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ANALYTICAL CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING MARCH 26, 1951

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ANALYTICAL CHEMISTRY DIVISION

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

QUARTERLY PROGRESS REPORT

for Period Ending March 26, 1951

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"Activation Analysis by Means of the Oak Ridge Reactor," G. W. Leddicotte and S. A. Reynolds, *Nucleonics* **8**, No. 3, 62 (1951).

ORNL-755 *Polarographic Determination of Sulfates,* P. F. Thomason and A. D. Horton (Feb. 19, 1951).

ORNL-839 *Spectrophotometric Determination of Inorganic Fluorides,* A. D. Horton, P. F. Thomason, and F. J. Miller (Mar. 26, 1951).

Y-B31-227 *Stability of Dow Corning Silicone Fluid 550 in the Presence of Sodium,* Robert Rowan, Jr. (Jan. 17, 1951).

Y-B31-233 *Cooperative Analyses of Standard Samples. Report No. 2, Uranium and Zirconium in Sulfuric Acid Solutions,* C. D. Susano (Feb. 15, 1951).

Y-B31-241 *Cooperative Analyses of Standard Samples. Report No. 3, Analyses of Zirconium Metal, Zirconium Hydride, and a Hydrided Alloy of Zirconium and Uranium,* C. D. Susano (Mar. 16, 1951).

Y-714 *Corrosion Resistance of Zirconium Metal and Stainless Steels on Exposure to Concentrated Solutions of Uranyl Fluoride,* C. D. Susano (Feb. 9, 1951) (previously issued as Y-B31-217 as a tentative draft and cited in ORNL-955).

ABSTRACT

ANALYTICAL CHEMISTRY DIVISION — X-10 SITE

Ionic Analyses — Research and Development. The automatic simultaneous semimicro titration of uranium and iron with ceric sulfate has been satisfactorily effected by performing the titration at 60°C. The feasibility of the procedure on a micro scale and on MTR samples containing aluminum nitrate is under study. Two methods were investigated for rapid determination of uranium(IV) in HRE solutions, a spot test using Thoron reagent or chloranilic acid in perchloric acid, and a solvent extraction followed by a Thoron colorimetric test. The former was not sufficiently sensitive, and the corrosion products of stainless steel interfered with the latter.

Submicrogram and microgram quantities of uranium(VI) were satisfactorily isolated by the technique of filter paper partition chromatography using 2-methyltetrahydrofurane containing aqueous nitric acid as the mobile liquid phase. The immobility of most other metal ions in the system indicates the possibility of separating U(VI) from other nonradioactive or radioactive cations by this technique. A separation of Fe(III) and U(VI) demonstrated this. The use of radioisotopes together with radioautography and alpha counting methods gave a highly sensitive method for locating solute sorption bands on the chromatograms. Work is being continued to make the method quantitative for nonradioactive uranium.

Use of the highly sensitive recording polarograph, provided with the "curve follower," was extended to determine microgram and submicrogram amounts of metal ions as follows: Uranium(VI) at concentrations of 0.5 and 1.0 γ/ml in 0.1 *M* HNO_3 was determined with high accuracy; rapid procedures were developed for determining trace quantities of lead in blood, urine, and air; polarograms of indium (0.02 and 0.04 γ/ml) were obtained, a special technique being required to overcome difficulties in the potential region of the electrocapillary zero; an indium-thorium alloy was successfully analyzed polarographically for indium.

Experimental work was begun on an indirect polarographic method for determining potassium as potassium cobaltinitrite.

A special hood has been put in use which facilitates plutonium titrations by providing protection for the personnel performing them.

Radiochemical Analyses — Research and Development. Studies of the disintegration of Cr^{51} have shown very little β^- or e^- to be associated with the decay. Data showed the presence of two gamma rays, 0.33 and 0.27 Mev in the ratio of 3 to 1. Gamma radiation was found to accompany 15% of the total disintegration, decay thus appearing to be 11.3% through 0.33 Mev, 3.8% through 0.27 Mev, and 85% directly to the ground state. A value for the half-life of 27 ± 0.4 days was indicated.

Decay studies on Sr^{85} indicated that the radiation was composed entirely of Rb X-rays and electromagnetic radiation of 0.52 Mev. The amount of activity due to conversion of electrons appeared to be of the order of 0.2%. The decay of Sr^{85} was found to occur 77% directly to the ground state and 23% accompanied by the 0.5-Mev gamma ray.

A study of the thermal cross-section for Fe^{55} and Fe^{59} production is underway.

Geometries have been obtained on five different Geiger-Mueller counters by use of Na^{24}, Co^{60}, and Nb^{95}. Variance in the Co and Nb geometries is discussed.

Two methods are suggested for the routine assay of low-level liquid wastes (10^{-8} to 10^{-5} μc/ml), e.g., that of Healy at Hanford and the more promising method of using a standard, established to have the same beta characteristic as typical waste. Two radionuclides, 127-day Tm^{170} and 2.7-year Tl^{204}, are mentioned as possible standards.

A bibliography on counting methods for liquid wastes and low-level counting in general was prepared for issue as a separate report.

Dishes of four designs have been studied to replace those in current routine use as sample mounts for gross beta counts. One design, which prevents solids from being deposited in one large mass, is recommended.

A method for the separation of americium and curium from the rare earths is being studied which consists in extracting them from an aqueous phase of *p*H 5 with 0.5 *M* TTA-xylene and then "stripping" the organic phase with Versene for americium and curium. The effect of *p*H on the selectivity of the stripping of americium is shown.

As a part of the activation-analysis program of all 14 rare earths, a second steam-heated ion-exchange column was installed. Preliminary runs on both columns using Tm^{170}, Tb^{160}, and Ce^{141} gave good results.

Paper chromatography is shown to have promise for the separation and qualitative identification of a series of a dozen metal ions for which R_f values were obtained using various radioactivities as tracers. Close agreement of the R_f values with those reported in the open literature was found.

Spectrochemical Analyses — Research and Development. Working curves and procedures were developed for the spectrographic determination of a series of seven metals in specific concentration ranges and media. Continued work on the spectrographic line-width method for determining small amounts of lithium in the presence of 500 to 1000 times as much sodium by weight showed the method to be less sensitive to the presence of other alkalies than the intensity ratio method.

Service Analyses. A new Activation Analyses Group was organized. The method of activation analysis was compared with spectrographic and spectrophotometric methods for determining several metals and found to be of high accuracy. New applications of the method to dental research and industrial problems are being made. Information relative to neutron activation analysis is being organized for issue in report form.

A total of 54,021 analyses were made during the quarter.

Inorganic Preparations. In connection with the Thorium Breeder Salts Program a number of reactions for producing anhydrous thorium fluorophosphates were studied. Several showed promise and are being considered further. Pure Mn_2Sb was prepared, in larger quantities than reported previously, by the use of newly designed equipment. Neodymium ethyl sulfate and a series of phosphors were prepared for use by the Physics Division.

Analytical Chemical Control of Homogeneous Reactor Solution. A modification of the Princo Densitrol is being evaluated for continuous control of the HRE soup solution. Work on the electromagnetic densitometer and high-frequency coil for Q measurement continued. Pile irradiation tests are continuing on glasses developed for the purpose of being neutron absorbing.

Optical and Electron Microscopy. A rapid method of removing deposited oxide layers or films from stainless steel was developed. A film pack for the Vickers microscope was designed and fabricated to allow the more rapid taking of sequence pictures using films with a higher speed rating. A summary of the service work is given.

ANALYTICAL CHEMISTRY DIVISION — Y-12 SITE

Research and Development. *Aircraft Nuclear Propulsion.* The *n*-butyl bromide method has been found to be a suitable replacement for the Pepkowitz and Judd method for determining oxygen in sodium. A complete evaluation of the *n*-butyl bromide method is reported and its advantages are enumerated. The oxygen contents of cylinders of helium and argon were determined spectrophotometrically, the results indicating the necessity for purifying these gases if they are to be used as protective atmospheres for liquid alkali metals. The continued study of the stability of Dow Corning Silicone Oil 550 at elevated temperatures indicated that DC-550 is unstable at temperatures above 1200°F because of polymerization, even when not in contact with sodium. The determination of carbon in chlorinated silicones, as requested for the NEPA project, was shown by the analysis of known compounds to be feasible with a micro combustion apparatus and procedure. A gravimetric perchlorate method was developed for determining potassium in the eutectic mixture formed in phase studies of sodium, potassium, and uranium fluoride systems.

A method for semimicro determination of uranium in minerals and ores by use of a cellulose-alumina column which retains all metals except uranium is under study.

The pyrohydrolysis method for the determination of fluoride in certain metallic fluorides is recommended as an improvement over the Willard and Winter steam-distillation method.

To meet the need for a method of separating titanium from niobium and tantalum, fractional distillation of the chlorides of the metals was investigated. The study of various chlorinating agents, resulting in the selection of heptachloropropane, is reported. Niobium chloride was almost quantitatively recovered in the higher boiling fraction. Chlorination of the titanium was incomplete, and procedure modifications are suggested to remedy this.

Homogeneous Reactor Project. Analytical problems of the HRE project are discussed in general, composition of the uranyl sulfate solutions as sampled during operation of the system, stability of uranium(IV) in uranyl sulfate solutions, and methods of separating trace elements from uranium and their subsequent determination receiving special attention.

Y-12 Technology. The ultraviolet spectrophotometric absorption method for the determination of phthalate ion in recycle liquors from the zirconium refining process was shown in a comparative study to be sufficiently accurate for routine use.

The sulfur in propane gas was suggested to be the cause of failure, by embrittlement or cracking, of a number of nickel reactor tubes. A study of the propane gas in use in the Y-12 area showed its total sulfur content to be far below 20 grains/cu ft, the tolerance value reported by the manufacturer of the reactor tubes.

Special Problems. A report is given of the spectrographic determination of trace elements in the human body in connection with the program of the Health Physics Division. The anticipated problems of analysis of body tissues are discussed briefly.

A sample of bonded graphite (Carbate) was bombarded with electrons in connection with experiments at X-10 and submitted for hydrogen analysis. A micro combustion technique showed a difference in hydrogen content of the Carbate before and after bombardment, the bombardment having effected a decrease in the hydrogen content.

