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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING APRIL 20, 1953

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ANALYTICAL CHEMISTRY DIVISION

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FOR PERIOD ENDING APRIL 20, 1953

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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

for

Period Ending April 20, 1953

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

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ABSTRACT

ANALYTICAL CHEMISTRY DIVISION
X-10 SITE

In the field of ionic research, the derivative polarographic system of end-point detection has been applied to the automatic microtitration of plutonium by use of the ORNL model Q-945 titrator. Nickel in HRE fuel solutions has been determined polarographically after ion-exchange separation from uranium. The spectrophotometric determination of aluminum in Thorex-process feed solutions, after extraction with a carbon tetrachloride solution of 8-quinolinol, is described. The determination of fluoride ion by use of the Dow Precision Recordomatic titrator is being investigated. The effect of volume on the extraction of carbamate complexes of copper, cobalt, and nickel was investigated. The usefulness of the method of vacuum-fusion analysis has been extended to the determination of oxygen in lead.

New developments and modifications in analytical instrumentation are reported. A shielded, filter photometer that is designed to protect the analyst and also the instrument from radiation damage has been built and put into service for the colorimetric analysis of radioactive solutions. The servo-controlled pipetor has been adapted for use in determining the densities of radioactive aqueous solutions by the falling-drop method. A precision instrument for determining the density of D_2O by the falling-drop method has now been assembled and is being tested and developed further. A laboratory-model oscillator for the study of solutions by high-frequency analysis has been built and it has been applied to the analysis of several types of solutions, including salts in organic liquids, water in organic liquids, and an aqueous electrolyte. The electronic sections of four automatically recording, internal-standard, flame photometers are being built by the Fabrication Section of the Instrumentation and Controls Division. Development of the optical section of this photometer is still in progress. A single-beam, automatically recording, flame photometer has been designed and put into service. It is used for the analysis of 75 to 100 samples per shift. The electronic section of a continuously recording, automatic, coulometric titrator has been designed and tested. It is planned to monitor the laboratory air for a basic gas with this instrument. The current that is required to continuously titrate the basic gas that enters the monitor is recorded and is directly proportional to the concentration of the basic substance in the air.

Radiochemical research has yielded new data on properties of Dy^{157}, Co^{57}, and As^{77}. Standards and standardization methods for scintillation counters and ionization chambers are discussed briefly. Certain new or unusual radioisotope products have been analyzed. A method of analyzing for Nb^{95} in the presence of large concentrations of Pa^{233} has been developed. Further progress in the assay of plutonium by alpha counting is reported. Significant results have been obtained in cyclotron research; abstracts of papers are included. Flux measurements for ANP and HRP have been done. Identifications of radioactive species in several types of samples are reported. Some applications of ion exchange and chromatography in radioisotope analysis have been found useful. The determination of uranium in solutions by x-ray absorption by employing a *K*-capture source of x rays appears promising.

The application of activation analysis to the determination of trace quantities of rare-earth elements, arsenic, aluminum, sulfur, cobalt, iron, tantalum, silicon and zinc, and of trace quantities of several elements in aluminum and petroleum is discussed. Inquiries regarding new applications of activation analysis are summarized.

The spectrochemical determination of boron was studied further, and the effects of several variables on the accuracy and precision of the method are discussed. New procedures for the spectrochemical determination of traces of metals in

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native iron and of platinum in solution are reported. A technique that extends the usefulness of microspark analysis is described.

Several inorganic compounds, including Mn_2Sb, UI_3, samarium compounds, and a group of phosphors, were synthesized for the Physics Division.

Optical and electron microscopy studies included examination of corrosion films of interest to the HRP, REED, and Chemistry Division; particle-size determinations on a variety of samples; and surface examination of electrolytically polished nickel and "fall-out" particles from the recent Nevada bomb test.

New methods that have been prepared for the *ORNL Master Analytical Manual* are listed.

Service analyses are summarized in tabular form, special problems being discussed briefly. Of particular interest is the summary of inquiries and requests for activation analyses, which indicates the extent of interest in this service.

ANALYTICAL CHEMISTRY DIVISION Y-12 SITE

Analytical studies for the ANP program have included five major problems: (1) determination of oxygen in metallic oxides by fluorination with bromine trifluoride, (2) volumetric determination of zirconium, (3) determination of reduced species in reactor fuels, (4) determination of traces of hydrogen fluoride in used helium, and (5) anodic dissolution of metallic fuel containers.

Work on the Raw Materials program included the complete analysis of raw lignites and a study of the molybdenum and fluoride concentrations throughout the various steps in the recovery process. The Raw Materials Analytical Laboratory was established as a separate entity to handle all requests of the Raw Materials Group.

In connection with investigations for the HRP, methods were studied for analyzing both the aqueous and solid phases of slurries of uranium trioxide and thorium oxide. The colloidal nature of these slurries required that they be separated, prior to the analysis, in a high-speed ultracentrifuge or by the addition of suitable salting agents. A rapid polarographic method has been adapted for determining traces of uranium dissolved in the aqueous phase of these slurries, and a sensitive method employing phenoldisulfonic acid reagent was developed for determining nitrate in the range 1 to 100 micrograms. Suitable separations and colorimetric methods have also been developed for determining phosphate, nickel, iron, thorium, and chromium in both phases of the slurries.

A colorimetric method based on the qualitative benzedine-acetic acid test was perfected for estimating the persulfate content of uranyl sulfate solutions from the HRE loop experiments. Technitium, an additive to these solutions, may be determined by separation as the sulfide and counting its beta activity.

A brief review of the quality control data for the past 12 months is presented in tabular form.

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PUBLICATIONS

G. W. Leddicotte and S. A. Reynolds, "The Determination of Trace Elements by Neutron Radioactivation Analysis," *ASTM Bulletin* **188**, 29 (February 1953).

P. F. Thomason, *The Spectrophotometric Determination of Lithium*, ORNL-1521 (April 17, 1953).

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ANALYTICAL CHEMISTRY DIVISION - X-10 SITE

RESEARCH AND DEVELOPMENT

IONIC ANALYSES

P. F. Thomason

Derivative, Polarographic, Microtitration of Plutonium (A. D. Horton, P. F. Thomason). The derivative, polarographic system of end-point detection[1] was applied to the ORNL model Q-945 automatic microtitrator in the Isolation Laboratory to determine 50 to 200 μg of plutonium because the routine potentiometric titration of plutonium was producing erratic potential breaks for the Cr(II)-Cr(III) and Pu(IV)-Pu(VI) oxidations.

Use of the derivative, polarographic end-point detection improved the plateaus of the Cr(II)-Cr(III) and Pu(IV)-Pu(VI) breaks, but the end points, as indicated by a reversal in direction of the potential breaks, were not sharp enough. A reduction from 500 to 200 μl in the volume of the sample titrated and a corresponding reduction in the size of the titration cell increased the sharpness of the breaks. The derivative, polarographic system has not yet been applied routinely by the Isolation Laboratory.

Polarographic Determination of Nickel in HRE Solution (M. T. Kelley, P. F. Thomason, A. D. Horton). Nickel in HRE solution has been determined polarographically, after separation from uranium by ion exchange, in a concentration of 2 μg/ml with an average deviation of a single determination of 0.09 μg. The HRE solution is pipeted onto an ion-exchange column of Dowex A-1 resin that has been treated with 6 *M* HCl. Uranium and some of the fission products are retained by the column, and nickel passes through. If suction is applied to the column, approximately 98% of the nickel can be removed from the column without rinsing. The volume of the eluted nickel solution is reduced by evaporation to about 1 ml, and the HCl is neutralized with NH_4OH. Sufficient HCl and pyridine are added to give a solution of 0.1 *M* pyridine-0.1 *M* pyridinium chloride when the solution is diluted to 5 ml. In this supporting electrolyte, nickel gives a fairly well-defined polarographic wave at an $E_{1/2}$ of −0.78 volt vs. the S.C.E.

[1] A. D. Horton, P. F. Thomason, and M. T. Kelley, "Automatic Derivative Polarographic Titration of Uranium and Iron with Ceric Sulfate," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 1.

Aluminum in Thorium-Containing Solutions (F. J. Miller). The method of Margerum *et al.*[2] for the spectrophotometric determination of aluminum in thorium has been used for the determination of as much as 60 μg of aluminum in solutions that contain thorium. By means of 8-quinolinol in chloroform, the aluminum is extracted from an aqueous nitrate solution that is buffered to pH 4.7 to 5.0 by an CH_3COONH_4-CH_3COOH buffer. Purification of the 8-quinolinol–chloroform solution by extraction with 0.5 *M* NH_4Cl–0.5 *M* NH_4OH solution is required. The transmittancy of the chloroform extract is read at 395 mμ.

Fluoride, Automatic Potentiometric Titration (J. M. Chilton). The determination of microgram amounts of fluoride by automatic, potentiometric titration that employs the Dow Precision Recordomatic titrator was investigated. A literature search disclosed that aluminum or thorium would be the most satisfactory titrant and that end-point detection would be possible by measurement of either the potential change of the Fe(II)-Fe(III) couple, as influenced by the fluoride ion, or of pH change. The pH change gave sharper and more reproducible results. The fluoride content of samples that contained as little as 50 μg of fluoride was determined by titration with potassium alum solution, pH end-point detection being used, with an average deviation of a single determination of 1%. The determination of smaller amounts of fluoride will be studied and the accuracy of the method established.

Simultaneous Determination of Copper, Cobalt, and Nickel (J. M. Chilton). Further investigation of the diethyldithiocarbamate colorimetric method for the simultaneous determination of copper, cobalt, and nickel[3] showed that the solution of nickel diethyldithiocarbamate obeyed Beer's law in solutions as concentrated as it is possible to measure with the model DU Beckman spectrophotometer, that is, the equivalent of 30 μg of nickel in 10 ml of CCl_4. Also, it was found that

[2] D. W. Margerum, W. Sprain, and C. V. Banks, "Spectrophotometric Determination of Aluminum in Thorium," *Anal. Chem.* 25, 249 (1953).

[3] J. M. Chilton, "Simultaneous Spectrophotometric Determination of Copper, Cobalt, and Nickel as Diethyldithiocarbamates," *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p. 8.

sample aliquots of 5- to 50-ml volume could be analyzed without difficulty. Larger aliquots, 75- to 100-ml, sometimes required as many as five extractions for complete removal of all the dithiocarbamates.

