5340 results. Over 95% of the samples were from the Chemical Technology Division and consisted of nitric acid solutions and organic solutions that contained either an organonitrogen or an organophosphorus extractant. The samples were derived from several solvent-extraction processes which include Purex-type decontamination experiments on simulated reactor waste solution; the extraction of zirconium-niobium tracer with tributyl phosphate; the selective extraction of the transuranium elements; the separation by selective extraction of uranium, neptunium, and technetium from Paducah leach solutions; and the separation of radioactive strontium and rare-earth elements from reactor waste solutions. Samples from the strontium separation experiments accounted for one-third of the results reported. Samples from the Reactor Chemistry Division, which accounted for 4% of the analyses, consisted of mixtures of fluoride salts that contained a radioactive tracer. These samples were counted on a well-type scintillation spectrometer for gross gamma activity.

A variety of methods were used. Plutonium, americium, and curium were determined by alpha counting. Calcium, rare-earth elements, technetium, and gross beta activity were determined by

¹R. L. McCutchen, B. J. Ginocchio, and C. D. Susano, "Quality Control," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959*, ORNL-2866, p 41.

²M. T. Kelley, *Statistical Quality Control Report, Analytical Chemistry Division, January through September, 1960*, ORNL CF-60-10-129 (Oct. 15, 1960).

Table 22. Distribution by Laboratory of Control Results for
October 1959 Through September 1960

Laboratory	Number of Control Results		Quality Level (%) ^a	
	Total	Outside Fixed Limits	1959	1960
Pilot Plant Control	667 ^b	34	89	95
Reactor Analyses	426 ^b	19	84	96
High-Alpha Analytical	34 ^c	6	75	82
Special Analyses	769	67	95	91
Process-Development Analytical	1324	58	95	96
Reactor Projects Analytical	170	0	99	100
Thermal Breeder Reactor Project Analytical Chemistry	353	5	99	99
Raw Materials	488	45	96	98
Miscellaneous Analyses	84	2	96	98
Total	4315	236	Av 92	Av 95

^aPer cent of control data inside fixed limits.

^bOctober 1959 through January 1960.

^cOctober through December 1959.

beta counting. Gamma counting was used to determine Ru, Zr, Nb, Am, and gross gamma activity. Approximately half the analyses were made by means of nonradiochemical methods on solutions that contained one or more radioactive tracers. Iron, uranium, thorium, cerium, samarium, and neodymium were determined spectrophotometrically. Uranium was also determined fluorometrically at concentrations <0.1 mg/ml. Flame photometric methods were used for the determination of strontium and sodium. Free acid in both aqueous and organic samples was titrated potentiometrically with standard sodium hydroxide solution. Other methods included the volumetric determination of cerium(III), cerium(IV), and total cerium by titration with ferrous solution and the gravimetric determination of cerium, neodymium, and samarium by oxalate precipitation. Lead was determined polarographically. In order to carry out these analyses, an ORNL model Q-1160 polarograph was installed; over 300 determinations of lead have been made with it. The lead concentration ranged from <1 µg/ml to 0.3 mg/ml in the aqueous and organic samples. A 2 M nitric acid solution was found to be suitable for re-extraction of lead from organic solutions.

Miscellaneous Analyses Laboratory

L. J. Brady

E. C. Lynn

The staff of the Miscellaneous Analyses Laboratory analyzed some 2300 samples. Approximately 63% were from the Chemistry, Reactor Chemistry, Health Physics, and Metallurgy Divisions.

Table 23. Distribution by Analysis of Control Results for
October 1959 Through September 1960

Type of Method	Constituent	Number of Control Programs	Number of Control Results
Colorimetric (spectrophotometric)	Aluminum	2	8
	Chromium	4	140
	Iron	7	185
	Molybdenum	2	74
	Nickel	4	152
	Nitrate	1	23
	Phosphate	2	4
	Thorium	8	818
	Uranium	9	971
	Vanadium	4	22
		43	2397
Coulometric	Copper	5	211
	Nickel	3	192
	Uranium	8	419
		16	822
Electrogravimetric	Copper	1	45
		1	45
Fluorometric	Uranium	7	499
		7	499
Potentiometric	Free acid	1	91
	Sulfate	2	154
	Uranium	1	122
		4	367
Volumetric	Aluminum	2	3
	Iron	2	2
	Thorium	3	61
	Uranium	4	110
	Vanadium	1	9
		12	185
Total		83	4315

Specification testing of metals, alloys, oils, inks, paints, and other samples was continued. Where possible, standard ASTM procedures were used. Soils and plants, submitted by the Ecology Department of the Health Physics Division, were analyzed for carbon, hydrogen, nitrogen, and moisture. Oil samples were tested for acidity, sulfur, and water. Compliance with specifications was established before the oils were transferred from the tank cars to storage tanks. The high-temperature fluorination process was used to determine the oxygen content of various metals, oxides of metals, and fluoride salts. Gas samples, many of which were off-gases from the ignition

of graphite, were analyzed by means of gas chromatography. Components usually determined were oxygen, carbon monoxide, methane, and nitrogen.

Raw Materials Laboratory

J. R. Lund

Approximately 9200 samples were analyzed by the staff of the Raw Materials Analytical Laboratory, and 12,600 results were reported. About 55% of the samples were analyzed in a laboratory near the point of origin of the samples. Almost 60% of the samples were aqueous solutions, 30% were organic extracts, and 10% were solids. The solid samples consisted principally of granite that had been leached with sulfuric acid. The liquid samples were derived from studies of solvent-extraction processes. In these processes organophosphorus compounds or high-molecular-weight amines, dissolved in an inert solvent (Amsco), were used to extract a variety of elements from dilute solutions of sulfuric acid, practically neutral nitrate or sulfate solutions, or strongly basic solutions of ammonium carbonate.

The methods used and the constituents determined are tabulated below. Analyses were made for nearly 40 different constituents, but only those that account for at least 5% of the analyses by a given method are included in the tabulation.

Method	Per Cent of Total Analyses	Constituents
Spectrophotometric	60	Th, U, Mo, V, Fe, Ti
Volumetric	15	U, NH ₃ , Th, H ⁺ , Cl ⁻ , NO ₃ ⁻ , V, free acid
Gravimetric	10	SO ₄ ²⁻ , CO ₃ ²⁻ , Mo
Fluorometric	10	U
Other	5	H ₂ O, Na, pH

Analyses and other services carried out near the point of origin of samples included: counting of the gross gamma activity, fluorometric determination of uranium, nonaqueous titration of amines and organic acids, and preparation of solutions.

IONIC ANALYSES (X-10)

P. F. Thomason

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

LOW-LEVEL RADIOCHEMICAL LABORATORY (X-10)

C. L. Burros

The Low-Level Radiochemical Laboratory has made 2660 more analyses this year than last year.