An attempt was made to synthesize iodoacetylene for the Stable Isotopes Division, and the product was submitted to them for measurement of its microwave rotational absorption spectrum.

Service Analyses. A total of 7550 determinations were made during the quarter. In addition, 79 samples were analyzed for the NEPA plant.

ANALYTICAL CHEMISTRY DIVISION — X-10 SITE

1. IONIC ANALYSES — RESEARCH AND DEVELOPMENT

AUTOMATIC SIMULTANEOUS SEMIMICRO TITRATION OF URANIUM AND IRON WITH CERIC SULFATE

P. F. Thomason

Many of the solutions from the various processes (Purex, Metal Recovery, HRE, etc.) which are to be analyzed for uranium contain iron as a contaminant. This is usually due to the corrosion of the stainless steel equipment. The iron does not cause trouble with the NH_4SCN colorimetric uranium method normally used for control analyses, but when a more precise determination of uranium is required, a volumetric estimation is used. The ferric sulfate procedure[1] can be used on macro samples as iron does not interfere with this method. However, the method is not very adaptable to an automatic micro titration as the titration must be carried out at 90 to 95°C, and the high temperature makes the control of small volumes of solution difficult. Nitrate-free uranium solutions in 5% H_2SO_4 are usually reduced with a Jones reductor to a mixture of U(III) and U(IV). The U(III) can be oxidized to U(IV) by bubbling air through the solution, and U(IV) can then be titrated potentiometrically with a standard solution of potassium dichromate or ceric sulfate. The oxidation is of U(IV) to U(VI). The automatic titrator is well adapted for this titration with ceric sulfate. If the uranium is reduced with a Jones reductor and titrated without air oxidation (under an inert atmosphere of CO_2), two breaks in potential are obtained, U(III) to U(IV) and U(IV) to U(VI). It has been found that uranium reduction with an excess of chromous sulfate or titanous chloride is as complete as with the Jones reductor. The two breaks in the potential show the oxidation of the excess chromous ion [also U(III), if present] and the oxidation of U(IV) to U(VI). The amount of titrant used between the two breaks is a measure of the uranium present.

When iron is present and the titration is carried out at room temperature, the iron causes high results for uranium. Rogers[2] suggested titrating at higher temperatures in order to obtain an iron break. Several workers[3] have

(1) G. J. Nessle, C. C. Casto, E. F. Orlemann, W. R. Grimes, and C. E. Larson, *Potentiometric Titration of Uranium with Ferric Sulfate*, MDDC-1123 (May 29, 1947).

(2) L. B. Rogers, personal communication.

(3) I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*, p. 293, Wiley, New York, 1931.

reported the successful simultaneous titration of uranium and iron with ceric sulfate at 80 to 90°C. However, this temperature range would cause the same volume troubles as a micro automatic ferric sulfate titration. It was therefore decided to titrate mixtures of uranium and iron in 5% H_2SO_4 with ceric sulfate at increasing temperatures from 30°C in order to obtain good breaks for each at the lowest possible temperature. Solutions containing 10 mg of U(VI) and 5.58 mg of Fe(II) in a total volume of 10 ml of 5% H_2SO_4 were reduced with chromous sulfate and automatically titrated at different temperatures with standard ceric sulfate, approximately 0.1 *N*.

It was found that a temperature of 40°C was required before three breaks in potential could be obtained. The second break showing the U(IV) to U(VI) oxidation was not very pronounced at this temperature, but at a temperature of 60°C three good breaks were obtained. The U(IV) to U(VI) break in potential was of the order of 80 mv. The final break due to the iron was approximately 300 mv.

These preliminary titrations were done with the Dow Recordomatic Titrimeter, using a water bath to heat the solutions. This titration will also be tried with the micro automatic titrator, since a 60°C temperature should not greatly affect the micro volumes of solution used with this instrument.

AUTOMATIC SIMULTANEOUS MICRO TITRATION OF URANIUM AND IRON WITH CERIC SULFATE IN SOLUTIONS CONTAINING ALUMINUM NITRATE

F. J. Miller

In anticipation that analyses of MTR samples containing iron and uranium in the presence of relatively large amounts of aluminum nitrate will be required, some exploratory work has been done.

Previously, iron has been determined separately and uranium calculated by applying a correction to the total uranium-iron titer. According to Furman and Schoonover[4] separate breaks may be obtained for the U(III) to U(IV), U(IV) to U(VI), and Fe(II) to Fe(III) oxidations when these ions have been

(4) N. H. Furman and I. C. Schoonover, "The Volumetric Determination of Uranium. Potentiometric Titration of Reduced Uranium Solutions with Ceric Sulfate, or with Potassium Permanganate. Application of the Differential Method," *J. Am. Chem. Soc.* 53, 2561 (1931).

obtained by reduction with zinc amalgam and subsequently titrated with ceric sulfate. The essential requirements are titration under an inert atmosphere, proper choice of electrode system, and keeping the solution at 80 to 90°C during the titration.

Thomason[5] has repeated this work on a semimicro scale using titanous chloride as a reducing agent. To date good results have not been achieved on a micro scale, but, with improvement in technique, the feasibility of the procedure has been demonstrated. The chief difficulty encountered is the removal of nitrates. Fuming with sulfuric acid is the usual procedure, but spattering has given difficulties in the past. At the suggestion of Dr. H. H. Willard[6] perchloric acid fuming has been tried and seems to offer some improvement. In fuming with perchloric acid caution must be observed not to dehydrate the aluminum. Once fumed to the point of dehydration, aluminum can be brought back into solution only with much difficulty.

INVESTIGATION OF RAPID METHODS FOR DETERMINING URANIUM(IV) IN HOMOGENEOUS REACTOR SOLUTIONS

A. D. Horton

Two methods were attempted for rapid determination of U(IV) in HRE solutions, (1) a spot test using Thoron or chloranilic acid in perchloric acid, and (2) a solvent extraction followed by a Thoron colorimetric test. It has been established by previous polarographic U(IV) determinations that the U(IV) concentration in HRE solutions will be between 0 and 100 γ of U(IV) per milliliter.

Spot Test. Synthetic uranium solutions containing, per milliliter, 30 to 85 γ of U(IV) and 32 to 40 mg of U(VI) were prepared from standard UO_2SO_4 solutions and UO_2SO_4 solutions reduced to $U(SO_4)_2$ by a Jones reductor.

Two-inch squares of filter paper (Whatman No. 42) were impregnated with 0.3% Thoron reagent, which gives a red color with tetravalent cations, and

(5) P. F. Thomason, "Automatic Simultaneous Semimicro Titration of Uranium and Iron with Ceric Sulfate," this report, p. 17.

(6) H. H. Willard, personal communication, Mar. 6, 1951.

100-λ aliquots of the uranium solutions were dropped on the treated paper. The difference in color intensity between spots obtained with the minimum and maximum U(IV) concentrations was very slight. Although U(IV) gives a brilliant red color with Thoron reagent, U(VI) in large quantities also gives the red color.

The same procedure was repeated using a saturated solution of chloranilic acid in 2 *M* perchloric acid. The resulting purple spot was good for the higher amount of U(IV) but was scarcely visible in the middle and lower ranges.

Solvent Extraction and Colorimetric Test. Hexone, ethyl ether, and dibutyl cellosolve were tested for extracting U(VI) from U(IV) in solutions which were predominant in U(VI) and which had been salted with 1 *M* $Al(NO_3)_3$.

Aliquots of solutions of uranium concentrations varying between 30 and 90 γ of U(IV) per milliliter and 32 and 40 mg of U(VI) per milliliter were placed in separatory funnels. Sufficient $Al(NO_3)_3$ solution was added to make the final solution 1 *M* in $Al(NO_3)_3$. A volume of solvent equal to the total water solution was added, and the mixture was shaken vigorously. The water layer, from which an estimated 90% of the U(VI) had been removed, was drained into a centrifuge cone and acidified with 5 drops of 13 *M* HCl. A volume of 250 λ of 0.3% Thoron reagent was added, and the solution was diluted to a volume of 10 ml. The percent transmittance of the solution was determined in the Beckman spectrophotometer, Model DU, at 545 mμ by comparing with a reference containing only 5 drops of 13 *M* HCl and 250 λ of Thoron reagent diluted to 10 ml. A curve, percent transmittance vs. micrograms of U(IV), was plotted for a series of values obtained from standard solutions. The result was a straight line originating near the zero point.

However, further tests using HRE solutions which contained corrosion products of stainless steel show that transmittance values for predetermined U(IV) concentrations do not fall on the curve. It is known that ferric iron will alter the color produced with Thoron reagent and U(IV). Other corrosion products also may interfere. Therefore, this method, which holds good for pure uranium salts, is not satisfactory for solutions which contain contaminants that affect Thoron reagent.

Further work on this project is awaiting developments in the engineering phase of the HRE.

ISOLATION OF URANIUM(VI) BY FILTER PAPER PARTITION CHROMATOGRAPHY AND DETECTION OF THE URANIUM(VI) LOCUS

H. P. Raaen

There is a general need for a method of separation and quantitative estimation of microgram and submicrogram quantities of uranium(VI). Filter paper partition chromatography offers a separation method of high resolving power, which is likewise rapid, sensitive, adaptable, and reliable. The method was first applied to the detection and estimation of uranium(VI) by Arden *et al.*[7] They selectively extracted uranyl nitrate from its solutions by use of 2-methyltetrahydrofurane containing aqueous nitric acid, carrying out the extraction on a strip of absorbent paper. The chromatograms obtained were developed with potassium ferrocyanide reagent, thus permitting estimation of uranium(VI). The method was reported to be sensitive to as little as 0.1 γ of uranium and semiquantitative for 0.25 to 200 γ with an accuracy of ±30%.

The maximum amount of a substance which may be handled successfully by paper partition chromatography is of the order of 1 mg, according to Burstall *et al.*[8] The minimum amount is determined by the suitability of the technique for detecting the locus of the sorbed solute and the accuracy of the method for its estimation either in situ or after removal from the paper.