Chromatographic Separation of Mercury (W. D. Shults II, P. F. Thomason, H. P. Raaen). The study of the chromatographic separation of mercury by use of 2-methyltetrahydrofuran as the eluting solvent[4] has been continued. The effects of variables, such as acid, water, and nitrate contents of the solvent, valence state of the mercury, and elution time, have been investigated. No sharp separation of mercury was obtained with 2-methyltetrahydrofuran alone, but somewhat better results were obtained with a mixture of 2-methyltetrahydrofuran and *n*-butanol. The optimum conditions for movement of the mercury have been found, and the effectiveness of the separation of mercury from other metals is being studied by the use of radioisotopes.

Vacuum-Fusion Analysis of Metals and Alloys (W. J. Wolkowitz). The usefulness of vacuum-fusion analysis has been extended. By the analysis of reagent grade lead oxide, the method has been shown to be applicable to the determination, with a negative error of approximately 6%, of oxygen in lead. The dissimilarity between type 347 stainless steel and a substitute that was claimed to be its equivalent was indicated by the vacuum-fusion determination of the nitrogen and oxygen contents of the steels. Recent changes in the techniques and apparatus that are used in vacuum-fusion analyses include the use of nickel capsules instead of gold foil as containers for powdered samples and the replacement of graphite powder by $\frac{1}{16}$-in.-dia graphite particles as an insulator in the vacuum-fusion furnace.

ANALYTICAL INSTRUMENTATION

D. J. Fisher H. L. Hemphill

Shielded Filter Photometer. (M. T. Kelley, R. M. Farnham,[5] H. L. Hemphill). The HRE feedstream is analyzed colorimetrically for elements such as copper and nickel. Samples from this source are highly radioactive and present hazards to both the operator and the instrument. Commercial instruments are inadequate for the analysis of radioactive samples; therefore a shielded, filter photometer of a special design (Fig. 1) has been built and put into service.

The instrument consists of an exciter light source, filter, mirrors, cuvette holder, phototube, galvanometer, and appropriate housing. The cuvette holder is located out of line with the light filters and the phototube in order to protect these components from the direct beam of radioactivity. Light is directed by mirrors along a circuitous path through the filter, the test specimen, and to the phototube. Optical-density readings are taken from the galvanometer.

The components of this instrument were selected from parts of commercial instruments. The exciter light-source assembly and the cuvette holder are the same as those that are used in the model DU Beckman spectrophotometer. The phototube and the galvanometer are parts from a Welch Densichron. The filter is a composite made from Corning glass absorption filters.

Servo-Controlled Pipetor for Use in Determining the Density of Aqueous Solutions by the Falling-Drop Method (M. T. Kelley, H. L. Hemphill, A. L. Ennis). A servo-controlled pipetor has been adapted for use in the determination of the densities of aqueous solutions by the falling-drop method. This instrument features the monoliquid, positive-delivery, pipet control. The plunger is motor-driven and servo-controlled, which enables the operator to work at a distance from a radioactive sample.

Precision Instrument for Determination of the Density of Deuterium Oxide by the Falling-Drop Method (M. T. Kelley, H. L. Hemphill, W. Pruessner, N. D. Lee, L. Bate). The instrument for the determination of the densities of aqueous solutions that was discussed in a previous report[6] has been assembled and refined to meet the requirements of routine control. Reproducible calibration curves are obtained when the voltage of the metering condenser is plotted against density. In order to extend the range of the instrument, work is now

[4] H. P. Raaen and W. D. Shults II, "Separation of Mercury from Other Metals by Filter-Paper Partition Chromatography," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 5.

[5] Instrumentation and Controls Division.

[6] M. T. Kelly, P. F. Thomason, and W. Pruessner, "Instrumentation for the Determination of Densities of Aqueous Solutions by the Falling-Drop Method," *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p. 8.

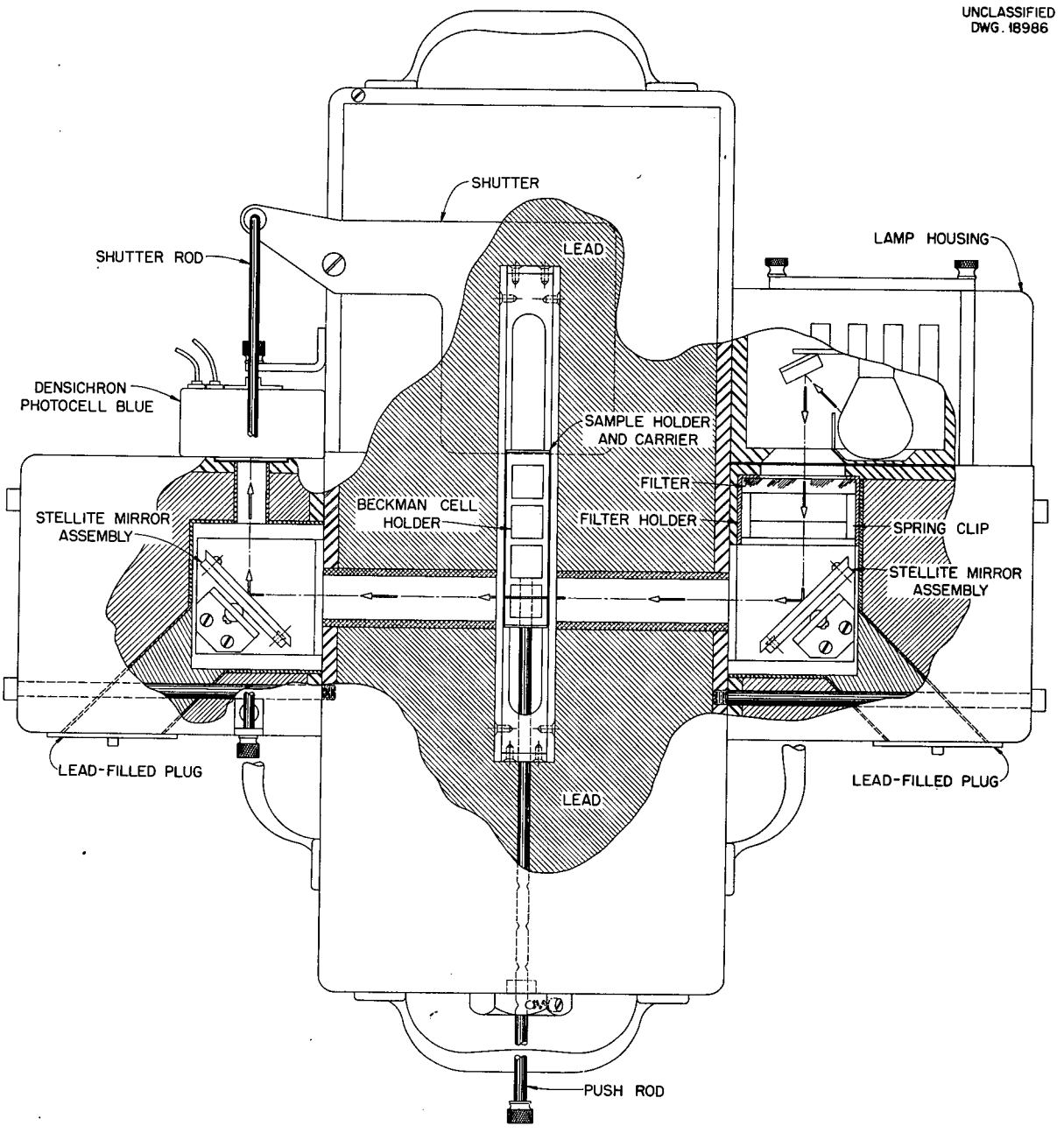

Fig. 1. Diagram of Shielded, Filter Photometer. Shows lead housing and location of components.

under way to provide a means for varying the density of the reference solution.

Analytical Applications of High-Frequency Oscillators. III. Laboratory Model Oscillator (M. T. Kelley, E. B. Wagner, D. J. Fisher). In a previous quarterly report,[7] it was stated that a general-purpose, laboratory-model oscillator (LMO) was planned. It had become apparent that in order to find optimum conditions for the study of various types of solutions within a reasonable time, an

[7] M. T. Kelley, E. B. Wagner, and D. J. Fisher, "Analytical Applications of High-Frequency Oscillators. II. ORNL Gridos," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 12.

oscillator that would be more flexible than the Gridos was needed. The LMO has now been built and evaluated initially.

The LMO is designed so that, by means of switches on the front panel and plugs for various coils, band-condensers, and coaxial cables, it can be changed to either a Colpitts or a Clapp-type oscillator. The design also permits variation in circuit parameters, in frequency over a wide range, of cells for the test solution, and of monitoring devices, such as microammeters and Brown recorders. Because optimum circuit conditions of high sensitivity can usually be determined and because the oscillator has good mechanical stability, adequate over-all stability can be obtained by the use of a voltage-regulated plate supply (*B*+) and a 6-volt Sola transformer for heater current.

The LMO has worked satisfactorily in tests that have been performed on several types of solutions.[8] It appears that the instrument will meet the need for a laboratory oscillator that should be versatile, stable, sensitive, and usable for quickly finding the conditions for the study of different types of solutions. A more detailed report on the instrument will follow.

Development of an Automatically Recording, Internal-Standard, Flame Photometer (M. T. Kelley, D. J. Fisher, H. L. Hemphill, N. D. Lee, C. Feldman[9]). Previous developmental work on the automatically recording, internal-standard flame photometer has been described.[10] From data obtained with standard solutions and from electronic tests of the ratio circuit, it was decided that the revised electronic design is satisfactory but that the optical system can be improved. The electronic units for four instruments are being built in the Fabrication Section of the Instrumentation and Controls Division.

The original electronic circuit was revised to permit the use of two modified Brown amplifiers. Because the recording instrument is a 50-mv Brown recorder, it was found feasible to convert a standard Brown amplifier from transformer to high-impedance input, thus eliminating the need for an ORNL model Q-1160 high-impedance preamplifier. Other revisions made possible the use of a second modified standard Brown amplifier in place of the special internal-standard-signal inversion amplifier previously required.[11] This flame photometer may be switched to record the single-beam output of either multiplier phototube, as well as the ratio of the two. The principle of the revised circuit is the same as before.

Work is being done on the optical units of the flame photometer. The positioning device for a Bausch and Lomb, wedge-type, interference filter has now been built, and the performance of this monochromator compares favorably with that of individual interference filters. However, it is not so good as that of the monochromator that is used in the model-B Beckman spectrophotometer. When a small amount of a substance such as potassium or magnesium, that has a weak emission, is to be determined in the presence of a very large amount of sodium, interference filters do not completely remove sodium-emission background at the emission wavelengths of the weakly emitting substance. Since it is desirable to have both multiplier phototubes "see" the same flame area under like conditions, the optical system that is used in the Perkin-Elmer flame photometer is being considered. Also, the relative merits of multiplier phototube types 1P21, 1P22, and 6217 are being determined. Results of this work on the optical system will be reported in the next semiannual report.