A variety of samples were analyzed, for example: leaves, grass, mulberries, rats, mice, muskrats, clamshells, grasshoppers, river water, mud, and silt. Most of the analyses were for the

Health Physics Division in connection with their ecological, waste-disposal, and area-monitoring programs.

In order to expedite the handling of samples, a new fume hood for the wet-ashing of plant and animal tissues and another low-background beta counter are being added to the laboratory.

MASS SPECTROMETRIC ANALYSES (Y-12)

J. R. Sites

The Analytical Mass Spectrometry Group reported 35,096 analyses from 4300 samples. About one-third of these analyses were for the Reactor Division, and about one-fifth were for the Isotopes Division.

A set of samples was studied in order to determine the possibility of separating mercury isotopes by a photo-ionization process. It was possible to see a change of 1% in the 204/200 relative isotopic abundance ratio.

For the Isotopes Division, successful techniques were developed for analyzing elements that previously were very difficult to analyze.

SPECTROCHEMICAL ANALYSES LABORATORY (Y-12)

J. A. Norris

Some 2200 samples were analyzed in the Spectrochemical Analyses Laboratory, and about 22,000 results were reported. The majority of the samples originated in the Isotopes Division and included the stable isotopes of Ni, Pb, Ru, B, Sm, Nd, Cu, Fe, Br, Sr, Sn, Zn, Cr, Ge, Si, Te, Ca, In, Ti, Li, K, Ba, Zr, Yb, and Ga. The Radioisotopes Production Department of the Isotopes Division submitted samples of Pm^{147} for the determination of neodymium and samarium and 1000 samples of rare-earth-element mixtures from separation studies in which ion exchange columns were used. The Reactor Chemistry Division submitted samples of graphite for boron determinations; fluorides of iron, chromium, nickel, and other metals for impurities; and beryllium oxide preparations for impurities. Numerous other samples were received from the Metallurgy, Physics, Reactor, and other research divisions.

PROCESS ANALYSES (X-10)

L. T. Corbin

Decontamination Studies Laboratory

H. C. Meyer

An investigation is being conducted to determine the significance of surface contamination and of the effectiveness of various methods now used to determine the extent of the contamination. This investigation is designed to provide relationships between transferable contamination, as determined by smears, and nontransferable contamination. A correlation is being sought between

surface activity and the quantity of activity that can be spread by typical maintenance and normal traffic. The investigation is being made first for alpha contamination on typical construction materials, such as steel, tile, and concrete.

High-Alpha Analytical Laboratory

J. H. Cooper

Approximately 95% of the analyses made by the High-Alpha Analytical Laboratory were for the Chemical Technology Division relative to processing transuranium materials. Paint, soil, concrete, and asphalt were analyzed for plutonium after the incident occurred in Building 3019.

A 256-channel analyzer, made by Radiation Counter Laboratories, is in service for alpha- and gamma-energy analyses. A Frisch grid chamber is used as the detector for alpha radiation. A resolution of about 100 kev is normally obtained on alpha sources prepared in the manner prescribed for determination of gross alpha activity.³ A 3 × 3 in. scintillation crystal has been obtained for analyzing gamma spectra on the multichannel instrument. A single-channel, well-type, manually operated gamma spectrometer has been put in use.

Twenty-one new glove boxes have been installed in the new facility in Building 3508 and are being equipped. Six of the boxes will be used without attached gloves for operations in which the level of radioactivity is relatively low. Radioactivity of higher levels will be isolated in the gloved boxes. Exhaust air is doubly filtered at the box and again before leaving the building.

High-Radiation-Level Analytical Facility (HRLAF)

L. G. Farrar

Several minor modifications have been made in the HRLAF. The small open area at the north end of the cell block was enclosed to provide an additional line of containment and to furnish a clothes change area. The entire facility, including the cells, was decontaminated. The cells and the east working zone were painted. Dampers in the off-gas ducts of each cell were modified to permit maximum air flow when needed, and particle collectors were installed on the off-gas outlets of the cell in order to prevent backflow of contaminated material. An inert-gas supply system has been installed for use inside the cells.

In an effort to decrease manipulator down time, heavy-duty hand grips were installed on the manipulators, and new canting switches have been in use on a trial basis. Total-enclosure disposable boots for the manipulators were fabricated. The design for a new decontamination facility in the HRLAF has been completed, and funds to purchase additional radiation-monitoring instruments have been requested.

³R. L. Walker, "Gross Alpha," Method Nos. 9 002301 and 9 0733000 (R. 7-14-60), *ORNL Master Analytical Manual*; TID-7015, suppl 3.

The operating procedures of the facility were modified to permit closer control of access to contamination and to radiation zones and to prevent contamination of the operating area. The use of radiation-zone entry permits was initiated.

Pilot-Plant Control Laboratory

C. E. Lamb

The major responsibility of the Pilot Plant Control Laboratory has been the analysis of samples received from ORNL pilot plants and related development groups involved in processing highly radioactive materials. In November 1959, process and development work on large quantities of radioactive material was suspended. After several months, work was partially resumed on a reduced and limited scale. During the interim, existing rules, policies, and controls relative to the safe handling of radioactive materials in the Pilot-Plant Control Laboratory were re-examined. Limits for exposure of persons to radiation and for area contamination were reduced. New and revised rules, methods, and procedures for operations involving radioactive materials were formulated and issued.

The curtailment of pilot-plant work resulted in the Pilot-Plant Control Laboratory receiving only approximately 55% as many samples in 1960 as had been received in 1959. However, compliance with the new measures for the control of radiation and contamination necessitated a longer time to perform many of the analytical operations.

Special analytical services have included work for Atomics International, Reactor Experimental Engineering Division (REED), Metallurgy Division, and the Radiochemical Processing Pilot Plant. The work for Atomics International⁴ included the dissolution of irradiated and unirradiated uranium wafers, the separation and measurement of components, and the distribution of dissolved portions to other groups for special work. The work for REED included the separation of uranium from irradiated aluminum-uranium capsules and the decontamination and preparation of the separated uranium for mass isotopic analyses. For the Metallurgy Division, the uranium content of irradiated coupons of UO₂ sandwiched between two layers of stainless steel was measured, and the uranium was isolated for isotopic analysis. For the Radiochemical Processing Pilot Plant, plutonium was isolated, decontaminated, and purified for isotopic analysis; also, precipitates present in their feed and first-column raffinate solutions were analyzed.⁵

A corrosion-resistant pipetter for remotely controlled measurement of radioactive samples (see "Corrosion-Resistant Pipetter for Remotely Controlled Measurement of Radioactive Solutions," this report), especially those containing halides, was put into operation. Mobile work benches were obtained for use in cell decontamination and instrument repair in the HRLAF. A Fisher Gas Partitioner was installed for the determination of hydrogen in samples of off-gas from the Volatility Pilot Plant.

⁴M. J. Gaitanis, *Analysis of Uranium Fuel-Element Wafers from Atomics International for Uranium, Plutonium, and Samarium*, ORNL CF-60-12-43 (Dec. 27, 1960).