The use of radioactive tracers is the most sensitive technique for identifying the locus of the resolved substance, being sensitive to as little as a few hundred atoms or molecules.[9] This technique combined with radioautography has been used by Fink and Fink in biological studies with radioisotopes[10,11] and in determining traces of nonradioactive or weakly radioactive substances in mixtures by formation of their radioactive derivatives.[12] In the latter work they attempted to determine natural uranium quantitatively in situ on the chromatogram by forming a salt of uranium containing a radioactive anion and subsequent measurement of beta radiation. The method was not satisfactory.

(7) T. V. Arden, F. H. Burstall, and R. P. Linstead, *Detection and Estimation of Uranium in Minerals and Other Products by Extraction Analysis on Absorbent Paper,* Montreal Report CRL-AE-3 (no date).

(8) F. H. Burstall, G. R. Davies, and R. A. Wells, "Inorganic Chromatography on Cellulose. Part III. The Use of Columns of Cellulose for the Separation and Determination of Metals," *Discussions Faraday Soc.* 7, 179 (1949).

(9) H. H. Strain, "Chromatographic Systems," *Anal. Chem.* 23, 25 (1951).

(10) R. M. Fink and K. Fink, *Radiocarbon and Filter Paper Partition Chromatography,* MDDC-1486 (Oct. 27, 1947).

(11) R. M. Fink and K. Fink, *Use of Radioactive Reagents in Filter Paper Partition Chromatography,* MDDC-1487 (Oct. 28, 1947).

(12) R. M. Fink and K. Fink, *The Possible Use of Paper Chromatography and Radioactive Reagents in Ultramicro Inorganic Analysis, with Special Reference to Uranium and Plutonium,* UCLA-30 (June 14, 1949).

For determining natural uranium in trace quantities the fluorescence method is the most sensitive known.[13] Of the reagents for colorimetric estimation of uranium, potassium ferrocyanide has been found to be the most satisfactory.[7,14]

A study was undertaken to determine the optimum conditions and useful range of paper partition chromatography for the isolation and detection of uranium. The following were considered for identification of the uranium locus:

1. Colorimetric reagents, e.g., potassium ferrocyanide, 8-hydroxyquinoline, and ammonium thiocyanate.
2. Fluorescence measurement, (*a*) by visual observation under ultraviolet light after enhancement of the fluorescence with phosphoric acid, or (*b*) by fluorophotometric measurement of the melt formed by fusion of the ashed chromatogram with sodium fluoride.
3. The radioactive isotope U^{233} (alpha emitter), combined with radioautography and alpha count measurement of the chromatograms.

None of the selected colorimetric reagents were sensitive to microgram quantities of uranium(VI) adsorbed on filter paper (Whatman No. 1, ashless) as indicated by spot tests. The lower limit of sensitivity was found to lie between 1×10^{-3} and 1×10^{-4} g/ml, the 8-hydroxyquinoline being the most sensitive but forming a yellow color which would be impossible to detect against the yellow color imparted to the paper by the 2-methyltetrahydrofurane. This is in disagreement with the results reported by Arden *et al.*[7]

The work of Sill and Peterson[15] suggested the treatment of the adsorbed uranium with phosphoric acid followed by visual observation of the enhanced uranium fluorescence under ultraviolet light. Spot tests showed that a spot made with 200 λ of a solution containing 1×10^{-3} g of U(VI) per milliliter gave excellent fluorescence after treatment with 25 and 50% H_3PO_4. The test was negative at 1×10^{-4} g/ml.

Another fluorescence method considered was the ashing of sections of the chromatogram beneath a sodium fluoride pellet, fusion, and measurement of the fluorescence of the melt by the fluorophotometer. A chromatogram was prepared by depositing 100 λ of a solution of 5.0 γ of U(VI) per milliliter and 0.1 *M* in HNO_3 along a line 3.5 in. from the end of a strip of Whatman No. 1 ashless filter paper (1.5 by 12 in.). After the spot was air-dried, the strip was

(13) C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, NNES Div. VIII, Vol. 1, p. 122, McGraw-Hill, New York, 1950.

(14) Elinor Ware, *Organic Reagents for Uranium Analysis*, MDDC-1432 (August, 1945).

(15) C. W. Sill and H. E. Peterson, "Fluorescence Test for Uranium in Aqueous Solution," *Anal. Chem.* 19, 646 (1947).

placed in the chromatographic apparatus of design described by Burstall *et al.*[16] The strip was eluted with 2-methyltetrahydrofurane containing 0.25% HNO_3, according to the recommendation of Arden *et al.*[7] The fluorophotometric measurements indicated a sorption gradient of uranium terminating abruptly in a section of the chromatogram coincident with a narrow dark band of brownish color which trailed behind the solvent front by almost 1 in. This band marks the boundary between two solvent phases[16] which exist on the paper strip: an upper, strongly acid and water-saturated phase and a lower, dry, solvent region almost free from acid. The position of the wet solvent front was found to be a function of acidity (Fig. 1). The results of this method were of qualitative value in indicating the distribution of uranium along the chromatogram. The method was time-consuming.

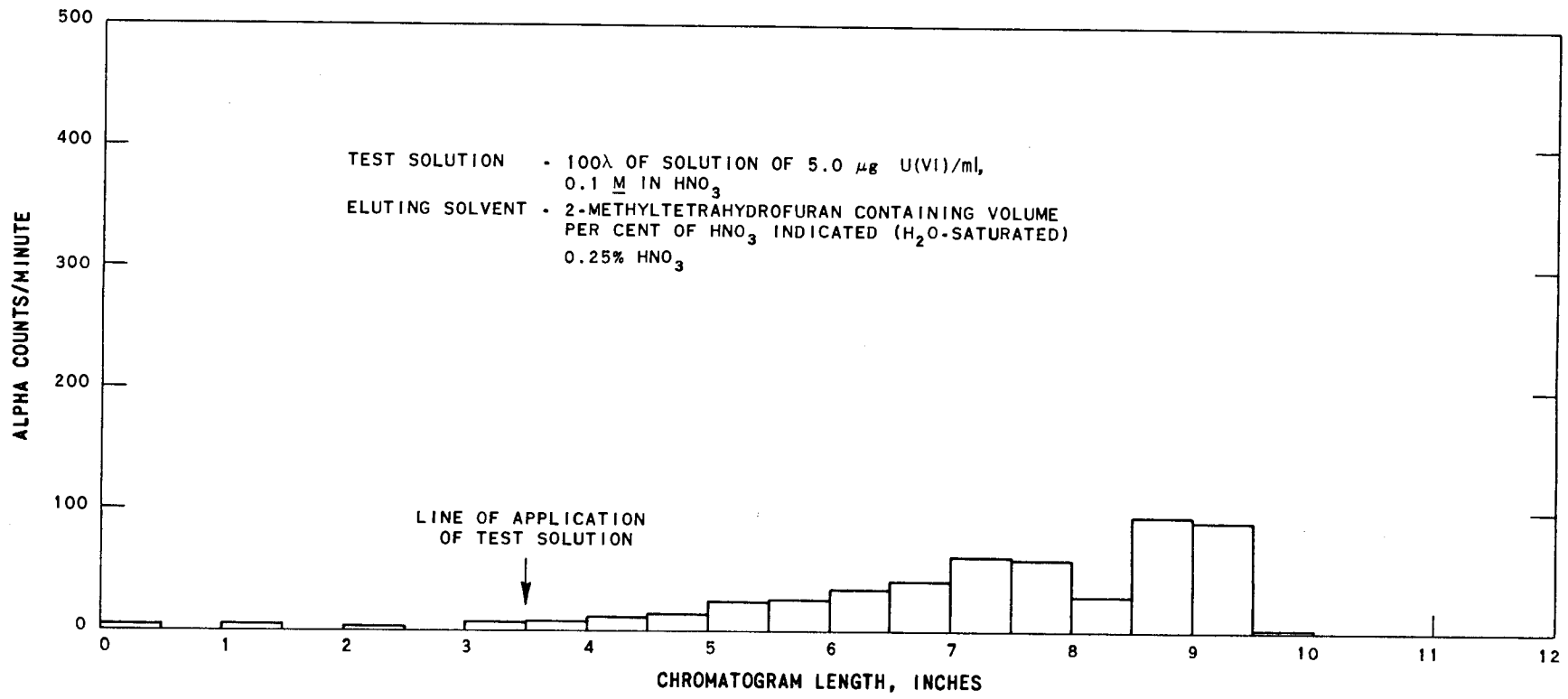
With the failure of chemical methods and the slowness of the fluorophotometric procedure in detecting the locus of natural uranium on the chromatogram, it was decided to substitute the radioactive isotope U^{233} for the natural uranium and to study its sorption gradient on the chromatogram by measurement of the alpha count of consecutive ½-in. segments of one-half of the chromatogram, and to prepare a radioautograph of the other undisturbed half. Alpha counts were made with the proportional alpha counter at 52% geometry. The radioautographs were made by stapling the chromatograms to X-ray film, weighting them with a ½-in.-thick lucite sheet, enclosing the assembly in a special light-tight box, and permitting contact for about 65 hr. Fogging of the film indicated the U^{233} locus. The analysis of reagent blanks by both techniques gave satisfactory results. Both techniques were found useful in indicating the sorption gradient of U^{233} in the chromatograms, the counting technique being more sensitive. This is shown in Fig. 2, where the alpha count data are presented graphically for a chromatogram of a solution containing 0.1 γ of U^{233}(VI) per milliliter. No radioautograph of this chromatogram was detectable even after about 65 hr of film contact.

Arden *et al.*[7] report the use of 2-methyltetrahydrofurane containing both 0.25 and 2.5% HNO_3, without indicating what acid concentration is optimum. The work of Aronoff[17] has shown that the sorption gradient of the solute may be a function of the acid content of the solvent, and that the presence of

(16) F. H. Burstall, G. R. Davies, R. P. Linstead, and R. A. Wells, "Inorganic Chromatography on Cellulose. Part II. The Separation and Detection of Metals and Acid Radicals on Strips of Absorbent Paper," *J. Chem. Soc. London* 1950, 516.

(17) S. Aronoff, "Separation of the Ionic Species of Lysine by Means of Partition Chromatography," *Science* 110, 590 (1949).