Single-Beam, Automatically Recording, Flame Photometer (M. T. Kelley, D. J. Fisher). A single-beam, automatically recording, flame photometer was needed; therefore an instrument was designed, built, and tested. It is now in routine use for the determination of several cations at the rate of 75 to 100 samples per shift.

A Beckman burner is used, and the optical system of a model-B Beckman spectrophotometer constitutes the monochromator. According to the emission wavelength that is used in the analysis, either a 1P21 or a 1P22 multiplier phototube is used. When it is available, a type 6217 will be tried; therefore an adapter has been built to mount a 6217 phototube on the monochromator. The electronic circuit is

[8] ORNL CF-53-4-122 (in press) (limited access).

[9] Spectrochemical Analysis Group.

[10] M. T. Kelley, D. J. Fisher, H. L. Hemphill, N. D. Lee, C. Feldman, and W. Pruessner, "Development of an Automatically Recording, Internal-Standard, Flame Photometer. III. Evaluation," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 8.

[11] M. T. Kelley and D. J. Fisher, "Development of an Automatically Recording, Internal-Standard, Flame Photometer. I. 100% Feedback, Impedance-Matching, Direct-Current Amplifier," *Anal. Chem. Quar. Prog. Rep. June 26, 1952*, ORNL-1361, p. 4.

similar to that of the automatically recording, internal-standard, flame photometer. The 50-mv Brown recorder is modified to register negative-going inputs. The input of the standard Brown amplifier is changed from transformer coupling to high-impedance coupling so that an ORNL model Q-1160 high-impedance preamplifier is not required. A battery-type, high-voltage power supply is used. The instrument is mounted in a standard enclosed relay rack.

Continuously Recording, Automatic, Coulometric Titrator (M. T. Kelley, D. J. Fisher, P. F. Thomason,[12] J. M. Chilton[12]). A request was received for a method of monitoring the concentration of a certain basic gas (an aliphatic amine) in laboratory air; therefore the continuously recording, automatic, coulometric titrator (CRACT) was designed, built, and applied to this analysis. The Instrumentation and Controls Division is designing and building the air-sampling device.

The CRACT consists of a two-compartment, coulometric, titration cell, a modified Leeds and Northrup pH indicator, catalog No. 7664, a modified Brown amplifier, an Esterline-Angus 1-ma recorder, and an air-sampling device. The titration cell is filled with Na_2SO_4 electrolyte. Air that contains the basic gas is bubbled through one compartment of the titration cell, and the resulting increase in the pH of the electrolyte is detected by a glass-calomel electrode system that is connected to the modified Leeds and Northrup pH indicator. The output of the indicator is amplified in the modified Brown amplifier. The current output of the amplifier is delivered to platinum electrodes in the titration cell, one electrode being in each compartment, and is recorded by the Esterline-Angus recorder. Because the positive platinum electrode is in the compartment that contains the pH electrodes and the air inlet, the incoming basic gas is titrated by coulometrically generated acid. The second compartment of the titration cell contains only the electrolyte and the negative platinum electrode. The total, coulometrically generated base in this compartment indicates the total equivalents of base received by the cell. When the CRACT is in operation, the current that is required to keep the entering substance titrated is recorded on the Esterline-Angus recorder and is directly proportional to the concentration of the basic substance in air. The same apparatus could monitor the concentration of an acidic substance in air.

[12] Ionic Analyses Group.

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Nuclear Properties

Dysprosium-157 (T. H. Handley). The nuclear properties of Dy^{157} are discussed under *Cyclotron Research* of this report.

Cobalt-57 (W. S. Lyon). The nuclear properties of Co^{57} are discussed under *Analysis of Radioisotopes* of this report.

Arsenic-77 (S. A. Reynolds, G. W. Leddicotte,[13] H. A. Mahlman[13]). Forty-hour As^{77} has been reported to decay by beta emission only.[14,15] By the study of a quantity of this nuclide that was prepared by the neutron bombardment of germanium, the nuclide was found to contain 1.4 ± 0.4% 0.25-Mev gamma radiation. The findings will be reported in detail in *The Physical Review*.

After this work was completed, a report[16] was received which indicated that similar research had been done at Los Alamos. The Los Alamos investigation reported gammas of 86-, 160-, 246-, and 524-kev energy.

Instrumental Methods

Standards and Standardization of Instruments for Radioactivity Measurement (W. S. Lyon). Natural-uranium standards and Cs^{137} standards for use throughout the Division with the well-type, sodium iodide, scintillation counters have been prepared, circulated for counting, calculated, and distributed.

NBS standard samples of Co^{60}, I^{131}, and P^{32} have been analyzed recently. The results indicate that the routine laboratory methods for the determination of Co^{60}, I^{131}, and P^{32} are accurate to about ± 3%.

With the assistance of G. N. Case,[17] the high-pressure ionization chamber in Building 4501 has

[13] Activation Analysis Group.

[14] Y. H. Woo, C. E. Mandeville, M. V. Scherb, and W. B. Keighton, "The Slow Neutron Induced Activities of Germanium," *Phys. Rev.* 75, 1286 (1949).

[15] C. E. Mandeville, Y. H. Woo, M. V. Scherb, W. B. Keighton, and E. Shapiro, "Radiations from Ge^{77} and Ge^{71}," *Phys. Rev.* 75, 1528 (1949).

[16] "Exerpts from the Progress Report, Los Alamos Scientific Laboratory, December 20, 1952," WASH-86, p. 4 (April, 1953).

[17] Radioisotopes Laboratory.

been calibrated, and the calibration of the ionization chamber in Building 3038 has been rechecked.

Analysis of Radioisotopes

New and Unusual Products (W. S. Lyon). The development of assay methods for new radioisotopes that are produced by the Operations Division has continued. Among unusual nuclides received for assay have been Te^{125m}, I^{125}, Co^{58}, Co^{57}, Eu^{152}-Eu^{154}, Ta^{182}, and Ir^{192}. Of particular interest has been the nuclide Co^{57} that is produced by the reaction Ni^{60} (p,α) Co^{57} on a normal Ni target. Cobalt-57 has been reported[18] to emit positrons and three gamma rays. By use of a thallium-activated, sodium iodide, gamma-ray spectrometer and an argon-methane, proportional-counter, x-ray spectrometer, it has been found that Co^{57} decays almost entirely by orbital-electron capture. In addition, the approximate branching ratios and the internal conversion coefficients of two of the gamma rays have been obtained. This work will be described in a separate report.

Rare-Earth Analyses (W. A. Brooksbank). The ion-exchange method of Boyd and Ketelle[19] has been used to analyze $Eu^{152,154}$ products for rare-earth impurities.

Fission Products

F. L. Moore

A new liquid-liquid extraction method for the separation of protactinium from niobium and for the determination of niobium has been developed for Thorex analyses. The method will be described in a forthcoming topical report.

Analysis for Heavy Elements

G. W. Smith

Plutonium Determination by Alpha Counting. Previous determinations of the plutonium content of L. T. Corbin's "standard" plutonium solution by alpha counting[20] were based on specific activities that were calculated from the Los Alamos estimate of Mwd/t and gave an assay of 10.69 ± 0.2 mg of plutonium per milliliter. The specific activity of this plutonium solution, when calculated by use of mass spectrographic and alpha-pulse analyses, gives an assay of 10.07 mg of plutonium per milliliter, which value agrees well with the titration value of 10.2 mg of plutonium per milliliter.

Synthetic uranium-dissolver solutions have been prepared and exchanged between the Oak Ridge and the Chalk River sites. The plutonium assay data that are now available on these solutions are given in Table 1. These data seem to indicate that counting and titration assays should agree when pure plutonium solutions of known specific activity are used.

Cyclotron Research

T. H. Handley

Assistance has been given to the Electromagnetic Research Division in the performance of the radiochemical phases of the following studies: yield distribution in proton fission of uranium, (p,pn) and $(p,\alpha n)$ excitation functions, and angular distribution of deuterons from Be^9 (p,d) Be^8. The first two topics will be presented at the April 30 to May 2 meeting of the American Physical Society in Washington. The latter is to be discussed in the April 15 issue of *The Physical Review*.

Dysprosium-157 (T. H. Handley, E. L. Olson[21]). The radiochemical properties of Dy^{157} were studied and will be discussed in the May 1 issue of *The Physical Review*. Highly purified terbium was bombarded with 24-Mev protons in the 86-in. cyclotron. Separations were made by ion exchange, and two radioactive species were found with the dysprosium fraction. By use of an excitation function, an 8.2-h activity was assigned to Dy^{157} and a 134-d activity to Dy^{159}. Terbium-157, which has been reported to have a 4.7-d half life,[22,23] was not observed as the daughter of Dy^{157}. A half life of less than 30 m, or greater than 100 y, was assigned to Tb^{157}. The gamma spectrum of Dy^{157} showed that the 8.2-h activity decays by K-capture with the emission of a 325-kev gamma ray.

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[18] K. Way, L. Fano, M. R. Scott, and K. Thew, *Nuclear Data* (Sept. 1, 1950) and *Supplements 1* (April 25, 1951), 2 (Nov. 26, 1951), and 3 (June 1952), NBS Circular 499.

[19] B. H. Ketelle and G. E. Boyd, "The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. IV. The Separation of the Yttrium Group Rare Earths," *J. Am. Chem. Soc.* 69, 2800 (1947).

[20] G. W. Smith, "Plutonium Analysis by Alpha Countings," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 19.

[21] Electromagnetic Research Division.

[22] G. Wilkinson and H. G. Hicks, *Radioactive Isotopes of the Rare Earths. III. Terbium Isotopes*, UCRL-421 (Aug. 18, 1949).

[23] G. Wilkinson and H. G. Hicks, "Radioactive Isotopes of the Rare Earths. III. Terbium and Holmium Isotopes," *Phys. Rev.* 79, 815 (1950).

TABLE 1. PLUTONIUM ASSAYS ON SYNTHETIC DISSOLVER SOLUTION

	OAK RIDGE SYNTHETIC (SCRUP) SAMPLE	CHALK RIVER SYNTHETIC SAMPLE
Titration at Oak Ridge, mg of Pu/ml	0.2694[a]	[b]
Counting at Oak Ridge, mg of Pu/ml, dpm/ml	0.269[c] 3.86×10^7	[d] 4.34×10^7
Titration at Chalk River, mg of Pu/ml	0.269[e]	0.284[e]

[a] Average of ten titrations.

[b] Data not available.

[c] Average of six plates, previously reported as 0.270 mg of plutonium per milliliter by slide-rule calculation. Specific activity calculated from mass and pulse analyses.

[d] Data not available for calculation of specific activity of plutonium.

[e] Average of four analyses.