⁵M. J. Gaitanis, *PRFR Pilot Plant*, memorandum to L. T. Corbin (Feb. 11, 1960).

A method of separating uranium from $\text{HNO}_3\text{-HCl}$ solutions of stainless steel by tri(isooctyl)-amine-xylene extraction⁶ was put into use for the future analysis of APPR and Darex samples in an HRLAF cell.

Process-Development Service Laboratory

G. R. Wilson

At the request of the Waste Disposal Group of the Chemical Technology Division, a spectrophotometric method was developed for the determination of ruthenium in the presence of stainless steel and nitric acid.⁷ The ruthenium is oxidized to the tetroxide with argentic oxide, and the ruthenium tetroxide is extracted into carbon tetrachloride. The extract is then equilibrated with an aqueous solution of sodium thiocyanate, with the result that the blue ruthenium thiocyanate complex is formed in the aqueous phase. The complex shows a broad absorption band with a maximum at about 590 $m\mu$. The relationship between ruthenium concentration and absorbancy conforms to Beer's law for ruthenium concentrations in the range from 0 to 15 $\mu\text{g/ml}$.

The Power Reactor Fuel Reprocessing Group of the Chemical Technology Division requested the determination of low concentrations of zirconium in aqueous solutions of nitric acid and in 30% tributyl phosphate-70% dodecane that had been equilibrated with a nitric acid solution of zirconium. Two spectrophotometric procedures were adapted by J. G. Surak,⁸ assisted by members of this group, from a method by Grimaldi and White;⁹ quercetin is the chromogenic reagent. The absorption is measured at a wavelength of 440 $m\mu$; the range of the method is 0.2 to 1 $\mu\text{g/ml}$.

Radioisotopes-Radiochemistry Laboratory

E. I. Wyatt

About half the work of the Radioisotopes-Radiochemistry Laboratory for the past year has been for the Isotopes Division. Specifications have been prepared and drawings are being made for the construction of five analytical hot cells in the laboratory of Building 3038. These cells will be used for analytical work on radioisotope products received from the Isotopes Division.

A new analytical procedure for the determination of radioantimony has been developed. It consists in the extraction of antimony from strong aqueous solutions of mineral acids, using diisobutylcarbinol, and the subsequent stripping of the antimony into a caustic solution for gamma counting. The total time required for analysis in duplicate is less than 30 min. Only one separatory funnel is needed, thus making the procedure well suited for remotely controlled work. A paper that describes the method has been submitted to *Analytical Chemistry* for publication.

⁶B. B. Hobbs, *Coulometric Determination of Uranium in Power-Reactor-Fuel-Dissolver Solutions*, ORNL-2987 (Nov. 18, 1960).

⁷W. L. Belew, "Ruthenium, Spectrophotometric Thiocyanate Method," Method Nos. 1 217312 and 9 00717312 (10-11-60), *ORNL Master Analytical Manual*; TID-7015, suppl 3.

⁸Summer employee from Marquette University, Milwaukee, Wis.

⁹F. S. Grimaldi and C. E. White, "Quercetin as Colorimetric Reagent for Determination of Zirconium," *Anal. Chem.* 25, 1886 (1953).

A monograph on the radiochemistry of ruthenium is being written for inclusion in the National Academy of Sciences – National Research Council *Nuclear Science Series*. It contains a collection of widely used radiochemical procedures and a bibliography on ruthenium chemistry.

Half-lives of five radionuclides have been determined (see Table 24); a gamma ionization chamber was used in making the determinations.

Table 24. Observed Half-Lives of Some Radionuclides

Nuclide	Half-Life	Method of Production	Duration of Observation (half-lives)
Na ²²	2.618 ± 0.016 y	Na ²³ _(p,pn) Na ²² Na ²³ _(p,2n) Mg ²² → Na ²²	1.3
Y ⁸⁸	107.4 ± 0.2 d	Sr ⁸⁸ _(p,n) Y ⁸⁸	> 3
Ba ¹³³	10.73 ± 0.14 y	Ba ¹³² _(n,γ) Ba ¹³³	0.35
Cs ¹³⁴	2.072 ± 0.017 y	Cs ¹³³ _(n,γ) Cs ¹³⁴	1.6
Ir ¹⁹²	74.19 ± 0.17 d	Ir ¹⁹¹ _(n,γ) Ir ¹⁹²	5.8

Reactor Analyses Laboratory

U. Koskela

Although the HRT was out of operation during most of this period, about 95% of the analyses performed were related to the HRP. Considerable time was spent in reconditioning the work cells in the HRLAF and in improving equipment for safer operations.

The previously reported method^{10,11} for the determination of free acid in HRT samples began to give erratic results during run 21 of the reactor. About halfway through the run, a conductometric method was introduced. It is based on the method of Pepkowitz, Sabol, and Dutina¹² as modified by Goldstein,¹³ and modified further by Corcoran *et al.*¹⁴ The last modification consisted in substituting methanol for sodium fluoride and adapting the method for remotely controlled operations. The average relative standard deviation for blanket and core samples was 1.4 to 2.5%. The method has been published.¹⁴ A completely automatic method is being evaluated.

During run 21 of the HRT, the aliquots of samples that were analyzed for sulfate became more radioactive as the run progressed. A remotely controlled conductometric titration of sulfate was

¹⁰O. Menis *et al.*, "Analytical Chemistry," HRP Progr. Rept. May 1 Through Oct. 31, 1959, ORNL-2879, pp 247–50.

¹¹F. J. Miller and H. E. Zittel, "Determination of Free Acid in Uranyl Sulfate Solutions by the Dowex 50 Resin Separation Procedure," Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1959, ORNL-2866, pp 10–11.

¹²L. P. Pepkowitz, W. W. Sabol, and D. Dutina, "Determination of Free Acid in the Presence of Hydrolyzable Ions," Anal. Chem. 24, 1956 (1952).

¹³G. Goldstein and O. Menis, *Determination of Free Acid in Uranyl Sulfate Solutions by Conductometric Titration*, ORNL CF-59-12-32, (Dec. 4, 1959).

¹⁴R. E. Corcoran *et al.*, *Determination of Free Acid in Highly Radioactive Solutions by Remotely Controlled Conductometric Titration*, ORNL CF-60-10-38 (Oct. 13, 1960).

investigated. The method consists in passing an aliquot of the sample through a column of Dowex 50 resin in methanol and titrating the effluent with an aqueous solution of barium acetate. The change in conductivity is followed on a Brown recorder. After the method has been evaluated, a report will be issued describing both it and the determination of free acid.

Special Analyses Laboratory

W. R. Laing

Changes in analytical requirements have necessitated that several new methods be put into use. Equipment for the measurement of the surface area of radioactive powders by the continuous-flow¹⁵ method has been used in a hot-cell area. The krypton adsorption method¹⁶ for surface area in the range from 0.02 to 0.7 m² of total surface is now in use. Other new methods were for the determination of oxygen in NaK and in potassium, dissolved oxygen and hydrogen in water from pressurized loops,¹⁷ carbonaceous material in aqueous solution, silicon in niobium metal, molybdenum in uranium-molybdenum alloys, boron in uranium-aluminum alloys, and sulfur in gamma-irradiated and unirradiated ion exchange resin. Attrition-rate tests and measurements of bulk density and pore volume were made on thoria pellets. Neutron-capture cross section targets of 65 elements were prepared.