DWG. 12364 [redacted]



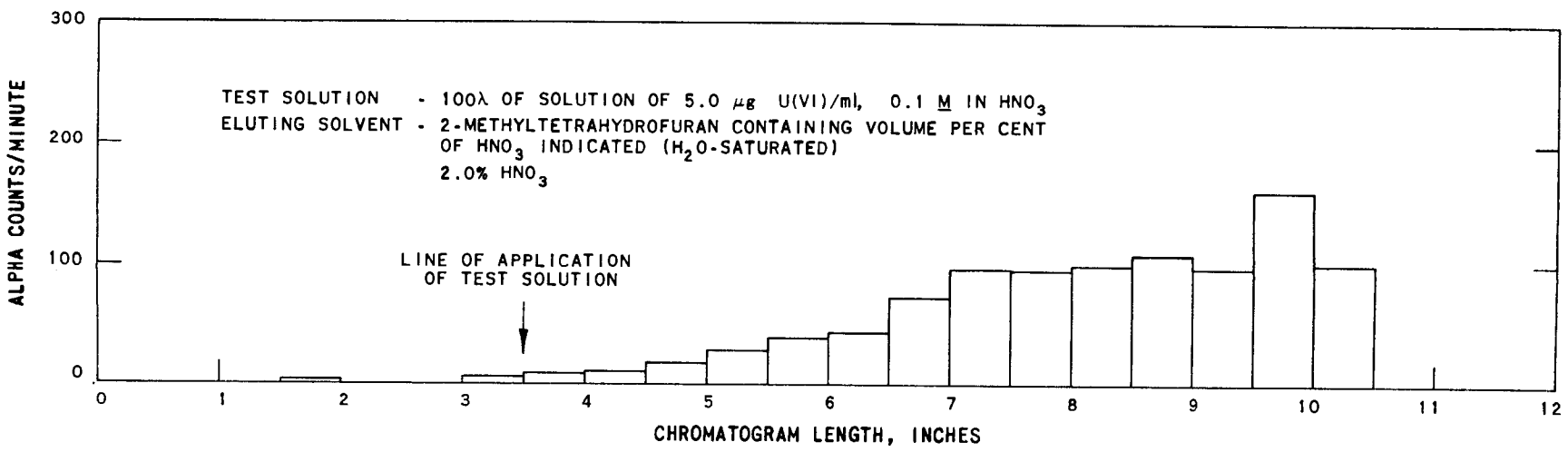
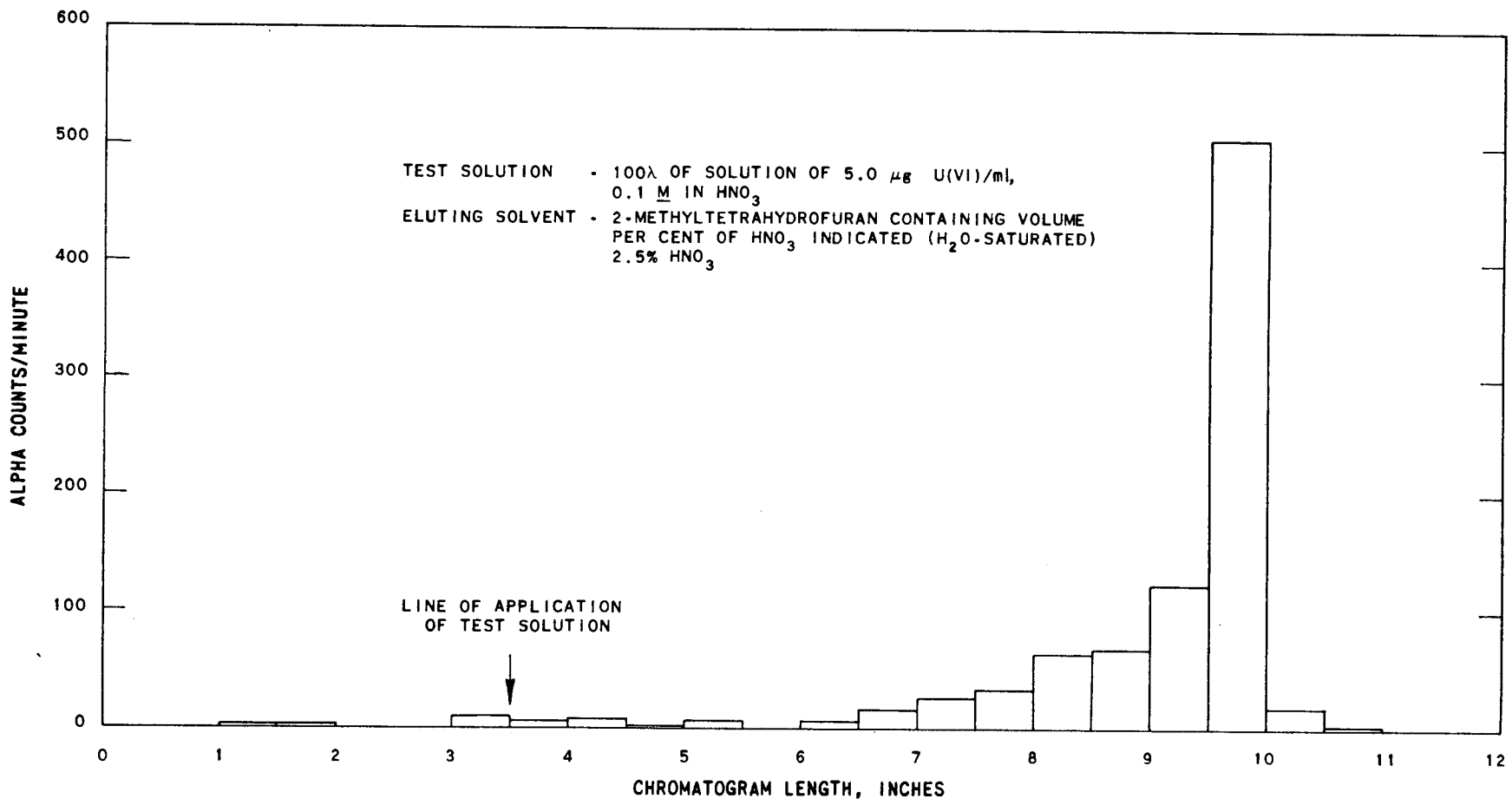


Fig. 1 (A and B) _ Effect of Acid Content of Eluting Solvent on Distribution of Uranium(VI) in Paper Chromatogram.

DWG. 12445 [redacted]



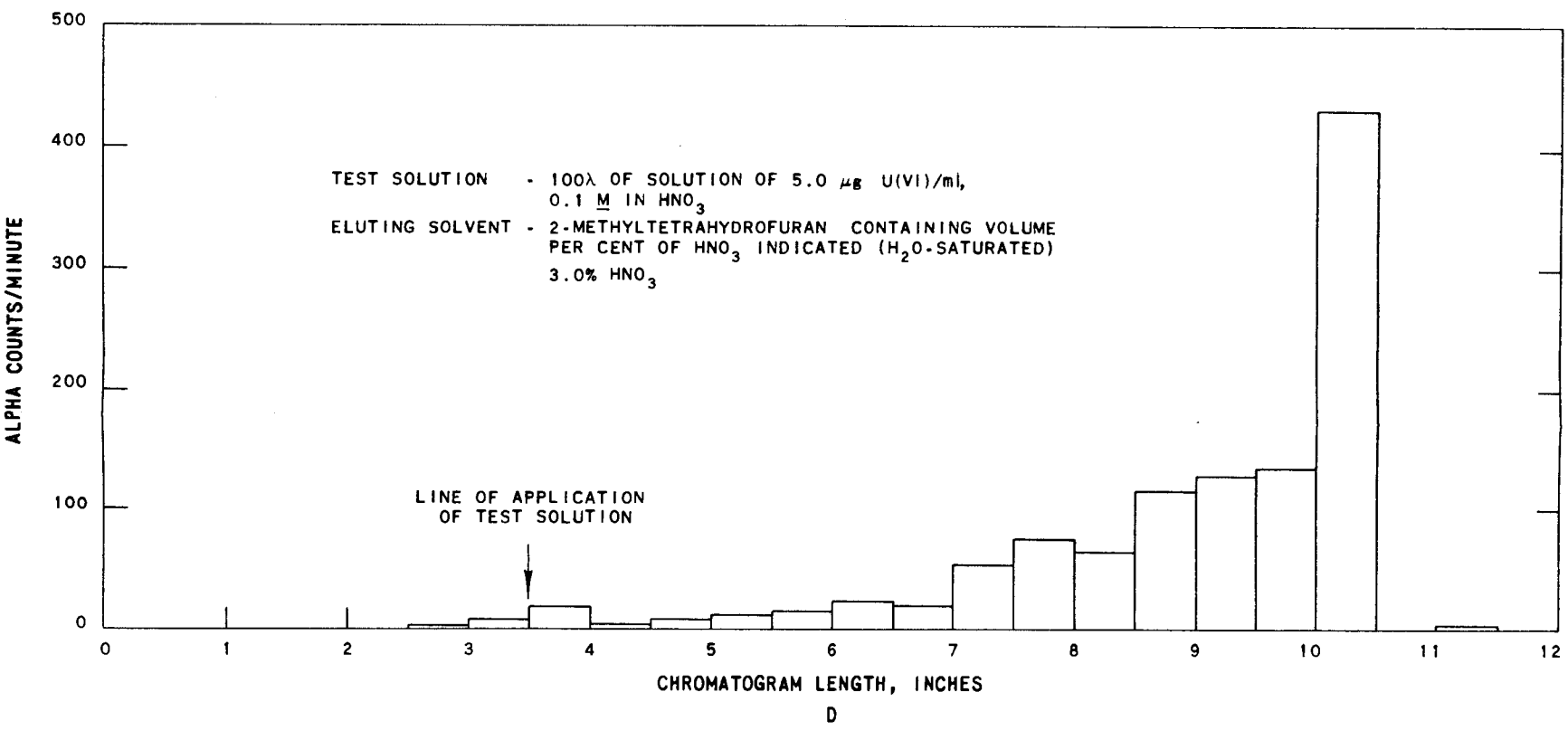


Fig. I (C and D) _ Effect of Acid Content of Eluting Solvent on Distribution of Uranium(VI) in Paper Chromatogram.