ANP and HRP Analyses

ANP Analyses (W. A. Brooksbank). Samples of ANP fuel that had been irradiated in the MTR were analyzed for Cs^{137} in order to determine the total number of fissions that had occurred. E. H. Turk of ANL made the radiochemical cesium determinations and calculated the number of fissions by comparison with his standards.[24,25,26] Turk's mounts of $CsClO_4$ that were used in the cesium determination are currently being used by the Division as the primary standard for the determination of total fission by radiochemical Cs^{137} determinations. The method consists of separating cesium from the material under consideration and comparing the beta counting rate of Cs^{137} with that of the ANL standards. The samples are mounted in the same manner as the standards. The method is rapid and accurate to ±10% for the determination of total fissions.

HRP Analyses (W. A. Brooksbank). The apparent neutron flux of the HR No. 1 has been determined by the method reported previously.[27] The data were reported to S. Visner of the REED for his calculation of the power level of the HR No. 1.

Identification of Radioelements

D. J. Coombe S. A. Reynolds

Several interesting samples have been submitted recently for identification of active constituents. The activity that "fell out" at ORNL on March 19, 1953 was positively identified as material from the Nevada bomb test that had been made two days earlier.[28]

Samples of water from the HR No. 1 and the LITR have been found to contain fission products. The HR No. 1 samples contained no detectable amount of induced activity,[29] but the water from the LITR

(24) D. Fredrickson, R. LaPorte, M. Homa, E. Reilly, E. H. Turk, and R. C. Vogel, "Determination of Burn-up by Fission," *Argonne National Laboratory Summary Report for July, August, and September 1952, Chemical Engineering Division*, ANL-4922, p. 45.

(25) D. Engelkemeir, T. Novey, and E. Turk, "Determination of Breeding Gain," *Argonne National Laboratory Summary Report for July, August, and September 1951, Chemical Engineering Division*, ANL-4720, p. 21.

(26) D. Engelkemeir, T. Novey, and E. Turk, "Determination of Breeding Gain in the Experimental Breeder Reactor," *Argonne National Laboratory Summary Report for October, November, and December 1951, Chemical Engineering Division*, ANL-4764, p. 39.

(27) W. A. Brooksbank, "Neutron Flux Determination of HR No. 1," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 22.

(28) S. A. Reynolds, *Analysis of "Fall-Out" Activity at ORNL*, ORNL CF-53-173 (March 20, 1953).

(29) S. A. Reynolds, *Analysis of Water Sample 7-M-173*, ORNL CF-53-3-117 (March 17, 1953).

contained significant amounts, particularly of Na^{24}.[30]

Techniques of decay measurements, absorption, gamma spectrometry, and radiochemical separation were used. Personnel of the General Radiochemistry Group made the radiochemical fission-product analyses.

Ion Exchange and Chromatography

G. W. Smith

Analysis for Rare-Earth Activities in Ba^{140}-La^{140}. As reported previously,[31] a method employing ion exchange, together with radiochemical procedures, was developed for rare-earth impurities in Ba^{140}-La^{140} product. The final method, which is relatively simple but which requires instrumentation in the form of a G-M tube detector, logarithmic count-rate meter, and Brown recorder, was put into memorandum form and copies were furnished to E. I. Wyatt.[32] If warranted by sufficient usage, the method will be prepared for the *ORNL Master Analytical Manual.*

Application of Paper Chromatography in Radioisotope Analysis. A method was requested for determining total nickel, including Ni^{63}, in Cr^{51} product. Preliminary experiments[31] indicated that a collidine-nitric acid mixture showed promise as an eluting solvent. Additional experiments were made with collidine, pyridine, and methanol-acetone mixtures that contained various amounts of nitric acid. A separation was effected with a 1:1 volume mixture of collidine and 0.4 N HNO_3. The chromium remained stationary and the nickel moved. The R_f value of the nickel was 0.8 to 0.9. Recoveries of known amounts of nickel from the chromatographic separation were roughly quantitative. The analysis of two lots of Cr^{51} product showed that Ni^{63} was absent in both; the lower limit of detection of the nickel by the method employed was approximately 2 μg. The separation procedure and the methods for detecting the nickel and chromium loci are described in a memorandum to E. I. Wyatt,[32] and a method will be prepared for the *ORNL Master Analytical Manual.*

(30) S. A. Reynolds, *Analysis of LITR Water Samples*, ORNL CF-53-4-12 (April 3, 1953).

(31) G. W. Smith, "Ion Exchange and Chromatography," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 23.

(32) Radioisotopes Laboratory.

Miscellaneous Activities

Determination of Uranium in Solution by X-Ray Absorption (S. A. Reynolds, D. J. Coombe). The determination of uranium in solution by x-ray absorption, which employs G-E x-ray photometers as sources of x rays, has been described.[33,34,35] The instruments are expensive and not readily available; however, radionuclides offer a possible alternate source of monochromatic x rays. An apparently suitable nuclide now being studied is Cd^{109} that is produced by the reaction Cd^{108} (n,γ) Cd^{109} under long bombardment of cadmium oxide enriched to approximately 28.4% Cd^{108}. An x-ray detector that consists of a Tracerlab model 64 scaler and a North American Philips Co. x-ray tube operated in the Geiger voltage range has been assembled. The detector is so arranged that samples, sources, and absorbers can be inserted from the top rather than from the front in the conventional way. Standard uranium curves will be prepared from data obtained by counting the Cd^{109} source through standard solutions of uranium and other elements by means of this x-ray detector.

ACTIVATION ANALYSES

G. W. Leddicotte

Trace Quantities of Rare-Earth Elements (W. A. Brooksbank, G. W. Leddicotte). The study of the quantitative determination of the rare-earth elements by the combined use of ion-exchange separation and neutron-activation analysis[36] has been continued. The practical limits of sensitivity have been determined, and the optimum conditions for elution with citrate buffer have been established for all the rare earths except cerium and praseodymium. These elements are now under study. Analysis time has been decreased appreciably by

(33) T. W. Bartlett, R. B. Bauder, J. H. Lykins, E. B. Olszewski, and R. H. Lafferty, Jr., *The General Electric X-Ray Photometer and its Application to the Determination of Uranium. I. Instrument Modifications*, AECD-2765 (March 4, 1949).

(34) T. W. Bartlett, *The General Electric X-Ray Photometer and its Application to the Determination of Uranium. II. Determination of Uranium in Solutions*, AECD-2766 (Oct. 28, 1949).

(35) W. F. Peed and H. W. Dunn, *Preliminary Investigation of Monochromatic X-Ray Absorption as a Method of Analysis for Uranium*, ORNL-1265 (April 8, 1952).

(36) W. A. Brooksbank and G. W. Leddicotte, "Determination of Trace Quantities of the Rare-Earth Elements," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 23.

the use of a LaF_3 precipitation instead of a volume-reduction column for the recovery of the radioactivity. Animal tissue will be the first material to be analyzed by this method, and it is now being irradiated.

Trace Quantities of Arsenic in Germanium and Germanium Compounds (H. S. Mahlman, G. W. Leddicotte). The procedure of Smales and Pate[37] for the determination of submicrogram quantities of arsenic by radioactivation has been adapted to the assay of trace amounts of arsenic in germanium metal and germanium compounds. In this method, radioactive arsenic, that is, 26.8-h As^{76} and 40.0-h As^{77}, is isolated by evolution as $AsCl_3$ and precipitated as $NH_4MgAsO_4 \cdot 6H_2O$ for yield-determining purposes. The beta radiations of the precipitate are counted through a 300 mg/cm^2 aluminum absorber in a Geiger-Mueller counter. The As^{77} beta radiations that are formed by the reaction Ge^{76} (n,γ) $Ge^{77} \xrightarrow{\beta-} As^{77}$ are completely absorbed by this absorber, and the attenuated portion of the As^{76} beta radiations formed by the reaction As^{75} (n,γ) As^{76} is counted.

Compilations of nuclear data indicate that gamma radiation is not associated with As^{77}.[38] Thus it was expected that a thallium-activated, sodium-iodide, scintillation counter would be useful for a rapid determination of arsenic in samples of germanium metal and its compounds because only the gamma radiation from the As^{76} would be detected. However, appreciable interference from a gamma component of 40-h half life was experienced. The results of several analyses indicate that this gamma radioactivity is associated with As^{77}, the product of the (n,γ) reaction on Ge^{77}. A more complete discussion of the work is given in the section *Arsenic-77* of this report.

Trace Quantities of Aluminum (H. A. Mahlman, G. W. Leddicotte). The direct-counting method for the determination of trace amounts of aluminum that was described previously[39,40] is not always applicable to aluminum determination in certain materials, for example, metals and alloys. Therefore a separation of the aluminum before neutron bombardment is being investigated. A technique is used in which the aluminum is carried on a non-isotopic carrier, such as Fe(III), which will not form an appreciable amount of radioactivity other than aluminum in the bombardment time used, that is, less than 10 minutes. The carrier, plus the aluminum, is precipitated with an organic reagent, the precipitate is bombarded with neutrons, and the analysis is effected by the direct counting method already described.[40]

Trace Elements in Aluminum (H. A. Mahlman, G. W. Leddicotte). The determination of traces of Cu, Ni, Fe, Ca, Mg, Mn, and Si contaminants in electrolytic aluminum is being studied. The results for Cu are in good agreement with those reported by the manufacturer of the aluminum, and excellent reproducibility has been achieved.

Simultaneous Determination of Cobalt, Iron, and Zinc in Irradiated Material (H. A. Mahlman, G. W. Leddicotte). The feasibility of determining trace amounts of more than one element in a single irradiated sample by activation analysis has been demonstrated by the determination of Co, Fe, and Zn in animal tissue. The limitation is that the half lives of the radioelements measured must be sufficiently long to permit the separations and determinations of the separate elements.

Trace Elements in Petroleum (H. A. Mahlman, G. W. Leddicotte). The determination of trace amounts of Cu, Fe, Ni, and V[41] in petroleum by activation analysis is being investigated further as a result of increased interest in the method. Crude oil and oil fractions will be analyzed, and particular emphasis will be given to the nickel determination.

Trace Quantities of Sulfur (H. A. Mahlman, G. W. Leddicotte). The determination of trace amounts of sulfur in a variety of materials by the reaction S^{34} (n,γ) S^{35} has been complicated by the reaction Cl^{35} (n,p) S^{35}. Also, the weakness of the 0.16-Mev beta radiation that is associated with S^{35} makes difficult the isolation of S^{35} radioactivity in a form suitable for weighing. The feasibility of determining sulfur by use of the reaction S^{32} (n,p) P^{32} and

(37) A. A. Smales and B. D. Pate, "Determination of Submicrogram Quantities of Arsenic by Radioactivation," *Anal. Chem.* 24, 717 (1952).