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

RADIOCHEMICAL ANALYSES (X-10)

S. A. Reynolds

Over 90% of the service analyses made by the Radiochemical Analyses Group were performed for five ORNL divisions. Most of the analyses for the Health Physics Division were concerned with radioactive materials in filters and charcoal traps; gamma spectrometric techniques usually were employed. Work for the Metallurgy and Solid State Divisions included spectrometric analyses of fission product gases in mixtures. Many analyses of unusual radioisotope products were made for the Isotopes Division. For the Chemical Technology Division, measurements were made of P³², S³⁵, H³, and other nuclides by liquid-scintillation counting.

¹⁵F. M. Nelsen and F. T. Eggertsen, "Determination of Surface Area. Adsorption Measurements by a Continuous Flow Method," *Anal. Chem.* 30, 1387 (1958).

¹⁶A. J. Rosenberg, "Rapid, Precise Measurements of Krypton Adsorption and the Surface Area of Coarse Particles," *J. Am. Chem. Soc.* 78, 2929 (1956).

¹⁷F. C. Steiner, *Simplified Methods for Primary Coolant Gas Measurements*, KAPL M-SMS-71 (June 14, 1957).

REACTOR PROJECTS LABORATORY (Y-12)

J. C. White W. F. Vaughan

Some 4600 samples were analyzed by the Reactor Projects Laboratory. These were mostly fused fluorides that were mixtures of three or more of the fluorides of U, Zr, Li, Na, Th, Be, K, Mg, Cr, Ni, and Fe. Analyses were made primarily for the following corrosion products: Ni, Cr, Fe, Mo, and Cu. Approximately 35% of the salts were analyzed for one or more of the major constituents in order to ascertain the amounts precipitated out by the addition of excess quantities of the oxides of either beryllium, calcium, or magnesium. These samples were received in connection with basic research on fused salts. Approximately 12% of the fused salts were analyzed for the major constituents in order to determine exact compositions. Volumetric, gravimetric, and spectrometric methods were used.

The services (one-half man-year) of a technician were furnished to two of the research groups of the Reactor Chemistry Division for analyses and other work that had to be done at the sites of the experiments.

THERMAL BREEDER REACTOR PROJECTS ANALYTICAL CHEMISTRY LABORATORY (Y-12)

H. E. Zittel C. K. Talbott

The Thermal Breeder Reactor Projects Analytical Chemistry Laboratory made 31,300 analyses on some 6500 samples. Of these, approximately 82% were submitted by the Reactor Experimental Engineering Division and 8% by the Ecology Department of the Health Physics Division. Approximately 35% fewer samples were analyzed this year than last year. The samples consisted principally of solutions of uranyl sulfate (many of which contained copper sulfate), slurries of thorium oxide, mixtures of thorium oxide with small amounts of uranium oxides, soils, plant materials, and shells. Analyses were made less frequently on a wide variety of materials, including water samples and solutions of nitric acid, phosphoric acid, lithium chloride, and methylene blue. Methods of analysis included gravimetry, spectrophotometric and potentiometric titrations, spectrophotometry, flame photometry, polarography, thermogravimetry, gasometry, and coulometry. Physical measurements were made on many samples; these included pH, conductivity, particle-size distribution, specific gravity, and zeta potential.

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
Horton, C. A.	"Trends in the Determination of Fluorine," pp 151-97 in <i>Advances in Analytical Chemistry and Instrumentation</i> , vol 1, C. N. Reilley, ed.	Interscience, New York, 1960
Leddicotte, G. W. ¹	<i>Source Material for Radiochemistry</i> , Nuclear Science Series Report No. 27 (rev. 1), July 1960 (publ. 825)	National Academy of Sciences - National Research Council, Washington, D.C.
Maddox, W. L.	<i>Cathodic Stripping Voltammetry Investigation of Voltage-Stepping and Current-Stepping Methods for the Determination of Chloride Ion</i> (M.S. thesis)	University of Tennessee, June 1960
Menis, O., ² H. P. House	"Flame Photometry - Indirect Methods," pp 343-46 in <i>The Encyclopedia of Spectroscopy</i> , G. L. Clark, ed.	Reinhold, New York, 1960

Articles

Author(s)	Title	Publication
Apple, R. F., J. C. White	"Determination of Thorium Present in Fluoride Salt Mixtures"	<i>Chemist Analyst</i> 49, 42 (1960)
Ball, R. G., ³ D. L. Manning, O. Menis ²	"Determination of Chloride by Cathodic Stripping Polarography. Application to Solutions of Uranyl Sulfate"	<i>Anal. Chem.</i> 32, 621 (1960)
Cooper, J. H.	"The High-Alpha-Radiation Analytical Facility of the Oak Ridge National Laboratory"	<i>Talanta</i> 6, 154 (1960)
Dunn, H. W.	"X-Ray Absorption Edge Analysis"	<i>Ibid.</i> , p 42
Dyer, F. F., G. K. Schweitzer ⁴	"Effects of Temperature and Non-Aqueous Solvent Changes on Silver Dithizonate Extractions"	<i>Anal. Chim. Acta</i> 23, 1 (1960)

¹This material was written jointly with other members of the Subcommittee on Radiochemistry of the National Research Council.

²Nuclear Materials and Equipment Corp., Apollo, Pa.

³American Cyanamid Co., New Orleans, La.

⁴University of Tennessee, Knoxville.