DWG. 12365 [redacted]

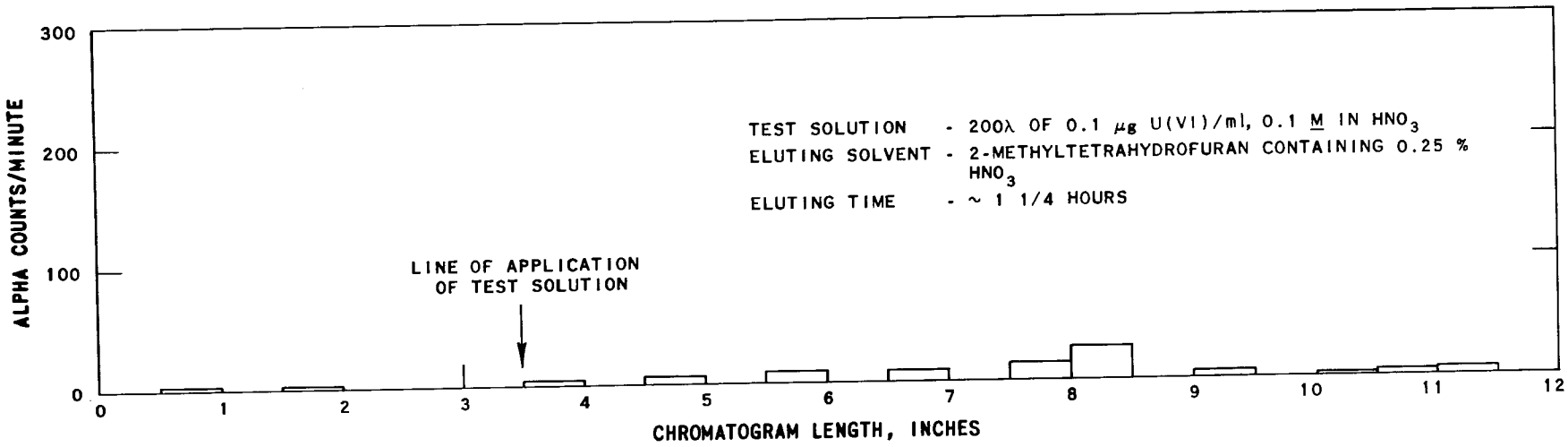


Fig. 2 - Distribution of Uranium(VI) in Chromatogram of 0.1 μg U(VI)/ml Solution

more than one locus may still be identified with a single substance. For this reason chromatograms were made for 100-λ samples of a U^{233} solution containing 5 γ/ml with solvents containing 0.25, 0.5, 1.0, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0% HNO_3. Elution was allowed to progress approximately 1.5 hr in all cases. The alpha count data for a selected group of these chromatograms and radioautographs shown in Fig. 1 indicate that the optimum nitric acid content of the solvent for producing the least diffuse band is 2.5%.

Studies are in progress to determine what elution time is required for obtaining maximum sharpness of the uranium band when the 2-methyltetrahydrofurane contains 2.5% HNO_3. Data taken to date are presented graphically in Fig. 3. These data show that the sorption zone does not migrate at a uniform rate, but that the lower portions of the zone, which contain the larger amount of adsorbed solute, migrate at a slower rate than the upper, a condition also characteristic of some column chromatograms.[9] The initial zone is compressed and the solute is concentrated as the elution proceeds. The minimum trailing is estimated to be reached between 1.5 and 2 hr, and may be independent of concentration, a factor yet to be investigated.

The successful use of tributyl phosphate in hexane solution for uranium extractions in plant operations suggested investigation of that solvent system as the mobile liquid phase in uranium chromatography. Chromatograms were made for a 100-λ aliquot of a U^{233} solution (5 γ/ml), 0.1 *M* in HNO_3, as described earlier, with solvent of the following composition: tributyl phosphate, 15 ml; concentrated nitric acid, 19.8 ml (of which about 15 ml remained immiscible); and hexane sufficient to make a total volume of 100 ml. The alpha count data and radioautographs are presented in Fig. 4. The results show that uranium is practically immobile with this liquid phase.

The separation of Fe(III) and U(VI) was effected on filter paper strips using 2-methyltetrahydrofurane containing 0.25% HNO_3 and qualitatively confirmed by radioautography and alpha count data. The reagents chosen for the experiment were U^{233}(VI) and a sample of irradiated $FeCl_3$ which contained Fe^{55}(III) and Fe^{59}(III) in such amounts as to give 500 beta counts per microgram of "dead" Fe(III). The separation of the Fe(III) and U^{233}(VI) bands on the chromatogram is clearly shown by the radioautographs, and the U^{233} locus by the alpha count data (Fig. 5). Increases in acid concentration to 2.5% and in elution time would have increased the distance traveled by the uranium. The

DWG. 12366 [redacted]

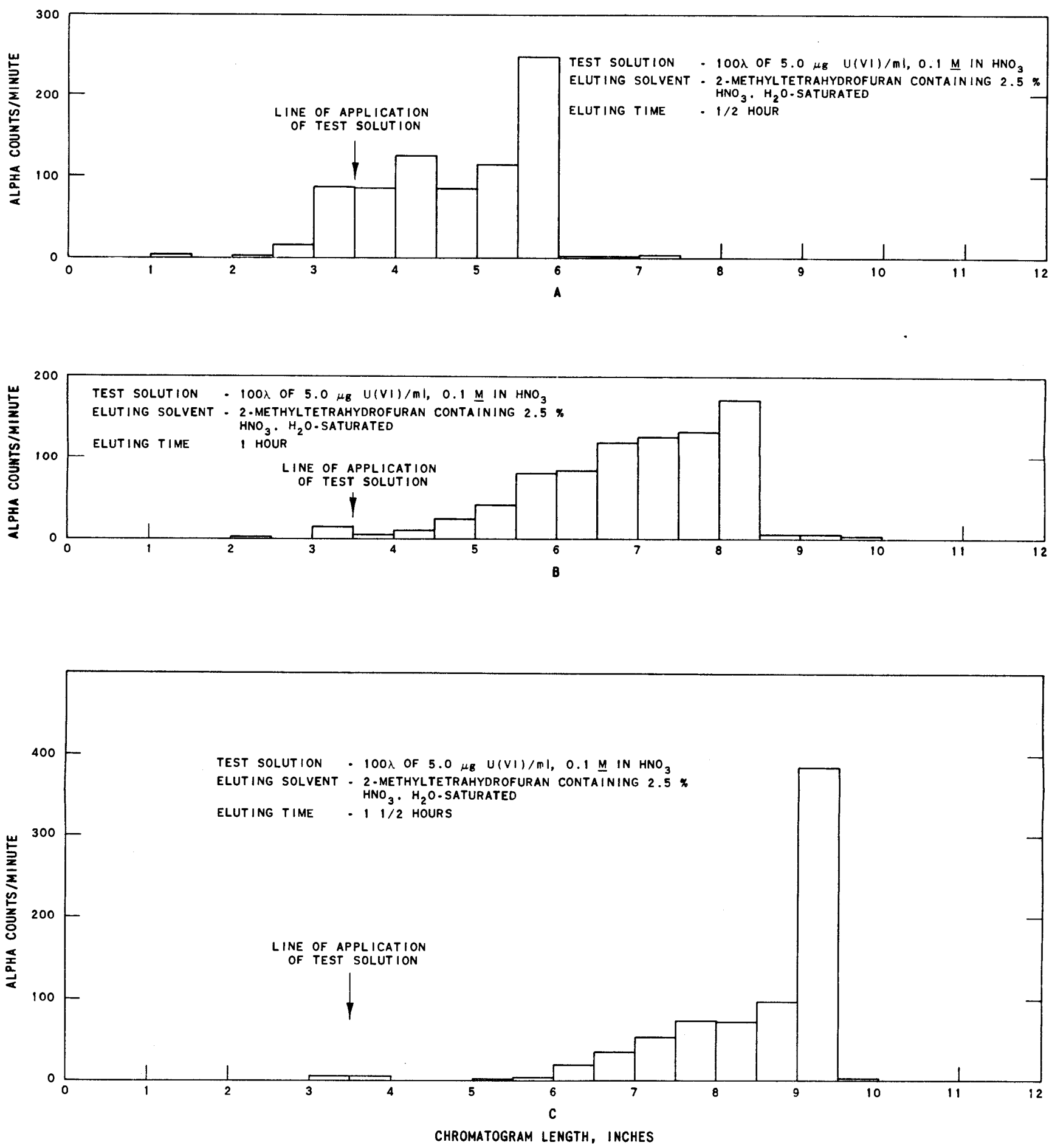
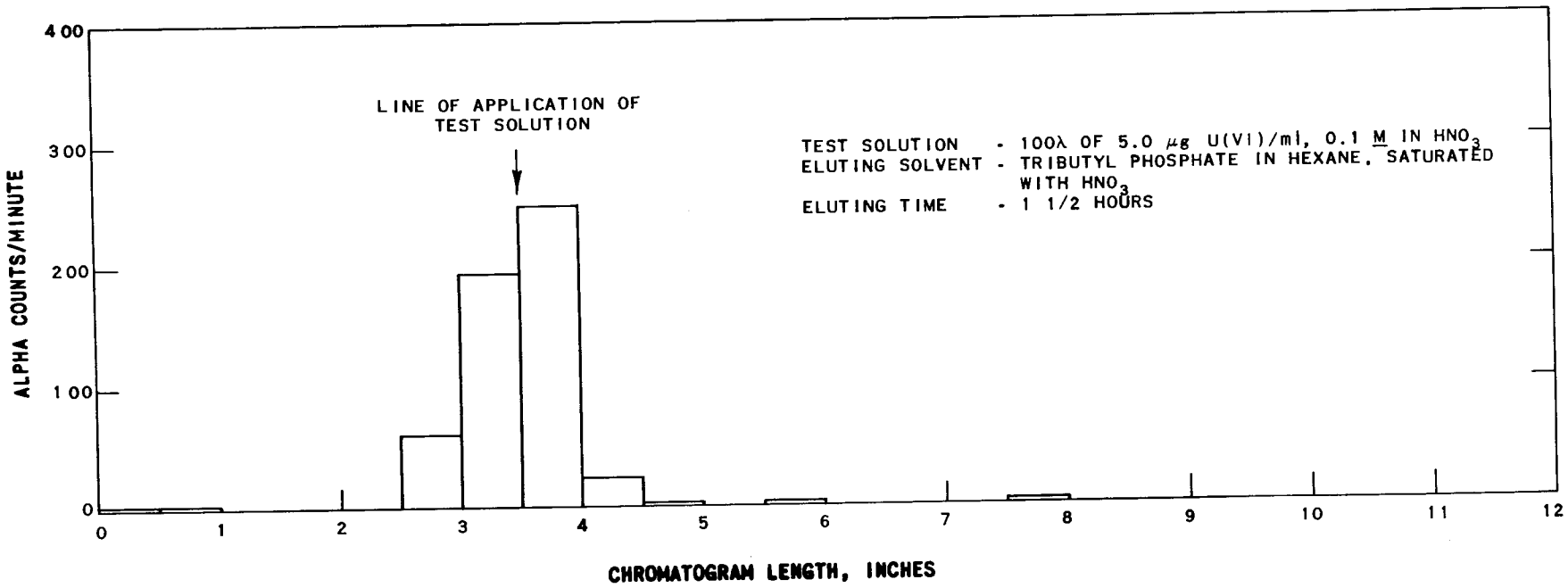