(38) K. Way; L. Fano, M. R. Scott, and K. Thew, *Nuclear Data* (Sept. 1, 1950) and *Supplement 3* (June, 1952), NBS Circular 499.

(39) W. A. Brooksbank and G. W. Leddicotte, "Determination of Trace Elements by Means of Their Short-Lived Radioisotopes," *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p. 24.

(40) H. A. Mahlman, "Determination of Trace Amounts of Aluminum in Rubber," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 27.

(41) W. A. Brooksbank and G. W. Leddicotte, "Determination of Trace Amounts of Vanadium in Petroleum Hydrocarbons," *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p. 25.

the measurement of the P^{32} radioactivity is under study.

Silicon in Germanium Compounds and Aluminum (T. C. Rains, G. W. Leddicotte). Activation analysis is being considered as a method for the determination of Si in germanium compounds and electrolytic aluminum. A separation procedure adapted from the work of Brabson *et al.*[42] and Jewsbury[43] was studied. It was found difficult to obtain a SiO_2 precipitate that was suitable for yield determination, mounting, and counting. The study will be continued.

New Applications of Activation Analysis (G. W. Leddicotte). Inquiries have been received regarding the suitability of the method of activation analysis for the determination of trace quantities of the following elements in the materials indicated: I in crude biological materials; Cu in animal heart tissue; metallic elements in methanol, catalytic reagents, and paints and pigments; Ta in tantalum-bearing ores; Al, P, Sb, In, and Cu in germanium compounds; rare earths in petroleum; and Mo in ores.

SPECTROCHEMICAL ANALYSES

C. Feldman
J. Y. Ellenburg M. Murray
A. J. Estepp M. K. Wittels

Traces of Boron. Study of the spectrochemical determination of boron has continued.[44] The precision and accuracy of the method in the lowest range appears to be limited by the occasional presence of residual boron in the carbon electrodes, although only those of highest purity are used. This difficulty has been eliminated by burning all electrodes before they are shaped and by using only those that are boron-free.

An internal standard that is usable for the determination of boron in all matrices is desirable, although gold behaved well in the determination of boron in carbon or graphite. The best substance found is finely powdered, metallic iridium, which appears to duplicate the volatilization behavior of boron in both constant-temperature and rising-temperature burns. A straight-line calibration curve has been constructed between 0.22 and 1.0 ppm of boron in graphite by the use of 30 ppm of iridium as the internal standard. The maximum spread of quadruplicate exposures, obtained by use of the line-pair B 2497/Ir 2543, was 3% of the value of the intensity ratio.

The removal of boron from uranium solutions by the use of carbonate ion to simultaneously hold uranium in solution and to precipitate $CaCO_3$, which carries down boron as $Ca_3(BO_3)_2$, proved impractical because of coprecipitation of uranium salts. Preliminary experiments show that calcium oxalate, which can be precipitated in the presence of uranyl ion without carrying down uranium, will coprecipitate boron as efficiently as $CaCO_3$.

Traces of Precious Metals in Native Iron. A procedure has been developed for the spectrographic determination of precious metals in native iron. The method provides for either the dissolution or nondissolution of microgram amounts of these metals; this is necessary because nothing is known about the chemical or physical form in which precious metals might occur. Preliminary tests have shown that the recovery of palladium, platinum, gold, silver, ruthenium, rhodium, and iridium from solution by the procedure is essentially complete.

Microspark Analysis. The usefulness of conventional microspark analysis is limited because of the lack of suitable metals and alloys for standards and because the spark avoids nonconducting particles. The semiquantitative technique of Bryan,[45] which employs microdrills as sampling tools for metallurgical specimens, has been modified and extended to permit quantitative analysis of 0.005 to 0.010-in.-dia areas in conducting (Inconel, stainless steel) and nonconducting (magnetite) specimens. Sample weights range from 20 to 100 μg.

Platinum in Solution. An analytical curve was constructed for determining 15 to 500 ppm of platinum in solution. Standard solutions were treated with 75 ppm of cobalt(II) and exposed spectrographically by the porous-cup technique. The curves were used to determine platinum in a

[42] J. A. Brabson, H. C. Mattraw, G. E. Maxwell, A. Darrow, and M. F. Needham, "Determination of Silica," *Anal. Chem.* 20, 504 (1948).

[43] A. Jewsbury, "A Rapid Photometric Determination of Silicofluoride in Hydrofluoric Acid, Ammonium Fluoride, Sodium Fluoride and Soluble Coloured Fluorides," *Analyst* 75, 256 (1950).

[44] C. Feldman, J. Y. Ellenburg, A. J. Estepp, M. Murray, and M. K. Wittels, "Determination of Traces of Boron," *Anal. Chem. Quar. Prog. Rep. Jan. 19, 1953*, ORNL-1474, p. 29.

[45] F. R. Bryan, "Metallurgical Microspectroscopy Using Microdrills," *J. Opt. Soc. Amer.* 41, 1061 (1951).

solution that was obtained by treating platinized alumina beads with aqua regia.

INORGANIC PREPARATIONS

D. E. LaValle R. H. Sampley

Special Preparations (D. E. LaValle). The following products were made for the Neutron Diffraction Group of the Physics Division: 26.4 g of Cr^{52} isotope was prepared in the metallic form by converting the oxide to chromic acid and electrolyzing; 50 g of Mn_2Sb was prepared by reaction of the elements at 950°C; and 20 g of pyrrhotite (Fe_7S_8) was prepared by union of the elements in an atmosphere of H_2S at 700°C.

A 110-g quantity of $Sm(C_2H_5SO_4)_3$ was made for the Low Temperature Group of the Physics Division by adding a solution of $Ba(C_2H_5SO_4)_2$ to a solution of $Sm_2(SO_4)_3$. Also, 75 g of UI_3 was prepared by direct union of the elements at 350°C, and another 75 g was made by passing CH_3I over UH_3 at 275°C.

Phosphors (R. H. Sampley). The following phosphors were prepared: purified methyl methacrylate monomer activated with 3% *p*-terphenyl and then polymerized; lithium iodide activated with each of the following compounds: $TmCl_3$, $TbCl_3$, $GdCl_3$, $PrCl_3$, $YbCl_3$, $CeCl_3$, NdI_3, Ho_2O_3, $Y(NO_3)_3$, $RuCl_3$, H_2SeO_3, and Dy_2O_3.

Purifications (R. H. Sampley). Large quantities of LiCl, $(NH_4)_2CO_3$, Li_2CO_3, LiI, HI, Na_2CO_3, and methyl methacrylate monomer were purified.

OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth
F. D. McNeer I. H. Gary

Corrosion Studies. The study of oxide corrosion films and the examination of metals that have been exposed to aqueous solutions of a corrosive nature has been continued for the HRP, REED, and Chemistry Division. Of general interest was the examination by optical and electron microscopy and electron diffraction of individual samples of type 347 stainless steel that had been immersed for 13 days in solutions that contained 300 g of UO_2SO_4 per liter at 300-psi partial oxygen pressure and at temperatures of 100, 130, 160, 190, 220, and 250°C. Optical examination disclosed colorless, thin films on the samples immersed at 100 and 130°C, and thick (2- to 4-μ), red to red-black films were found on the others. The approximate thicknesses of the two thin films were found by subsequent electron microscopic examination to be 500 to 1000 Å. Except for small areas, the films on the higher temperature samples were opaque to the electron beam. Electron-diffraction patterns provided lattice spacing values which indicated, within the limits of experimental error, that the films on the 100 and 130°C samples were primarily cubic gamma Fe_2O_3, and that those on the 160, 190, 220, and 250°C samples were mixtures of the hexagonal alpha Fe_2O_3 and Cr_2O_3. This would indicate that phase change from the gamma to the alpha form of Fe_2O_3 takes place in aqueous solutions under the stated conditions at a lower temperature than it does in air, that is, 225°C.

Other oxide films that were examined included those formed on type 347 stainless steel that was exposed for 116 hr at 250°C in a solution that contained 300 g of UO_2F_2 per liter, that was 0.2 *M* in LiOH, and that contained 800 to 1500 ppm of oxygen. The oxide film also formed on type 347 stainless steel in a solution that was similar except that the oxygen content was 100 ppm and the exposure time 49 hr; and the film formed on type 347, annealed stainless steel that was exposed in UO_2SO_4 solution at 250°C. Other corrosion studies included the examination of type 347 stainless-steel-clad samples and electropolished samples exposed for 20 hr to a solution that was 1.26 *M* in each of Na_2SO_4 and UO_2SO_4 at 250°C and of type 347 stainless steel decontaminated in both oxalic acid and $KMnO_4$ solutions.

Particle-Size Studies. The following materials were photographed in either the optical or the electron microscope, and particle-size measurements were made: ThO_2 produced from the oxalate; ThO_2 produced by the Ames method; ThO_2 from the carbonate; UF_4; irradiated and nonirradiated $UO_3 \cdot H_2O$; silica gel that was nonirradiated, irradiated in air, irradiated in H_2O, and irradiated in acid solution; "popcorn" exchange resins; KCl; and KCl in benzene.

Crystallography and Analysis by Electron Diffraction. Identification was made of the following by optical and electron-diffraction methods: corrosion products from SAE 1030 carbon steel after a nine-week exposure in the LITR; the corrosion product from natural uranium that had been immersed in deaerated, distilled water at 200°C; a

precipitate collected on a silver electrode in a chloride solution; and the contaminant found in $UO_3 \cdot 2H_2O$ produced from UO_2F_2. Electron-diffraction studies were made of PbO and $Cr_{23}C_6$.

Metallography and Surface Studies. Samples of nickel that had been polished electrolytically in phosphoric acid were examined to determine whether incongruities in the surface were the result of surface inclusions of foreign material or were a specific polishing effect caused by the electrolyte used. Also, various samples of type 347 stainless steel that had been exposed to corrosive solutions in which $KTcO_4$ was present as a corrosion inhibitor were examined for pitting and surface effects.

"Fall-out" particles collected in the vicinity of Oak Ridge after the recent Nevada bomb tests were observed optically for noteworthy structural and surface details. The particles examined were found to be approximately spherical and of 24-μ diameter. Most of them were black and opaque; one was found to be glassy and translucent. The surfaces appeared to be covered with small protrusions, approximately 1-μ in height, that imparted an "orange skin" effect.

Autoradiographs. Autoradiographs of tritium on zirconium-coated tungsten were made for the Operations Division to determine coating uniformity. To avoid air contamination effects, samples were given photographic exposure in an argon-filled dry box.