Author(s)	Title	Publication
Eldridge, J. S., W. S. Lyon	"Decay of Promethium-148"	<i>Trans. Am. Nuclear Soc.</i> 3, 89 (1960)
Feldman, C.	"Ammonium Bisulfate Fusion. Application to Trace Analysis by Spectrochemical and Other Techniques"	<i>Anal. Chem.</i> 32, 1727 (1960)
Goldberg, G., A. S. Meyer, Jr., J. C. White	"Determination of Oxides in Fluoride Salts by High-Temperature Fluorination with Potassium Bromotetrafluoride"	<i>Ibid.</i> , p 314
Goldstein, G., O Menis, ² D. L. Manning	"Extraction of Thorium with Thenoyltrifluoroacetone. Effect of Acetic Acid"	<i>Ibid.</i> , p 400
Handley, T. H., J. A. Dean ⁴	"Trialkyl Thiophosphates. Selective Extractants for Silver and Mercury"	<i>Ibid.</i> , p 1878
Harmatz, B., T. H. Handley,* J. W. Mihelich ⁵	"Nuclear Spectroscopy of Neutron-Deficient Lu, Ta, and Re Isotopes"	<i>Phys. Rev.</i> 119, 1345 (1960)
Jacob, K. P., ⁵ J. W. Mihelich, ⁵ B. Harmatz, T. H. Handley*	"Electron Capture Decay of Tm ¹⁶⁸ and Tm ¹⁶⁶ "	<i>Phys. Rev.</i> 117, 1102 (1960)
Kelley, M. T., D. J. Fisher, H. C. Jones	"Controlled-Potential Polarographic Polarizing Unit with Electronic Scan and Linear Residual Current Compensation"	<i>Ibid.</i> , p 1262
Kelley, M. T., D. J. Fisher, H. C. Jones, W. L. Maddox R. W. Stelzner	"Applications of Commercial Operational Amplifiers in Instrumentation for Chemical Analyses"	Preprint No. NY60-52, Instrument Society of America, Pittsburgh 22, Pa.
Kelley, M. T.,* D. J. Fisher,* E. B. Wagner	"Automatic Recording Velocity-Servo Potentiometric Titrator"	<i>Anal. Chem.</i> 32, 61 (1960)
Kelley, M. T., H. C. Jones, D. J. Fisher	"Electronic Controlled-Potential Coulometric Titrator for Plutonium Analysis"	<i>Talanta</i> 6, 185 (1960)
Kubota, H.	"Determination of the Stoichiometry of Uranium Dioxide. Polarographic Determination of Uranium(VI) in Uranium Dioxide"	<i>Anal. Chem.</i> 32, 610 (1960)
Lamb, C. E.	"The High-Radiation-Level Analytical Facility at the Oak Ridge National Laboratory"	<i>Talanta</i> 6, 20 (1960)
Leddicotte, G. W.	"Experience in the U.S.A. on the Use of Radioactivation Analysis"	<i>Pure and Appl. Chem.</i> 1, 61 (1960)
Macklin, R. L., G. DeSaussure, J. D. Kington, W. S. Lyon*	"Manganese Bath Measurements on η of U ²³³ and U ²³⁵ "	<i>Nuclear Sci. and Eng.</i> 8, 210 (1960)

⁵University of Notre Dame, Notre Dame, Ind.

Author(s)	Title	Publication
Manning, D. L., R. G. Ball, ³ O. Menis ²	"Determination of Molybdenum in Nitrotri-acetic Acid Medium by Derivative Polarography. Application to Solutions of Mixed Thorium-Uranium Oxides"	<i>Anal. Chem.</i> 32 , 1247 (1960)
Manning, D. L., O. Menis ²	"Some Applications of High-Frequency Titrimetry"	<i>Talanta</i> 6 , 30 (1960)
Menis, O., ² T. C. Rains	"Extraction and Flame Photometric Determination of Iron"	<i>Anal. Chem.</i> 32 , 1837 (1960)
Miller, F. J., P. F. Thomason	"Spectrophotometric Determination of Technetium(VII) with Thioglycolic Acid"	<i>Ibid.</i> , p 1429
Moore, F. L.	"Liquid-Liquid Extraction of Polonium-208 Tracer from Bismuth Target Solutions"	<i>Ibid.</i> , p 1048
	"Liquid-Liquid Extraction of Uranium and Plutonium from Acetate Solution with Triisooctylamine. Separation from Thorium and Fission Products"	<i>Ibid.</i> , p 1075
Rains, T. C., H. P. House, O. Menis ²	"Evaluation of Flame Photometry for the Determination of Elements of the Rare-Earth Group"	<i>Talanta</i> 6 , 274 (1960)
	"Flame Spectra of Sc, Y and Rare-Earth Elements"	<i>Anal. Chim. Acta</i> 22 , 315 (1960)
Ross, W. J., J. C. White	"Colorimetric Determination of Boron in Nitrate Solutions"	<i>Talanta</i> 3 , 311 (1960)
Surak, J. G., ⁶ D. J. Fisher, C. L. Burros, L. C. Bate	"Apparatus for Pyrohydrolytic Determination of Fluorides"	<i>Anal. Chem.</i> 32 , 117 (1960)
Susano, C. D.	"The Role of the Analytical Chemist in Nuclear Reactor Technology"	<i>Talanta</i> 6 , iii (1960)
Young, J. P., J. C. White	"Absorption Spectra of Molten Fluoride Salts. Solutions of Praseodymium, Neodymium, and Samarium Fluoride in Molten Lithium Fluoride"	<i>Anal. Chem.</i> 32 , 1658 (1960)
	"Absorption Spectra of Molten Salts. Solutions of Several Metal Ions in Molten Lithium Fluoride-Sodium Fluoride-Potassium Fluoride"	<i>Ibid.</i> , p 799
Young, J. P., J. C. White, R. G. Ball ³	"Spectrophotometric Determination of Yttrium with Pyrocatechol Violet"	<i>Ibid.</i> , p 928
Zingaro, R. A., ⁷ J. C. White	"The Extraction of Nitric Acid and Thorium Nitrate by Tri- <i>n</i> -octylphosphine Oxide in Cyclohexane"	<i>J. Inorg. & Nuclear Chem.</i> 12 , 315 (1960)

⁶Temporary summer employee from Marquette University, Milwaukee, Wis.

⁷Temporary summer employee from Agriculture and Mechanical College of Texas, College Station.

Reports

Author(s)	Title	Report No.
Bate, L. C., F. C. Burns, ⁸ G. W. Leddicotte	"Neutron Flux from the ORR Reactor Window into the Reactor Pool"	ORNL CF-60-11-31 (Nov. 3, 1960)
Bate, L. C., R. L. Ferguson	"Comments on Southeastern Regional Meeting of the American Chemical Society"	ORNL CF-59-12-27 (Dec. 4, 1959)
Biggers, R. E.,* 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)
Biggers, R. E., D. A. Costanzo	"Hazards and Experimental Procedure Evaluation For: Studies on the Polymerization and Hydrolysis of Plutonium in Uranyl Nitrate and Nitric Acid Solution at Elevated Temperatures"	ORNL CF-60-5-34 (May 9, 1960)
Boyd, C. M.	"Comments on the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 5 Through 14, 1960"	ORNL CF-60-5-44 (May 4, 1960)
Boyd, C. M., H. P. House, O. Menis ²	"Catalyzed Hydrolysis of Pyrophosphate by Thorium Oxide"	ORNL-2893 (Feb. 16, 1960)
Corcoran, R. E., ⁹ H. E. Zittel, S. R. Dinsmore, U. Koskela	"Determination of Free Acid in Highly Radioactive Solutions by Remotely Controlled Conductometric Titration"	ORNL CF-60-10-38 (Oct. 13, 1960)
Gaitanis, M. J.	"Analysis of Uranium Fuel-Element Wafers from Atomics International for Uranium, Plutonium, and Samarium"	ORNL CF-60-12-43 (Dec. 27, 1960)
Goldstein, G.	"A Study of Spectrophotometric Methods for the Determination of Osmium"	ORNL-2862 (Jan. 7, 1960)
	"Determination of Osmium in Molybdenite"	ORNL CF-60-5-77 (May 12, 1960)
Goldstein, G., O. Menis, ² D. L. Manning	"Indirect Determination of Sulfate by Non-Aqueous Titrimetry"	ORNL CF-60-2-47 (Feb. 3, 1960)
Hobbs, B. B.	"Coulometric Determination of Uranium in Power-Reactor-Fuel-Dissolver Solutions"	ORNL-2987 (Nov. 18, 1960)
Holsopple, H. L.	"Synthesis of Dimethyl Selenide"	ORNL CF-60-10-26 (Oct. 7, 1960)
	"Synthesis of Some Quaternary Ammonium Salts"	ORNL CF-60-5-134 (May 27, 1960)
Lund, J. R.	"Recording and Comparison of Gas Chromatograms of Treated and Untreated Amsco"	ORNL CF-60-8-20 (Aug. 5, 1960)
Lyon, W. S.	"Report of Foreign Travel"	ORNL CF-60-6-109 (June 20, 1960)