Fig. 3 - Effect of Elution Time on Distribution of Uranium(VI) in Paper Chromatogram

DWG. 12367

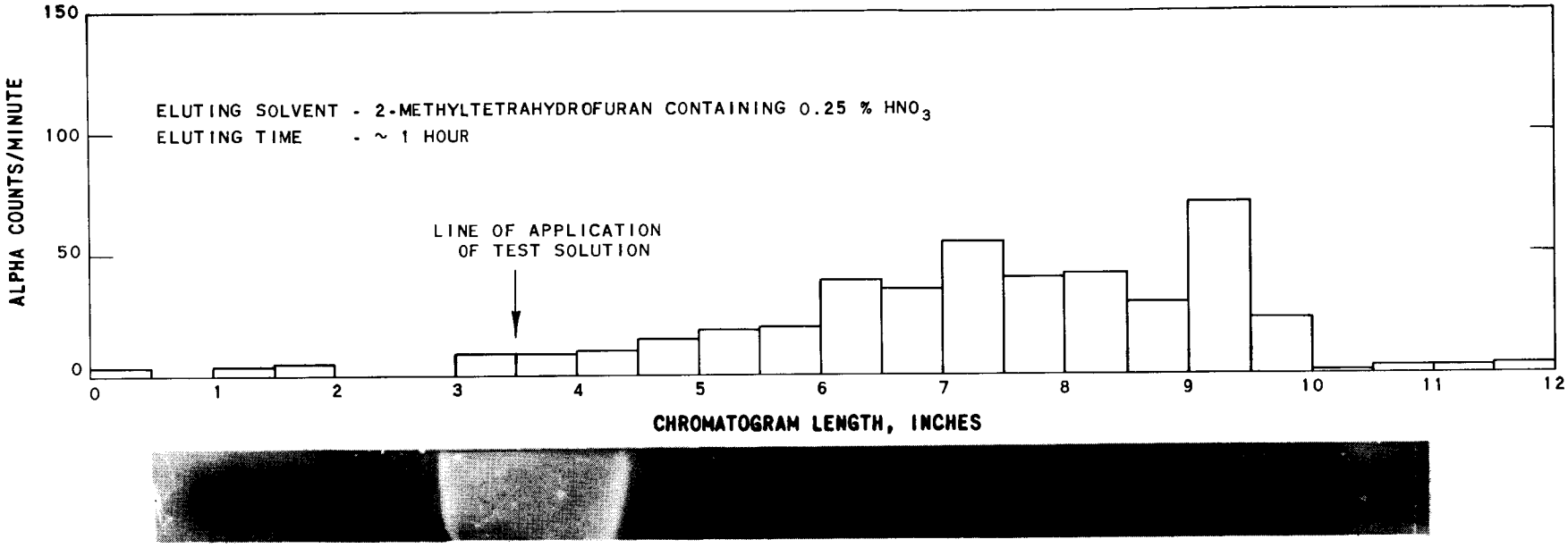
[redacted]



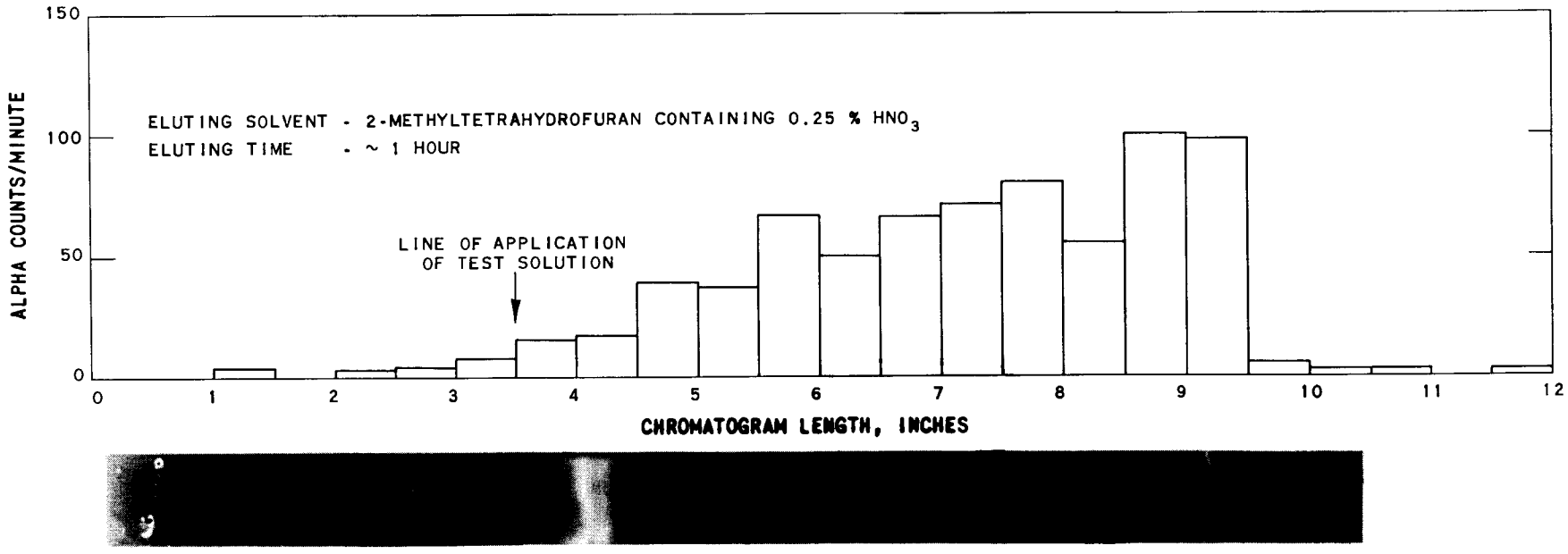
[redacted]

Fig. 4 - Ineffectiveness of Tributyl Phosphate in Hexane for Paper Chromatography of Uranium(VI)

DWG. 12368 [redacted]



A. TEST SOLUTION - 200λ OF SOLUTION CONTAINING 1 μg U(VI) AND 50 μg Fe(III)/ml, 0.1 M IN HNO_3



B. TEST SOLUTION - 100λ OF SOLUTION CONTAINING 4 μg U(VI) AND 100 μg Fe(III)/ml, 0.1 M IN HNO_3

Fig. 5 - Separation of Iron(III) and Uranium(VI) by Paper Chromatography

immobility of the Fe(III) is in accord with the results of Arden *et al.*,[18] who studied the movement of Fe(III) in a cellulose column eluted with diethyl ether containing nitric acid.

In summary, it may be said that filter paper partition chromatography with 2-methyltetrahydrofurane, containing aqueous nitric acid, as the mobile liquid phase, is an excellent method for the isolation of microgram and submicrogram quantities of U(VI). The reported immobility of most metal ions in this system indicates the good possibility of separating U(VI) from other nonradioactive or radioactive cations by this technique. The use of radioisotopes, together with radioautography and alpha counting methods, gives a highly sensitive qualitative method for locating the solute sorption bands on the chromatograms. Work is being continued to make the method quantitative for nonradioactive uranium.

POLAROGRAPHIC DETERMINATION OF URANIUM AT U(VI) CONCENTRATIONS OF 0.5 AND 1.0 γ/ml

H. P. Raaen

As discussed above, the most sensitive method known[13] for detecting natural uranium, i.e., the fluorescence method, was not satisfactory for accurate quantitative determination of microgram quantities of uranium in situ on filter paper. The necessity of removing the sorbed uranium for quantitative determination is therefore indicated. The polarographic method employing the "curve follower" instrument described recently[19] appeared attractive for analysis of chromatogram eluents containing uranium because of its high sensitivity range. It was therefore evaluated by the analysis of synthetic solutions of uranyl nitrate in 0.1 *M* HNO_3 having U(VI) concentrations of 0.50 and 1.0 γ/ml.

For the analysis of the 1.0 γ/ml solutions it was not necessary to use the curve follower. The standard addition technique[20] was used and the

(18) T. V. Arden, F. H. Burstall, R. P. Linstead, and R. A. Wells, *A New Method for the Separation and Purification of Uranium by Extraction of Uranyl Nitrate with an Organic Solvent in the Presence of Cellulose and Other Solid Absorbents*, Montreal Report CRL-AE-S-1 (Jan. 1, 1948).

(19) M. T. Kelley, H. H. Miller, and W. H. Davenport, Jr., "A Polarograph for Analysis of Very Dilute Solutions (10^{-6} *M*)," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part II. Analytical Chemistry*, ORNL-686, p. 24 (May 18, 1950).

(20) See "Polarographic Determination of Uranium," obtainable from files of P. F. Thomason, Ionic Analyses Group, Analytical Chemistry Division, ORNL.

instrument operated under the following conditions: sensitivity, 8 (0.02 μa); damping, 40.0; compensation, approximately 345; span, 1.0 volt. The test solutions were bubbled with nitrogen for a minimum of 10 min before each polarogram was taken. A method of interpreting the polarograms was established which is shown graphically in Fig. 6. A fresh test solution and standard were prepared for each analysis. The data are given in Table 1.