Miscellaneous. Composite lantern slides were made of autoradiographs from radioactive surfaces, together with the metal that contained the source material. A preliminary study of possible techniques for examining carbides precipitated in type 347 stainless steel has been started. Examination is also being made of a means of metering the magnetic lens currents in the Philips electron microscope to permit precision electron-diffraction work to be done with the instrument.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods and H. P. Raaen

The following methods, not reported previously, have been prepared for issuance in Section 9, "Process Methods," of the *ORNL Master Analytical Manual:*[46]

Method Title	Author
Gross Alpha Activity in Aqueous or Organic Solutions	R. L. Wolker
Gross Beta Activity in Aqueous or Organic Solutions	R. L. Walker
Tributyl Phosphate in Organic Diluents, Acid Equilibration	G. R. Wilson
Nonvolatile Material	E. I. Wyatt
Total Cation Concentration of Aqueous Solutions, Ion Exchange	E. I. Wyatt
Nitrates, Brown Ring Test	E. I. Wyatt
Total Reducing Agents	E. I. Wyatt
Heavy Metals, Spot Test	E. I. Wyatt
Chloride, Turbidimetric Method	E. I. Wyatt
Manganese, Spot Test	E. I. Wyatt
Product Analysis Guide for:	E. I. Wyatt
Barium-140	
Beryllium-7	
Calcium-45	
Carbon-14	
Chlorine-36	
Cobalt-60	
Iodine-131	
Neodymium-147–Promethium-147	
Niobium-95	
Phosphorus-32	
Promethium-147	
Ruthenium-103,106	
Scandium-46	
Sodium-22	
Sodium-24	
Strontium-89	
Sulfur-35	
Zirconium-95–Niobium-95	
Carbon-14, Beta Ionization Chamber Method	E. I. Wyatt
Phosphorus-32	E. I. Wyatt

Drafts of a number of other methods have been prepared for the "Ionic," "Radiochemical," and "Process" sections of the manual. Also, formal schedules for the writing of methods for the Purex and Orex processes have been issued.

[46] H. P. Raaen, "ORNL Master Analytical Manual," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 7.

SERVICE ANALYSES

A summary of the service analyses made at the X-10 Analytical Chemistry Division laboratories is given in Table 2.

IONIC ANALYSES

P. F. Thomason

The service work by the Ionic Research and Development Group consisted of analyses for the HRP and the Orex processes. The methods that were used have been discussed previously.[1,2]

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Most of the work of the Radiochemical Analyses Group was done for the Electromagnetic, Operations, and Chemical Technology Divisions. Radiochemical analyses were done for the Electromagnetic Division in connection with the cyclotron program. Assay and purity tests of new or unusual products were made for the Operations Division. The work for the Chemical Technology Division included special plutonium and fission-product analyses and identifications.

ACTIVATION ANALYSES

G. W. Leddicotte

The extent of interest that has been shown by the Oak Ridge plant sites and outside organizations in the activation analysis service, as indicated by inquiries and requests for analyses, is summarized in Table 3. The difference in number between the inquiries and the requests for analyses that have been received from outside organizations can be explained in part by the normal time lag required for the submission of samples.

Analyses have been made for Cu in aluminum; Co, Fe, and Zn in animal tissue; U on paper chromatograms; and As in germanium metal and germanium compounds.

GENERAL ANALYSIS LABORATORY

J. H. Edgerton

The Metallurgy and Chemical Technology Divisions requested the determination of low concentrations of silica in uranium alloys and salts. The silica is being determined[3] by extracting the uranium with tributyl phosphate and by measuring the silica that remains in solution by the ammonium molybdate spectrophotometric method.

A ter Meulen apparatus[4] is being constructed by the Glass Shop for the determination of nitrogen in organic liquids. The apparatus is expected to be in operation in the near future.

The Chemistry Division is studying the solubilities of metal oxides in UO_2F_2 and UO_2SO_4 solutions. The fluoride and sulfate were separated from the uranyl ion on a 1- by 4-cm column of 12% cross-linked, 200-mesh, Dowex-50 resin,[5] and then determined by heating the eluate to boiling to evolve CO_2 and titrating the hot solution with standard alkali by use of the ORNL model Q-945 automatic titrator.[6] The use of 0.4- by 3-cm ion-exchange columns is also being considered.

LABORATORY AND SEMI-WORKS CONTROL

L. T. Corbin G. R. Wilson
M. J. Gaitanis

Assistance was given to the Thorex Group of the Chemical Technology Division in their studies of the nitric acid concentration of the CW and CU streams of the Thorex process. The uranium capacity of the ion-exchange resin that is used in the Thorex process to separate uranium and thorium is a function of the acidity of the two streams.

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(1) P. F. Thomason, "Ionic Analyses – Development Group," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1951*, ORNL-955, p. 65.

(2) M. T. Kelley, *Analytical Chemistry for Orex Process for Period Ending December 26, 1952*, ORNL CF-53-2-236 (Feb. 7, 1953).

(3) W. B. Wright, Jr., *Determination of Silicon in Uranium Metal*, Y-893 (May 15, 1952).

(4) J. Holowchak, G. E. C. Wear, and E. L. Baldeschwieler, "Application of ter Meulen Nitrogen to Petroleum Fractions," *Anal. Chem.* 24, 1754 (1952).

(5) J. H. Edgerton and J. F. Emery, "Ion-Exchange Separation of Fluoride," *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p. 35.

(6) J. H. Edgerton and L. C. Henley, "Automatic Potentiometric Microtitration of Boron," *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p. 35.

TABLE 2. SUMMARY OF ANALYTICAL SERVICE WORK AT X-10 SITE FOR THE FIRST QUARTER OF 1953

	NO. OF PERSONNEL		ORNL DIVISIONS REQUESTING ANALYSES																OTHERS REQUESTING ANALYSES				
	TECHNICAL	NONTECHNICAL	ANALYTICAL CHEMISTRY	ANP	BIOLOGY	CHEMICAL TECHNOLOGY	CHEMISTRY	ELECTROMAGNETIC	ENGINEERING AND MAINTENANCE	HEALTH PHYSICS	HRP	LABORATORY PROTECTION	MATERIALS CHEMISTRY	METALLURGY	OPERATIONS	PHYSICS	REED	SOLID STATE	K-25	ORSORT	TVA	OTHERS	TOTAL DETERMINATIONS
GROUP MAKING ANALYSES			Number of Determinations																				
Activation Analyses	5	5	793	24		630	165			42	47				958			140	27				2,826
ADP Control	4	9				2,688	21																2,709
General Analyses	5	7				3,311	884		26		6			582	79	43		85	9				5,025
General Radiochemical	5	6	94			7,431				280								14			70		7,889
HRE	2	2															713						713
Ionic Analyses	7	1	10			146	27				62					2							247
Laboratory and Semi-Works Control	2	8		77		7,282	3				762			120	14				481				8,739
Optical and Electron Microscopy	3	1	24		8	208	85			8	7			18	16		149						523
Pilot Plant Control	3	5				7,060											514						7,574
Plutonium Isolation Laboratory	1	4				2,739		26								9							2,774
Radiochemical Analyses	6	1	22	2		50		295		18			11		99		23			20			540
Radioisotope Production Control	2	16				2,090	8								7,965	89		327				15	10,494
Spectrochemical Analyses	5	0	3			680	27		1		54	1		97	45	27	252						1,187
TOTAL	50	65	946	103	8	34,315	1,220	321	27	348	938	1	11	817	9,176	170	1,651	566	517	20	70	15	51,240

TABLE 3. SUMMARY OF ACTIVATION ANALYSIS SERVICES

PERIOD	INQUIRIES FROM OUTSIDE ORGANIZATIONS	REQUESTS FOR ANALYSES	
		From Oak Ridge* Plant Sites	From Outside Organizations
Before November 30, 1952**	88	68	30
December, 1952	10	7	4
January, 1953	9	8	2
February, 1953	8	8	2
March, 1953	13	7	4
Total	128	98	42

*Same as the number of inquiries.

**Memorandum to A. M. Weinberg from M. T. Kelley, December 18, 1952.

PILOT PLANT CONTROL

L. T. Corbin C. E. Lamb

Upon completion of the Purex process, the Hot Pilot Plant Group made a series of studies on the stainless steel equipment and submitted samples to be analyzed for gross beta and gamma activities, fluoride, iron, nickel, chromium, oxalic acid, hydrogen peroxide, and free acid. The results were used to check the degree of corrosion and decontamination. Iron and organic substances interfered in the chromium[7] determination and were eliminated by boiling with sulfuric-nitric acid and by the use of phosphoric acid to stabilize the iron. Fluoride interfered with the nickel[8] determination and was eliminated by boiling the solution with hydrochloric acid.

Calibration curves of the vibrating-reed ionization chambers in the Building-3019 Control Laboratory and in the Radioisotope Laboratory were compared. The results indicated that the ion chamber in the Radioisotopes Laboratory gave results that were 13.0% greater than those given by the ion chamber in Building 3019.

[7]E. B. Sandell, *Colorimetric Determination of Traces of Metals* 2d ed., p. 260, Interscience, New York, 1950.

[8]Ibid., p. 470.

[9]Du Pont Co.

[10]R. W. Foster, *A Brief Study of Uranium and Iron Interferences in the Plutonium TTA Methods*, DPO-53-120 (March 23, 1953).

HRE ANALYSES

U. Koskela

The work of the HRE Analyses Group has consisted primarily of colorimetric, titrimetric, and gravimetric determinations of uranium. Also, the HR fuel has been analyzed for chloride and silver by use of the ORNL model Q-945 automatic titrator.

Very high levels of radiation were attained in samples during the power-producing operation of the HRE on March 18. The activity of samples was 75 to 100 r at distances of 2 to 3 ft, which is somewhat greater than can be handled safely with present equipment. Various members of the Division are assisting in designing better tools and in modifying existing procedures for more remote operations.

ISOLATION ANALYSES

L. T. Corbin J. H. Cooper

The Isolation Analyses Group has continued uranium and plutonium analyses on the single-channel "Bluenose" samples, in addition to routine control and product samples.

An investigation by C. E. Pietri[9] and R. W. Foster[9] showed that iron and uranium do not interfere in the TTA extraction method for plutonium.[10]

Tests of induction fusion of sodium fluoride pellets for fluorometric uranium determination were

made by C. E. Pietri.[9] Fusion with an induction heater is a more rapid technique than the gas-flame fusion now in use.[11] A report on the technique and results is being prepared.

The method for preparing Scrup dissolver solutions for plutonium titration has been revised to include two diisopropyl ether extractions for the removal of iron. A synthetic Scrup dissolver solution was prepared and analyzed for uranium and plutonium. A duplicate of the synthetic solution was sent to the Chalk River laboratories for analysis. The results obtained at ORNL agreed with those at Chalk River within acceptable limits.