⁸National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio.

⁹Now associated with Martin Co., Baltimore, Md.

Author(s)	Title	Report No.
Manning, D. L.	"Summary of Lectures Attended at the 138th National Meeting of the American Chemical Society, September 12 Through 16, 1960"	ORNL CF-60-9-115 (Sept. 29, 1960)
Mullins, W. T.	"Second Annual Texas Conference on the Utilization of Atomic Energy"	ORNL CF-60-4-107 (Apr. 22, 1960)
Norris, J. A.	"A New Spectrographic, Controlled-Atmosphere, Excitation Chamber by R. E. Weekley"	ORNL CF-59-10-60 (Oct. 14, 1959)
	"Wavelength Table of Rare-Earth Elements and Associated Elements Including Zirconium, Thorium, Hafnium, Rhenium and Tellurium"	ORNL-2774 (Feb. 2, 1960)
Norris, J. A., R. L. McCutchen	"Investigation of Spectrochemical Solution-Methods of Analysis. The Use of Designed Experiments and Statistical Methods of Analysis in the Interpretation of Data"	ORNL-2927 (Apr. 25, 1960)
Reynolds, S. A.	"Determination of Thorium in Rock Samples by Gamma Spectrometry"	ORNL CF-60-6-37 (June 7, 1960)
	"Report of Foreign Travel"	ORNL CF-60-4-46 (Apr. 8, 1960)
Shults, W. D.	"Controlled Potential Coulometric Titration of Plutonium - Application to PRFR Samples"	ORNL-2921 (Apr. 11, 1960)
White, J. C., J. A. Norris	"Report of Trip to Atlantic City, New Jersey, June 29, 1960"	ORNL CF-60-8-139 (Aug. 31, 1960)
	"Report of Trip to National Spectrographic Laboratories and BeO Standards Meeting"	ORNL CF-60-4-22 (Apr. 4, 1960)
Winchester, J. W. ¹⁰	"Rare Earth Chromatography Using Bis(2-ethylhexyl)orthophosphoric Acid"	ORNL CF-60-3-158 (Mar. 14, 1960)
Wyatt, E. I., H. A. Parker, S. A. Reynolds, W. S. Lyon, R. H. Rodriguez ¹¹	"Assay Methods Used in the ORNL Radioisotope Program"	ORNL CF-60-2-39 (Feb. 1, 1960)
Young, J. P.	"Spectrophotometry of Molten Salts Status Report, May 1960"	ORNL CF-60-6-15 (June 2, 1960)
	"Spectrophotometry of Molten Salts Status Report, June 1960"	ORNL CF-60-7-45 (July 14, 1960)
	"Spectrophotometry of Molten Salts Status Report, July 1960"	ORNL CF-60-8-141 (Aug. 31, 1960)
	"Spectrophotometry of Molten Salts Status Report, August 1960"	ORNL CF-60-9-53 (Sept. 13, 1960)

¹⁰Massachusetts Institute of Technology, Cambridge.

¹¹Division of Radiochemistry of the National Commission of Atomic Energy, Argentina.

New Methods Issued to ORNL Master Analytical Manual

Author(s)	Title	Number(s)	Date
Apple, R. F.	"Oxygen in Metals, Inert-Gas-Fusion-Conductometric Method"	1 215895 9 00715895	5-19-60
	"Silicon in Beryllium Oxide, Spectrophotometric Molybdenum Blue Method"	1 217712 9 00717712	10-3-60
Attrill, J. E.	"Sulfur, Leco Combustion-Photometric Titration Method"	1 218180 9 00718180	10-20-60
Ball, R. G., ³ D. L. Manning	"Chloride, Cathodic-Stripping Polarographic Method"	1 212024 9 00712024	5-27-60
Belew, W. L.	"Ruthenium, Spectrophotometric Thiocyanate Method"	1 217312 9 00717312	10-11-60
Costanzo, D. A.	"Europium in Scintillation Crystals of Europium-Activated Lithium Iodide, Coulometric Titration Method"	1 212720 9 00712720	5-18-60
Feldman, C.	"Cesium, Flame Photometric Method"	1 211930 9 00711930	10-10-60
Goldberg, G.	"Oxygen in Fluoride Salts and Refractory Metals, Potassium Tetrafluorobromide Manometric Method"	1 215894 9 00715894	5-12-60
Goldstein, G.	"Sulfate, Indirect Potentiometric Barium Acetate Titration (Nonaqueous Medium) Method"	1 218121 9 00718121	5-11-60
Horton, A. D.	"Ruthenium, Spectrophotometric Thiourea Method"	1 217310 9 00717310	10-14-60
Layton, F. L.	"Chromium, Spectrophotometric 1,5-Diphenylcarbohydrazide (Sulfuric Acid Medium) Method"	1 212112 9 00712112	3-28-60
	"Phosphate, Spectrophotometric Vanadomolybdate Method"	1 216011 9 00716011	3-28-60
	"Thorium, Volumetric Disodium Dihydrogen Ethylenediaminetetraacetate-Xylenol Orange Method"	1 218771 9 00718771	3-29-60
	"Titanium, Spectrophotometric Hydrogen Peroxide Method"	1 219010 9 00719010	3-29-60
Leddicotte, G. W.	"Aluminum, Neutron Activation Analysis (Direct Measurement) Method"	5 11021	10-14-60
	"Arsenic, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11060	4-27-60
	"Barium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11080	5-3-60
	"Copper, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11230	2-5-60
	"Gallium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11310	5-9-60
	"Iron, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11410	2-29-60