TABLE 1

Polarographic Analysis of Uranyl Nitrate Solutions, 0.1 *M* in HNO_3, Containing 1.0 γ of U(VI) per Milliliter*

ANALYSIS NO.	CONCENTRATION OF URANIUM (γ/ml)	d_i
1	0.96	0.00
2	1.01	0.05
3	[1.12] **	[0.16]**
4	[0.76] **	[0.20]**
5	0.97	0.01
6	0.89	0.07
7	0.96	0.00
8	0.95	0.01
9	0.90	0.06
10	0.99	0.03
11	1.01	0.05
	9) 8.64	9) 0.28
	Avg. dev. = 0.96	Avg. dev. = 0.03
	% Error = 4.0	

*Prepared by dilution from a solution containing 10.04 mg U(VI)/ml, according to standardization by ignition analysis.

**Shown by statistical test[21] to be a deviate value.

For the polarographic analysis of the U(VI) solutions containing 0.5 γ/ml the standard addition technique[21] was also used and the sensitivity of the instrument was extended by use of the curve follower. The polarograms were made under the following conditions: sensitivity, 8 (0.02 μa); damping, 30.0; compensation, 298 to 302.5; span, 1.0 volt.

(21) I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, p. 276, Macmillan, New York, 1948.

DWG. 12369
NOT CLASSIFIED

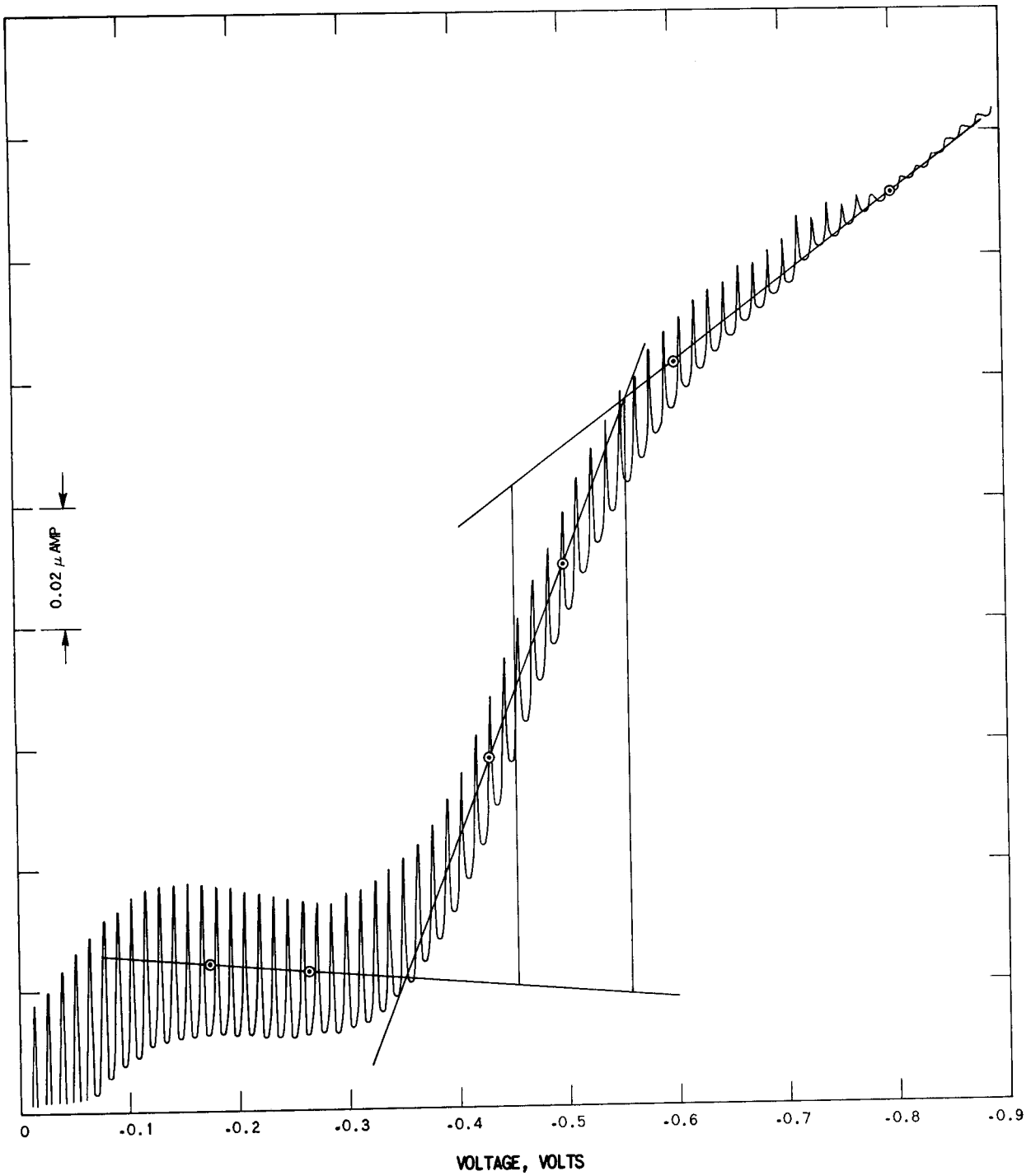


Fig. 6 - Polarogram of Solution of 1.0 μg U(VI)/ml in 0.1 M HNO_3

Test solutions were bubbled with nitrogen for at least 15 min before the polarograms were recorded. Fresh solution and standard were prepared for each polarogram. Typical curves for the blank on 0.1 *M* HNO_3, the test solution, and test solution plus standard addition are shown in Fig. 7. The data are given in Table 2.

TABLE 2

Polarographic Analysis of Uranyl Nitrate Solutions, 0.1 *M* in HNO_3, Containing 0.5 γ of U(VI) per Milliliter

ANALYSIS NO.	CONCENTRATION OF URANIUM (γ/ml)	d_i
1	[0.67]*	[0.17]*
2	0.50	0.00
3	0.51	0.01
4	0.50	0.00
5	0.48	0.02
6	[0.42]*	[0.08]*
7	0.52	0.02
8	0.51	0.01
9	0.51	0.01
10	0.51	0.01
11	0.49	0.01
	9)4.53	9)0.09
	Arith. mean = 0.503	Avg. dev. = 0.01
	% Error = 0.6	

*Shown by statistical test[21] to be a deviate value.

To check the data of Table 2, two unknowns, prepared by a coworker, were analyzed. The results are given in Table 3.

TABLE 3

Polarographic Analysis of Unknowns Containing Approximately 0.5 γ of U(VI) per Milliliter