D. Madinabeitia[9] has developed a method for the valence-state analysis of plutonium. An anion resin is used to separate Pu(III) from Pu(IV) and Pu(VI). Plutonium(IV) is separated from Pu(VI) by a TTA extraction[12] in which the Redox step is omitted. A report on this work is being written.

(11) M. T. Kelley, P. F. Thomason, L. T. Corbin, S. A. Reynolds, C. L. Burros, and E. J. Frederick, *Manual of Analytical Procedures for the U^{235} Recovery Process*, Method No. 12, ORNL-983 (Aug. 20, 1951).

(12) R. W. Foster, *Purex Control Manual – Total Plutonium in Aqueous Solutions – TTA Method*, Building 3019, ORNL.

ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

RESEARCH AND DEVELOPMENT

ANP ANALYTICAL LABORATORY

J. C. White J. E. Lee, Jr.
A. F. Roemer, Jr. D. L. Manning
W. J. Ross

The analytical problems that have been under study relative to reactor fuels and fuel components are the determination of oxygen in metallic oxides by fluorination with bromine trifluoride, the volumetric determination of zirconium, the determination of metallic zirconium and uranium trifluoride in reactor fuels, the determination of traces of hydrogen fluoride in used helium, and the anodic dissolution of metallic fuel containers. In addition, the preparation of kilogram quantities of uranium tetrachloride has been undertaken. These problems are discussed elsewhere.[1]

ANALYTICAL STUDIES FOR THE HOMOGENEOUS REACTOR PROGRAM

O. Menis M. L. Druschel
J. R. Lund C. K. Talbott

Analytical studies for the HRP consist of analyses relative to the uranium oxide and thorium oxide slurry program, and to the uranyl salt solution loop and static tests. In connection with the slurry program, analyses are made of the aqueous and solid phases of the slurry to determine the solubility of the slurry components and the concentration of the accumulated corrosion products. Determinations of traces of uranium(IV), uranium(VI), thorium(IV), nitrates, carbonates, phosphates, chromium, nickel, and iron in one or both phases are desired. The development of methods for these determinations has been largely completed; however, sampling techniques that are entirely satisfactory have not yet been established. The aqueous phase of some of the slurries contains a colloidal suspension that is not readily separated; also, the solid phase does not dissolve homogeneously in a perchloric acid medium but leaves a small insoluble residue that has not been identified. The analytical results must be furnished rapidly in order to serve as a guide in the loop experiments.

Some current problems in the analysis of the uranyl salt solutions are the determination of chloride and technetium, the elimination of interferences in the determination of traces of iron and nickel, and the estimation of the precision of methods for the determination of uranium.

Analysis of Uranium Oxide Slurries

Separation and Dissolution of Phases. The phases of the uranium oxide slurry are separated by filtration or centrifugation. The solid phase is then washed free of the original solution, dried at 110°C, dissolved, and analyzed. The colloidal nature of some of the slurries has caused special problems of separation and analysis. One method of separation was to centrifuge the colloidal suspension in a high-speed ultracentrifuge at 40,000 rpm. After the centrifugation, the liquid does not show any Tyndall effect that would result from colloidal particles when tested in a strong beam of light. Methods of salting-out with K_2SO_4 are also being investigated. The solid phase of a slurry that contained 0.1 *M* sodium dihydrogen phosphate and a high concentration of uranium(IV) had to be fumed with nitric-perchloric acid mixture before dissolution occurred. Aliquots of the solutions of the solid slurry phases were used for the following determinations.

Total Uranium (J. R. Lund). The Jones reduction-ceric sulfate titration is used for the determination of total uranium.

Uranium in the Dissolved Aqueous Phase (M. L. Druschel). A standard-addition polarographic method was adopted for the determination of dissolved uranium as uranium(VI) because of the speed and convenience it offered in the handling of a few samples per day. A mercury pool was used as the anode and 0.3 *N* nitric acid as the supporting electrolyte. With a series of uranium standards of 2 to 100 μg, a relative standard deviation of 5% was attained.

Nickel in the Presence of Large Amounts of Uranium (M. L. Druschel). Nickel was determined in the presence of as much as 12 mg of uranium(VI)

[1] J. C. White *et al.*, "Chemical Analysis of Reactor Fuels and Contaminants," *ANP Quar. Prog. Rep. March 10, 1953*, ORNL-1515, p. 171.

by the procedure used for HRE samples,[2] except that the concentration of ammonium citrate was increased.

Nickel in the Presence of Uranium and Iron Phosphates (C. K. Talbott). The phosphates of iron and uranium interfere in the determination of nickel;[2] therefore an anion-exchange column (Dowex-A1) was utilized to remove iron and uranium as the chloride complexes. According to Kraus and Moore[3] nickel is not adsorbed. A 7 *N* HCl solution of the solid oxides and phosphates is passed through Dowex-A1 resin and nickel is collected in the effluent. Because the development of the nickel dimethylglyoxime color is very slow in the presence of a high concentration of salts, the effluent is fumed with sulfuric acid to remove the chlorides as HCl. The relative standard deviation of the method was 2% as determined by the analysis of eight standard solutions.

Determination of Nitrate (O. Menis). Several methods for the determination of nitrate in the range of 1 to 100 μg in uranium oxide slurries have been investigated. The method of Wright[4] that employs nitrate reduction with DeVarda's alloy, Kjeldahl distillation, and a Nessler colorimetric procedure gave irreproducible reagent blanks and conditions for the Nessler reaction.

The second method tested was the chromous sulfate reduction of the nitrate to ammonia followed by a Kjeldahl distillation and potentiometric titration.[5] In this method, a slight excess of chromous solution over the stoichiometric amount required to reduce both uranium and nitrate is needed to assure quantitative recovery of NH_3. A relatively large excess of sodium tartrate is added to keep the solution that is in the Kjeldahl flask from becoming turbid and thus causing low results when ammonia is liberated by the addition of a 50% sodium hydroxide solution. The relative standard deviations of single measurements by this method were 4, 4, and 2% for 25, 50, and 100 μg of nitrate, respectively. The recovery was 20% low for the 25-μg sample, and the recoveries of 5- and 10-μg samples were erratic. In these tests, sample size was limited to 0.1 g of UO_3 by the size of the 150-ml, Kjeldahl, distillation flask.

A method that employs phenoldisulfonic acid reagent and a uranium separation by means of Dowex-50 resin offered the greatest sensitivity and reliability. The procedure described previously[6] was modified to include this separation prior to the final adjustment of pH. The dried sample is treated with the reagent under anhydrous conditions, diluted with water to give a solution less than 0.4 *N* in H_2SO_4, and passed through the resin column. Uranium is retained in the column and does not interfere in the remainder of the procedure. Less than 1 ppm of nitrate in UO_3 can be determined by this method with a relative standard error of less than 10%. Recent results indicate that improved precision is possible.

Phosphate (C. K. Talbott). The separation of phosphate from uranium oxide slurries that contained a relatively high concentration of corrosion products and that were 0.1 *M* in sodium dihydrogen phosphate was effected by use of a column of the hydrogen form of Dowex-50, which liberated the phosphoric acid and separated it from the cations. The acid was then titrated with standard alkali to a thymolphthalein end point. A relative standard deviation of 0.6% was attained in the analysis of ten standard samples. For the determination of microgram quantities of phosphates in the solid phase of the slurry in the presence of uranium, the phosphovanadomolybdate colorimetric method was used.[7]

Carbonate (J. R. Lund). The carbonate present in both phases of the slurry, as well as the carbonate present at equilibrium with the gas phase under the experimental conditions, was determined by the use of volumetric, gravimetric, and gasometric methods.

Equilibrium Carbon Dioxide (J. R. Lund). The CO_2 that was dissolved in the slurry at 1000-lb pressure and 250°C was determined by measuring the volume of gas, at STP, liberated from a sample

[2] M. L. Druschel, O. Menis, and R. Rowan, Jr., *Modifications of the Dimethylglyoxime Method for the Colorimetric Determination of Nickel Based on the Use of Potassium Persulfate as the Oxidant*, ORNL-1430 (Nov. 3, 1952).

[3] G. E. Moore and K. A. Kraus, "Anion Exchange Studies. IV. Cobalt and Nickel in Hydrochloric Acid Solutions," *J. Am. Chem. Soc.* 74, 843 (1952).

[4] W. B. Wright, Jr., *Determination of Ammonia and Nitrate Nitrogen Present in Uranyl Sulfate and Uranium Oxides*, Y-919 (Nov. 23, 1951).

[5] O. Menis and C. K. Talbott, "Determination of Trace Elements," *Anal. Chem. Quar. Prog. Rep. Dec. 26, 1951*, ORNL-1233, p. 74.

[6] O. Menis, "Analysis of Uranyl Sulfate and Uranium Oxide," *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p. 49.

[7] C. J. Barton, "Photometric Analysis of Phosphate Rock," *Anal. Chem.* 20, 1068 (1948).

that was collected in a steel bomb under the experimental equilibrium conditions. Also, on the same sample, the ratio of carbonate to uranium in the solid and liquid phases was determined by decomposing the carbonate with acid, measuring the volume of CO_2 evolved, and then determining the uranium content of the solution.

Uranium(IV) Determination (M. L. Druschel). Further investigation of the chloranilic acid method for the determination of uranium(IV) in UO_3[8] was concerned with increasing the sensitivity of the method without sacrificing reproducibility. Various organic solvents and protective colloids were tried without success as color stabilizers. The use of an inert atmosphere for sample preparation did not help to stabilize the uranium(IV) complexes. Finally, various organic and inorganic acids were tested as solvents for UO_3, and their concentrations were varied to assure the dissolution of UO_3 without the loss of uranium(IV). A 1:4 ratio of HCl to $HClO_4$ was found to be best because it assures rapid dissolution of the oxide and 60- to 90-min color stability. For standards from 1 to 5 μg of uranium(IV) in 50 mg of UO_3, a relative standard deviation of 10% is attained.

Analysis of Thorium Oxide Slurries

Dissolution of the Oxide (C. K. Talbott). In the analysis of thorium oxide, some of the very refractory oxide particles failed to dissolve after prolonged treatment with nitric acid that contained traces of fluoride. These particles readily dissolved after treatment with fuming perchloric acid, followed by the addition of traces of HF and a short fuming.

Determination of Constituents. Determinations of thorium and nitrate in both the aqueous and solid phases of thorium oxide slurries were carried out by methods similar to those used with uranium oxide slurries. Thorium in the solid was determined by the oxalate method and in the filtrate by the Thoron colorimetric method. The nitrate was determined by the phenoldisulfonic acid[4] method as described in the discussion on uranium oxide slurry.