Author(s)	Title	Number(s)	Date
	"Molybdenum, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11500	3-25-60
	"Silicon, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11770	3-11-60
	"Tungsten, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11910	3-3-60
Lynn, E. C.	"Amines in Organic Diluents, Potentiometric Perchloric Acid Titration Method"	1 221002 9 00721002	5-16-60
Menis, O. ²	"Fluoride, Separation by Fusion Pyrohydrolysis Method"	1 00707 9 00651	10-20-60
Meyer, H. C.	"Potassium, Flame Photometric Method"	1 216430 9 00716430	2-24-60
Moore, F. L.	"Radioactive Cesium, Sodium Tetraphenylboron Precipitation Method"	2 21194	10-14-60
	"Uranium-237, Triisooctylamine Extraction Method"	2 31920	10-17-60
	"Iron-59 in Homogeneous Reactor Fuel Solutions, Radiochemical Methods"	9 082212	10-14-60
	"Uranium-237 in Homogeneous Reactor Fuel Solutions, Radiochemical Methods"	9 082222	10-17-60
Mullins, W. T., G. W. Leddicotte	"Chromium, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11210	1-29-60
	"Cobalt, Neutron Activation Analysis (Isotopic Carrier Precipitation) Method"	5 11220	2-3-60
Rains, T. C.	"Iron, Flame Photometric Method"	1 214130 9 00714130	10-13-60
Reynolds, S. A., G. W. Leddicotte	"Growth of a Radioelement"	2 0028 5 10120	2-26-60
Shults, W. D.	"Plutonium, Automatic Controlled-Potential Coulometric Titration Method"	1 216220 9 00716220	9-22-60
	"Uranium, Automatic Controlled-Potential Coulometric Titration Method"	1 219225 9 00719225	1-29-60
Talbott, C. K.	"Copper, Spectrophotometric 2,9-Dimethyl-1,10-phenanthroline (Neo-cuproine) Method"	1 212311 9 00712311	6-2-60
Wyatt, E. I.	"Molybdenum Activity in Aqueous Solutions"	2 21502	6-13-60
Wyatt, E. I., R. R. Rickard	"Promethium and/or Yttrium Activity in Aqueous or Organic Solutions"	2 21661 2 21961	6-9-60
	"Ruthenium Activity in Aqueous Solutions, Non-distillation Method"	2 21733	6-13-60
	"Technetium Activity"	2 21831	6-8-60
Zittel, H. E.	"Barium, Amperometric Titration Method"	1 210820 9 00710820	10-4-60

Revised Methods Issued to ORNL Master Analytical Manual

Author(s)	Title	Number(s)	Date
Hemphill, H. L., D. J. Fisher*	"Fluorophotometer, ORNL Model Q-1165"	1 003080 9 003080	R. 1-14-60
Surak, J. G. ⁶	"Fluoride in the Presence of Nitrate, Pyrohydrolysis Method"	9 012207	R. 2-11-60
Walker, R. L.	"Gross Alpha"	9 002301 9 0733000	R. 7-14-60
Walker, R. L., C. E. Lamb	"Uranium, Fluorometric Method"	1 219240 9 00719240	R. 1-20-60
Wilson, G. R.	"Tributyl Phosphate in Organic Diluents, Acid Equilibration Method"	9 012206	R. 6-14-60
Wyatt, E. I.	"Free Acid Normality of Radioisotope Product Solutions"	9 0732005	R. 6-29-60
	"Antimony-124 HSA, Product Analysis Guide"	9 0733041	R. 6-15-60
	"Barium-140, Product Analysis Guide"	9 0733081	R. 6-15-60
	"Carbon-14, Product Analysis Guide"	9 0733171	R. 6-16-60
	"Niobium-95, Product Analysis Guide"	9 0733551	R. 6-15-60
	"Zirconium-95-Niobium-95, Product Analysis Guide"	9 0733981	R. 6-16-60
Wyatt, E. I., D. K. Smith ¹²	"Low Concentrations of Ruthenium-106 in Water"	2 21732	R. 7-11-60

¹²Now associated with Aloe Scientific Co., St. Louis, Mo.

ORAL PRESENTATIONS

The Analytical Chemistry Division sponsored a Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology at Gatlinburg, Tennessee, on October 12-14, 1960. The committee consisted of C. D. Susano (chairman), W. S. Lyon, W. R. Laing, and H. P. House. Forty-seven papers were presented.

This conference was held concurrently with the First Conference on Nuclear Reactor Chemistry. There were 367 registrants: 180 from Oak Ridge, 91 from industrial organizations, 31 from other AEC installations, 28 from foreign countries, 17 from colleges and universities, 12 from governmental agencies other than the AEC, 6 from the AEC, and 2 others.

The proceedings of this conference will be published, as were the proceedings of prior conferences in this series. The proceedings of the First Conference were published as document TID-7555, of the Second Conference as document TID-7568 (Parts 1, 2, 3), whereas the proceedings of the Third Conference were published by Pergamon Press as a special issue of *Talanta*, Vol 6, in September 1960.

A Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology has been scheduled tentatively to be held at Gatlinburg, Tennessee, on October 10-12, 1961.

At Meetings of Professional Societies

Author(s)	Title	Presented at
Apple, R. F., ¹³ J. C. White	"Separation and Colorimetric Determination of Trace Quantities of Mg in High-Purity BeO"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Bate, L. C., ¹³ J. F. Emery, G. W. Leddicotte	"Applications of Low-Level Gamma Scintillation Spectrometry"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Biggers, R. E., ^{13*} J. M. Chilton	"Mathematical Resolution of Complex Overlapping Absorption Spectra and Fine Structure by Means of High Speed Digital Computation"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Cooke, W. D., ^{13,14} M. T. Kelley, D. J. Fisher	"The Role of Capillary Behavior in High Sensitivity Polarography"	1960 Summer Symposium, Trace Analysis, sponsored by <i>Anal. Chem.</i> and the Division of Analytical Chemistry of the American Chemical Society, Houston, Tex., June 15-17, 1960

¹³Speaker.

¹⁴Research participant from Cornell University, Ithaca, N.Y.

Author(s)	Title	Presented at
Dunn, H. W.	"Recent Improvements in the X-Ray Absorption-Edge Method of Analysis"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
	"X-Ray Absorption Edge Analysis"	138th Meeting, American Chemical Society, New York, Sept. 11-16, 1960
Dyer, F. F., ¹³ G. W. Leddicotte	"Analytical Applications of Delayed-Neutron Counting"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Dyer, F. F., ¹³ G. K. Schweitzer ⁴	"The Effects of Temperature and Non-Aqueous Solvent Changes on the Solvent Extraction of Silver Dithizonate"	Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Nov. 3-5, 1960
Eldridge, J. S., ¹³ W. S. Lyon	"Decay of Promethium-148"	American Nuclear Society, Chicago, June 12-15, 1960
	"Techniques for Counting Low-Energy Beta Emitters"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Feldman, C.	"Ammonium Bisulfate Fusion. Application to Trace Analysis by Spectrochemical and Other Techniques"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 29-Mar. 4, 1960
	"Fundamental Processes in Spectral Excitation of Liquids"	Monthly Meeting, Society for Applied Spectroscopy, Chicago, May 10, 1960
Fisher, D. J., ¹³ M. T. Kelley, W. L. Belew	"A Corrosion-Resistant Pipettor for Remote Measurement of Radioactive Samples"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Goldstein, G., O. Menis, ² D. L. Manning ¹³	"Indirect Determination of Sulfate by Nonaqueous Titrimetry"	138th Meeting, American Chemical Society, New York, Sept. 11-16, 1960
Handley, T. H., ¹³ J. A. Dean ⁴	"Tri-Alkyl Thiophosphates. Selective Extractant for Silver and Mercury"	Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Nov. 3-5, 1960
Horton, C. A., ¹³ J. C. White	"Infrared Study of Some Organo-Phosphorous Extractants"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 29-Mar. 4, 1960
	"Infrared Study of Some Phosphine Oxide Adducts"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 29-Mar. 4, 1960

Author(s)	Title	Presented at
Kelley, M. T., D. J. Fisher, ¹³ H. C. Jones, W. L. Maddox, R. W. Stelzner	"Applications of Commercial Operational Amplifiers in Instrumentation for Chemical Analyses"	Instrument Society of America, Fall Instrument-Automation Conference and Exhibit, New York, Sept. 26-30, 1960
Koirtyohann, S. R., ¹³ C. Feldman	"The Spectrographic Determination of Trace Elements in Human Tissue"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Kubota, H.	"Automatic Potentiometric Titration of Rare Earths with EDTA"	138th Meeting, American Chemical Society, New York, Sept. 11-16, 1960
Kubota, H., ¹³ L. Hemphill, T. Tamura	"Disposal Into Salt: Laboratory Studies of Simulated Waste and Salt"	ORNL Health Physics Division Information Meeting, Oct. 27-28, 1960
Leddicotte, G. W.	"Radioactivation Analysis"	Graduate Symposium, Department of Engineering, Agricultural and Mechanical College of Texas, College Station, Mar. 28, 1960 Symposium, Division of Chemistry, National Bureau of Standards, Washington, D.C., Oct. 4-6, 1960 Annual Meeting of the Association of Official Agricultural Chemists, Washington, D.C., Oct. 9-10, 1960
	"Radioactivation Analysis and the Analytical Chemist"	Summer Symposium, American Chemical Society, Houston, Tex., June 15-17, 1960
	"Radioactivation Analysis Applications"	ORINS Symposium on Nuclear Medicine, Oak Ridge, Tenn. Oct. 28-29, 1960
	"Radioactive Isotopes in Analytical Chemistry"	St. Louis Society of Analysts, St. Louis, Mo., Sept. 27, 1960
	"Recent Advances in Activation Analysis"	Washington Section Symposium on Recent Developments in Research Methods and Instrumentation, Bethesda, Md., Oct. 4-7, 1960
	"Utilization of Computers in Radiochemical Analysis"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Leddicotte, G. W., L. C. Bate, ¹³ J. E. Strain	"Useful Routine Radioactivation Analysis Applications"	8th Detroit Anachem Conference, Detroit, Mich., Oct. 24-26, 1960
Lyon, W. S.	"Standardization in Radioisotopes at the International Level"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960

Author(s)	Title	Presented at
Maddox, W. L., ¹³ M. T. Kelley, J. A. Dean ⁴	"Cathodic Stripping Voltammetry. Current-Stepping and Voltage-Stepping Procedures for Chloride Ion"	8th Detroit Anachem Conference, Detroit, Mich., Oct. 24-26, 1960
McCutchen, R. L.	"Statistics for Spectrographers"	8th Annual Spectroscopy Seminar, University of Florida, Gainesville, Jan. 6-8, 1960
	"Technical Writing - Bridge or Barrier to Effective Communication"	Industrial Editor's Institute, University of Tennessee, Knoxville, Oct. 28-29, 1960
Meyer, A. S., Jr., J. C. White, I. B. Rubin ¹³	"Gas Chromatographic Determination of He in Neutron-Irradiated BeO"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Miller, F. J., ¹³ P. F. Thomason	"Spectrophotometric Determination of Tc"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Norris, J. A. ¹³ R. L. McCutchen	"Investigation of Spectrochemical Solution-Methods of Analysis"	8th Annual Spectroscopy Seminar, University of Florida, Gainesville, Jan. 6-8, 1960
Reynolds, S. A.	"Basic Radiochemical Techniques"	R. A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Feb. 15, Aug. 25, 1960
	"Determination of Significant Radionuclides"	R. A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Feb. 15, Aug. 25, 1960
	"Determination of Radium"	R. A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Feb. 15, Aug. 25, Nov. 14, Nov. 16, 1960
	"Fundamentals of Radiochemistry"	Army Nuclear Science Seminar, Oak Ridge, July 31-Aug. 13, 1960
Ross, W. J., ¹³ J. C. White	"Application of Pyrocatechol Violet as a Colorimetric Reagent for Tin"	138th Meeting, American Chemical Society, New York, Sept. 11-16, 1960
	"Extraction of Tin with Tris(2-ethylhexyl)phosphine Oxide and Its Determination in Nonaqueous Medium with Pyrocatechol Violet"	138th Meeting, American Chemical Society, New York, Sept. 11-16, 1960
Shaffer, J. H., ¹³ W. R. Grimes, G. M. Watson, D. R. Cuneo, J. E. Strain,* M. J. Kelly	"The Recovery of Uranium and Protactinium from Molten Fluoride Systems by Precipitation as Oxides"	1st Conference on Nuclear Reactor Chemistry, Gatlinburg, Tenn., Oct. 12-14, 1960

Author(s)	Title	Presented at
Stelzner, R. W.	"Single-Beam Gamma Absorptiometer"	4th Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 12-14, 1960
Strain, J. E., ¹³ G. W. Leddicotte	"Analytical Applications of Neutron Absorptiometry and Neutron Transmission"	8th Detroit Anachem Conference, Detroit, Mich., Oct. 24-26, 1960
White, C. C., H. Kubota ¹³	"Titrimetric Determination of Mixtures of Monobutyl-, Dibutyl-, and Orthophosphoric Acids"	138th Meeting, American Chemical Society, New York, Sept. 11-16, 1960
White, J. C.	"Separations in Analytical Chemistry by Solvent Extraction with Organophosphorus Compounds"	Analytical Group, Western New York Section, American Chemical Society, Buffalo, New York, Oct. 3-5, 1960
White, J. C., ¹³ W. J. Ross	"Solvent Extraction with Tris(2-ethylhexyl)phosphine Oxide"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 29-Mar. 4, 1960
Willmarth, T. E.	"Design and Applications of the Electron Microscope"	Society for Non-Destructive Testing, Oak Ridge, Oct. 11, 1960
Young, J. P., ¹³ J. C. White	"Absorption Spectra of Molten Fluoride Salts: Solutions of Several Rare-Earth Fluorides in Molten Lithium Fluoride"	1st Conference, Nuclear Reactor Chemistry, Gatlinburg, Tenn., Oct. 12-14, 1960 Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Nov. 3-5, 1960



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