Analysis of Uranyl Sulfate Solutions. The analysis of uranyl sulfate solutions required the determinations previously noted;[9] the determination of chloride, persulfate, technetium, and iron in the presence of large amounts of nickel; and a study of the precision of the specific gravity and volumetric methods for uranium determination.

Chloride (O. Menis). Microgram quantities of chloride were determined potentiometrically by titration with silver nitrate by a method described previously.[10]

Persulfate (M. L. Druschel). The qualitative, benzidine-acetic acid test was adapted for the rapid determination of persulfate ions in the concentration range of 6×10^{-4} to 6×10^{-2} M.[11] A Beckman spectrophotometer was used to determine the absorbancy at 600 mμ immediately after the development of color.

Technetium (O. Menis). The concentration of technetium in the microgram range was determined by separating it as the sulfide with a platinum carrier and counting the beta activity.[12]

Iron (C. K. Talbott). High concentrations of nickel interfere in the determination of iron by the α, α'-bipyridyl method. An anion-exchange procedure is now used instead of the isopropyl ether extraction to separate the iron prior to the colorimetric determination. The hazard arising from the use of ether is thus eliminated.

Specific Gravity Method for Uranium Determination (O. Menis). Ten samples that were obtained successively from a loop test were analyzed for uranium by the specific gravity method,[13] and by the Jones reductor-ceric sulfate titration method. The calculated variance ratio indicates no significant difference in precision between the two methods.

Special Analysis of Corrosion Products

Analysis of Propylenediamine Solutions (C. K. Talbott, J. R. Lund). Analysis of propylenediamine

[8] M. L. Druschel, "Determination of Uranium(IV) in Uranyl Oxide," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 46.

[9] O. Menis, "Analytical Studies for the Homogeneous Reactor Program," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p. 45.

[10] O. Menis, C. K. Talbott, F. E. Jenkins, and J. E. Lee, Jr., "Determination of Halides," *Anal. Chem. Quar. Prog. Rep. Sept. 10, 1951*, ORNL-1129, p. 66.

[11] F. Feigl, *Qualitative Analysis by Spot Tests*, 3rd ed., p. 242, Elsevier, New York, 1946.

[12] G. W. Parker, J. Reed, and J. W. Ruch, *Isolation of Milligram Amounts of Element 43 from Uranium Fission*, AECD-2043 (June 4, 1948).

[13] J. E. Lee, Jr., R. Rowan, Jr., C. D. Susano, and O. Menis, *The Density of Uranyl Sulfate Solutions and the Determination of Uranium Concentration by Density Measurements*, ORNL-1332 (June 18, 1952).

solutions for corrosion products of steel led to an investigation of the interference by this organic compound in the determination of iron and nickel by the established procedures. Propylenediamine in a 25 vol % concentration of the final solution does not interfere in the α, α'-bypyridyl method for iron when hydroxylamine hydrochloride is used as a reducing agent. However, if hydroquinone is used as a reducing agent, a deep, interfering color develops in this medium. Any interference with the dimethylglyoxime colorimetric nickel determination is eliminated by decomposing the propylenediamine with nitric acid and completely oxidizing the products by fuming with a nitric-perchloric acid mixture.

QUALITY CONTROL

R. L. McCutchen

The control programs for the Miscellaneous Analysis Laboratory, the ANP Analytical Laboratory, and the Analytical Chemistry Division laboratories at the X-10 site were all expanded during the period, the accuracy and precision of the reported test results being maintained either by daily control standards or by a combination of daily control standards and regular sample analyses. Early in the period the control program for the HRP Analytical Laboratory was suspended because of a temporary decrease in the work load of the Laboratory.

A total of 11,180 determinations for control purposes was reported by the five laboratories that participated in the control program. The distribution of the 11,180 determinations is shown in Table 4.

A review of the quality control programs for the Analytical Chemistry Division effected during the past 12 months revealed that the number of determinations evaluated for control purposes in-

TABLE 4. SUMMARY OF DETERMINATIONS EVALUATED FOR CONTROL PURPOSES DECEMBER 1952 THROUGH FEBRUARY 1953

	ANALYTICAL LABORATORY					TOTAL
	Y-12 Site			X-10 Site		
	Miscellaneous	HRP	ANP	Building 4500	Building 3019	
Number of standard determinations	664	52	369	584	628	2,297
Number of sample determinations used for control purposes	7,949	236	698			8,883
Total	8,613	288	1,067	584	628	11,180

TABLE 5. SUMMARY OF TEST RESULTS EVALUATED FOR CONTROL PURPOSES MARCH 1952 THROUGH FEBRUARY 1953

	NUMBER OF DETERMINATIONS PER QUARTER
March through May 1952	1,570
June through August 1952	2,778
September through November 1952	10,208
December 1952 through February 1953	11,180
Total	25,736

creased by a factor of 7. Such a rapid expansion of the quality control programs is indicative of the increased versatility of the laboratories because additional laboratory control programs are planned and instituted in order to maintain the accuracy and precision of test results for new types of materials and/or analyses.

The distribution, by quarters, of the 25,736 determinations evaluated for control purposes during the past year is given in Table 5.

SERVICE ANALYSES

ANP ANALYTICAL LABORATORY

J. C. White A. F. Roemer, Jr.

The service work of the ANP Analytical Laboratory has continued to consist mainly of the analyses of fluoride reactor fuels, uranium tetrachloride, and sodium-potassium alloys. The usual determinations of sodium, zirconium, uranium, fluorine, iron, nickel, and chromium were made on reactor fuels. The preparation of uranium tetrachloride by chlorination of uranium trioxide with hexachloropropene was assumed by the Laboratory. The purity of the product was established by determining the amount of uranium dioxide and uranous oxychloride present. The ratio of sodium to potassium in sodium-potassium alloys was determined, as well as trace quantities of beryllium. A detailed account of the work of this Laboratory is given elsewhere.[1]

RAW MATERIALS ANALYTICAL LABORATORY

J. C. White W. F. Vaughan
L. J. Brady

The number of samples received as a result of studies of various methods of processing uraniferous lignites for recovery of uranium has increased significantly. Complete analyses of the raw lignites have been made in addition to determinations of uranium, molybdenum, and fluoride in process residues and leach solutions. Fluoride is introduced as the ammonium bifluoride salt during one stage of the recovery process. The time required to distill the fluoride from these samples is prolonged because of the presence of aluminum in lignite. Fluoride is separated by a modified Willard and Winter[2] distillation method that employs constant-temperature, steam-distillation equipment of the type described by Huckabay, Welch, and Metler.[3] The final determination is made by the conventional titration method, which employs a standard solution of thorium nitrate and a sodium alizarinsulfonate indicator.

Because the lignites that are being studied contain molybdenum in sufficient quantities to be of interest, it has been worth while to follow the course of this element through the various steps of the recovery process. Molybdenum is determined colorimetrically by the thiocyanate-stannous chloride method. The transmittancy is measured at 470 mμ by a Beckman model B spectrophotometer.

The determination of the phosphate and uranium concentrations of Florida Leach Zone residues and leach solutions has continued. Recently, these samples have also been analyzed for carbonate content.

Uranium has also been determined in organic solutions. These samples are dilute solutions of such organophosphorus compounds as phosphinic and phosphonic acids, and phosphine oxides in kerosene or benzene. The solutions have been investigated as possible extractants of uranium from uranyl solutions. The synthesis of these organophosphorus compounds by the Raw Materials Group of the Materials Chemistry Division continued. These compounds were analyzed for carbon and hydrogen by microcombustion techniques. A second microcombustion train was purchased and is now in operation.

Macrocombustion methods were employed to analyze high-molecular-weight aliphatic amines that were prepared by the Raw Materials Chemistry Group. Samples of 50 to 100-mg weight were

(1) H. P. House, S. A. Reed, and A. F. Roemer, Jr., "Service Chemical Analyses," *ANP Quar. Prog. Rep. March 10, 1953*, ORNL-1515, p. 177.

(2) H. H. Willard and O. B. Winter, "Volumetric Method for Determination of Fluorine," *Ind. Eng. Chem., Anal. Ed.* 5, (1933).

(3) W. B. Huckabay, E. T. Welch, and A. V. Metter, "Constant-Temperature Steam-Distillation Apparatus for Isolation of Fluorine," *Anal. Chem.* 19, 154 (1947).

placed in tared bulbs, which were then weighed and introduced directly into the combustion tubes, thereby eliminating any exposure of the sample to moisture and air.

The Raw Materials Analytical Laboratory was established as a separate entity to handle all requests of the Raw Materials Group.

MISCELLANEOUS ANALYSIS LABORATORY

J. C. White L. J. Brady
W. F. Vaughan

The major portion of the work on miscellaneous samples consisted of the analysis of uranyl sulfate solutions for uranium, iron, nickel, and chromium, and the weekly preparation and standardization of 50-gal lots of dilute solutions of hydrochloric acid. A 50-gal stainless steel reactor equipped with a high-speed stirrer is now available and is being used to prepare large batches of the standard acid.

In addition, a number of metals and alloys have been analyzed. These analyses varied from simple identification tests that require only a few minutes to rather complete analyses that require many hours. A partial list of the metals and alloys tested includes the following: stainless steels, nickel metal and alloys, cadmium, titanium, aluminum, and alloys of silver and copper.

Samples of water were analyzed for mineral content, including uranium.

The Stores Department of the Y-12 Plant is submitting samples of lubricating oils for the determination of water and sediment by ASTM methods, and water by the Karl Fischer method. Other analyses requested are viscosity at various temperatures, neutralization number, carbon residue, dielectric strength, and specific gravity. These tests are being made to determine whether the purchased oils meet the requirements that are set forth by the Y-12 specifications for lubricants.

TABLE 6. SUMMARY OF ANALYTICAL SERVICE WORK AT Y-12 SITE

	NO. OF PERSONNEL		ORNL DIVISIONS REQUESTING ANALYSES					OTHERS REQUESTING ANALYSES				
	TECHNICAL	NONTECHNICAL	ANP	ELECTROMAGNETIC	STABLE ISOTOPE	MATERIALS CHEMISTRY	REED	Y-12 ADP PROCESS IMPROVEMENT	Y-12 STORES	GENERAL ELECTRIC CO.	MISCELLANEOUS	TOTAL DETERMINATIONS
LABORATORY MAKING ANALYSES			Number of Determinations									
HRP Analytical	2	6					6,626					6,626
ANP Analytical	3	9	2,143			5,000		41		53	8	7,245
Raw Materials	2	12				11,990						11,990
Miscellaneous Analysis	2	3		89	101		27		261			478
ADP Analytical Chemistry	9	5						589			844	1,433
Total	18	35	2,143	89	101	16,990	6,653	630	261	53	852	27,772