CONCENTRATION OF URANIUM (γ/ml)		% ERROR
PREPARED TO BE	FOUND POLAROGRAPHICALLY	
0.55	0.50	10.0
0.66	0.60	8.3

DWG. 12370
NOT CLASSIFIED

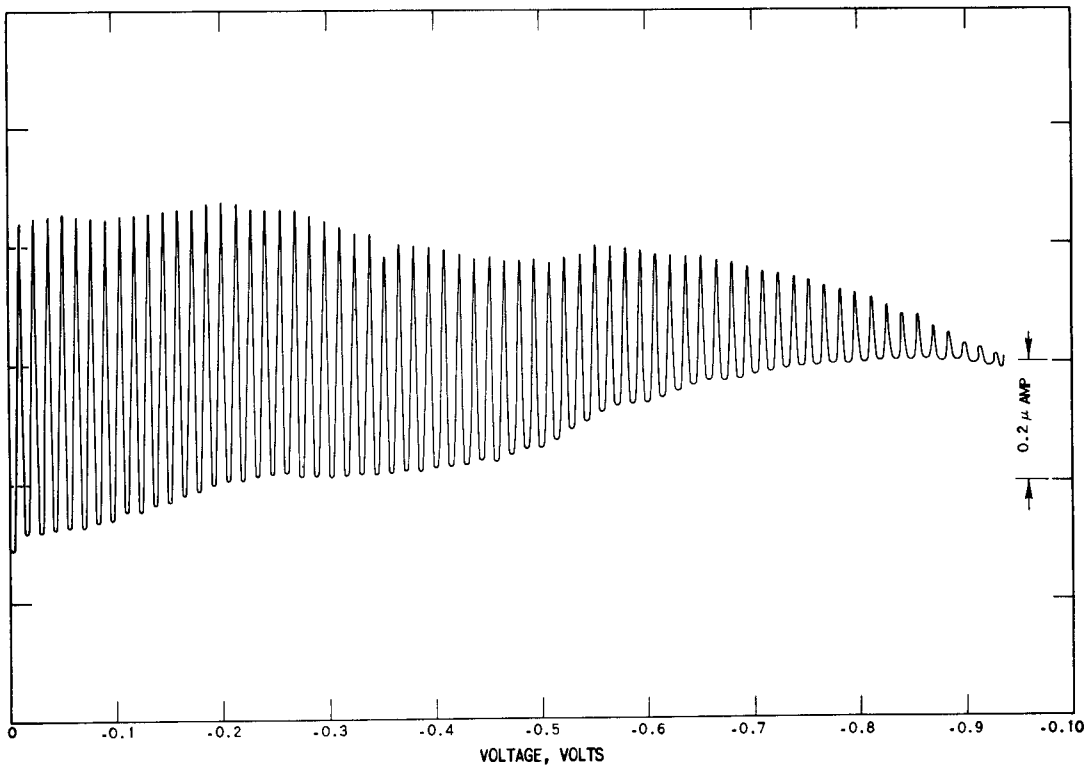


Fig. 7A - Polarogram of 0.1 M HNO_3 Using Curve Follower

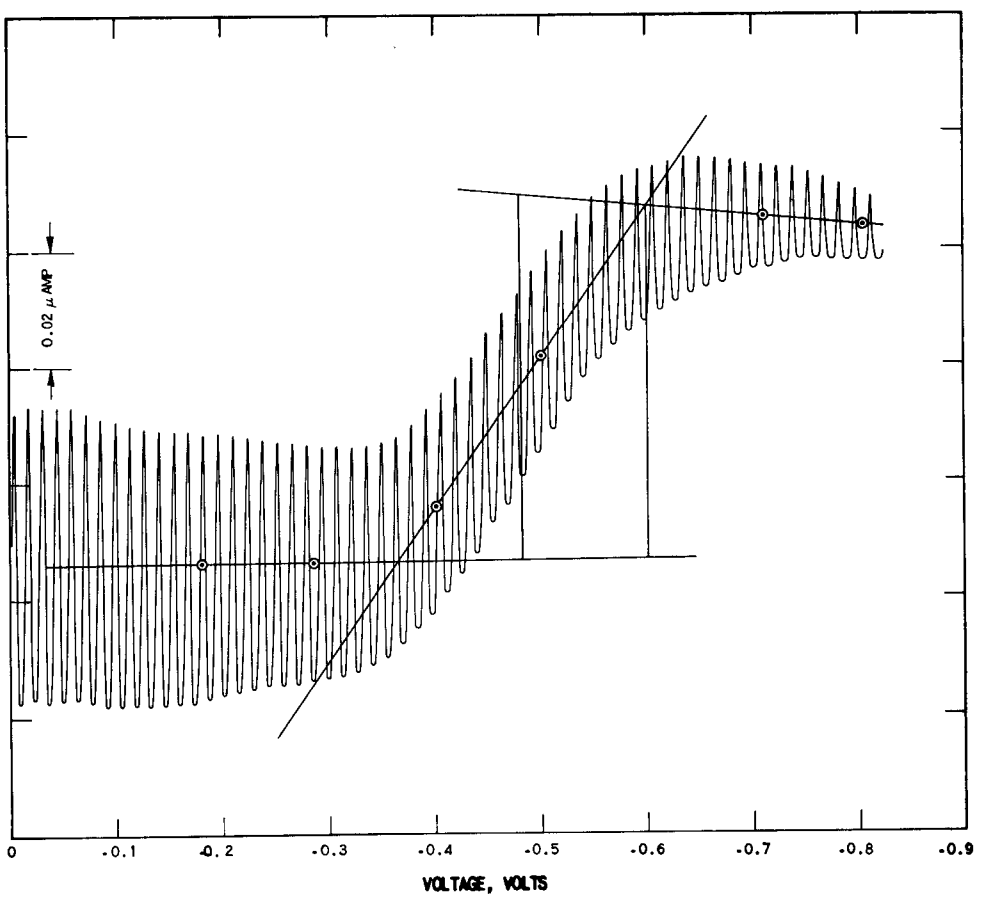


Fig. 7B - Polarogram of Solution of 0.5 μg U(VI)/ml in 0.1 M HNO_3 Using Curve Follower

The high errors obtained here compared with the results in Table 2 are unexplained, and the check analyses will be repeated.

The results of this study suggest that the polarographic method employing the curve follower may be suitable for determining uranium in chromatogram effluents. It challenges the fluorometric method for uranium with respect to sensitivity and surpasses it in accuracy, that of the photofluorometric procedure being only 15 to 20% in this concentration range.

POLAROGRAPHIC DETERMINATION OF LEAD IN BLOOD, URINE, AND AIR SAMPLES

H. H. Miller

Previously, the determination of lead in blood and urine has been done at ORNL by the colorimetric dithizone method. However, because this method is time-consuming, the Health Physics Division requested a more rapid method having an accuracy comparable to that of the dithizone method. From previous polarographic work[22] it has been found that an organic sample may be wet-ashed and a polarographic analysis made on the residue.

Preliminary investigation of the wet-ash residues from blood and urine samples indicated that the residues could be dissolved in 0.1 *M* HNO_3 and the lead extracted with a chloroform solution of dithizone after the *p*H had been adjusted to approximately 8.2 with NH_4OH. The lead could be stripped back into 0.1 *M* HNO_3 and run polarographically.

To shorten the procedure further by eliminating the extraction step, the residue from the wet ash was dissolved in 0.1 *M* HNO_3 and polarographed directly. However, when this was done, a wave beginning at zero applied potential was found which interfered with the lead wave. This interference was caused by the iron which is found in the hemoglobin of the blood and in urine. Ferric iron in acid solution can usually be reduced with hydroxylamine hydrochloride, but the large concentration of phosphate in blood and urine prevents complete reduction of iron to ferrous iron with this reagent by forming ferric phosphate complexes. However, if orthophenanthroline is added, its reaction with the small amount of ferrous iron present to form the ferrous orthophenanthroline

(22) H. H. Miller, "Polarographic Determination of Cadmium in Vinylite," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-788, p. 16 (Oct. 4, 1950).

complex causes a shift in the equilibrium of the phosphate-complex-forming reaction in such a way that all the ferric iron becomes available for reduction by hydroxylamine hydrochloride and subsequent complexing as ferrous orthophenanthroline, which is not reduced polarographically in 0.1 *M* HNO_3. This solution can then be polarographed directly.

Because of the low concentration of lead in blood and urine, a high-sensitivity recording instrument must be used for its polarographic determination.[23] For this technique only small samples are needed from the patient.

Lead removed from air samples by drawing the air through filter paper may also be determined by this procedure. The lead is extracted from the filter paper with 0.1 *M* HNO_3, and the extract is treated with hydroxylamine hydrochloride to reduce the ferric iron and analyzed polarographically.

POLAROGRAPHIC DETERMINATION OF INDIUM IN INDIUM-THORIUM ALLOY

H. H. Miller

In the investigation by the Metallurgy Division of various thorium alloys which have properties suitable for use in reactors, an indium-thorium alloy was made. Because of the low concentration of indium present, a polarographic method of analysis was developed for its determination.

Kolthoff and Lingane[24] have reported that, in the presence of 0.1 *M* KCl and a small amount of gelatin, 10^{-3} to 10^{-2} *M* indium gives a well-defined wave with a half-wave potential of approximately -0.5 volt vs. S.C.E. Polarograms of standard solutions of indium with In(III) concentrations between 5 and 20 γ/ml give well-defined waves and indicate that gelatin is not necessary as a maximum suppressor in this concentration range.

The indium-thorium alloy was treated with 10 ml of hot concentrated HCl and 4 to 5 drops of concentrated HNO_3. This solution was heated until no further reaction took place, and then 5 ml of concentrated HCl, containing ½ drop of concentrated HF, was added to the solution. Upon further heating the solution became clear. It was evaporated to near dryness and diluted to

(23) M. T. Kelley and H. H. Miller, *A High Sensitivity Recording Polarograph*, ORNL-942, in press.

(24) I. M. Kolthoff and J. J. Lingane, *Polarography*, rev. ed., p. 274, Interscience, New York, 1941.

volume with 0.1 *M* KCl. This solution was polarographed, the standard addition method of analysis being used. The samples were found to contain 0.22% indium. From the limited number of analyses made, the accuracy of the polarographic method for determining indium in indium-thorium alloy is estimated to be about ±3%.

POLAROGRAPHIC STUDIES OF SUBMICROGRAM QUANTITIES OF INDIUM

H. H. Miller

To obtain polarographic waves of submicrogram quantities of metals it has been found necessary to use the curve-follower technique to extend the range of sensitivity of the polarograph. The curve follower has been very useful when the sensitivity of the polarograph is of the order of 0.02 μa per full scale deflection on the Brown recorder chart.

Previous studies of the determination of submicrogram amounts of metals which have used the curve-follower technique have included lead[25] and uranium.[26] In the continuation of these studies indium has been selected because it gives a well-defined wave and because it has a three-electron change in the reduction.

Before a wave could be obtained for indium, a blank of the supporting electrolyte, 0.1 *M* KCl, was drawn on the polarograph and transcribed to the curve follower. The indium wave was then obtained by running the curve follower and polarograph simultaneously.

Since the half-wave potential of indium in 0.1 *M* KCl is -0.56 volt vs. S.C.E., the curve was drawn from -0.3 to -0.7 volt. When an aliquot of 0.1 *M* KCl was polarographed to obtain a blank for the curve follower, the oscillations at -0.3 volt were large; as the curve progressed the oscillations became smaller until the curve reached the electrocapillary zero (approximately -0.55 volt in 0.1 *M* KCl), at which point the charge on the mercury drop becomes zero. When this curve was transferred to the curve follower and both the curve follower and the polarograph were run to obtain a corrected blank, the

(25) H. H. Miller, "Using the Curve Follower in the Determination of Low Concentrations of Lead and Iron in Ammonium Oxalate," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part II. Analytical Chemistry*, ORNL-686, p. 30 (May 18, 1950).

(26) H. P. Raaen, "Polarographic Determination of Uranium at U(VI) Concentrations of 0.5 and 1.0 γ/ml," this report, p. 30.

curve follower refused to follow the blank at the time it reached the electrocapillary zero, making the blank useless for low-concentration curves. This had not been observed before in the cases of lead ($E_{1/2}$ = -0.41 volt) and uranium ($E_{1/2}$ = -0.18 volt) because the half-wave potentials precede the electrocapillary zero by several millivolts.

In order to overcome this difficulty a small amount of uranium was added to the supporting electrolyte (approximately 50 γ to 10 ml of electrolyte) and this solution was polarographed. The polarogram was then started at -0.3 volt, which is in the region of the limiting diffusion current of the uranium reduction. On rerunning this solution a good blank was obtained because the charge on the mercury drop was prevented from changing by the reduction of uranium, even though the capillary zero remained constant. A good corrected blank could be obtained under these conditions.

Polarograms of indium at concentrations of approximately 1.7×10^{-7} *M* (0.02 γ of indium per milliliter) and approximately 3.5×10^{-7} *M* (0.04 γ of indium per milliliter) were obtained. The latter is shown in Fig. 8.

Future work will include determining diffusion coefficients and diffusion currents over a range of indium concentrations.

INDIRECT POLAROGRAPHIC DETERMINATION OF POTASSIUM AS POTASSIUM COBALTINITRITE

A. D. Horton

As an indirect method for determining potassium it is proposed to precipitate potassium as potassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6 \cdot xH_2O$, and determine cobalt polarographically. Potassium has been determined volumetrically[27] using this method of precipitation.

The proposed polarographic procedure consists in precipitating solutions containing micro amounts of potassium in centrifuge cones by adding a large excess of sodium cobaltinitrite solution. The precipitate formed is then separated from the mixture by centrifuging at full speed in a clinical centrifuge. The precipitate is washed twice with small amounts of water or dilute

(27) W. C. Böttger (ed.), *Newer Methods of Volumetric Chemical Analysis*, by Erna Brennecke *et al.*, tr. by Ralph Oesper, p. 40, Van Nostrand, New York, 1938.

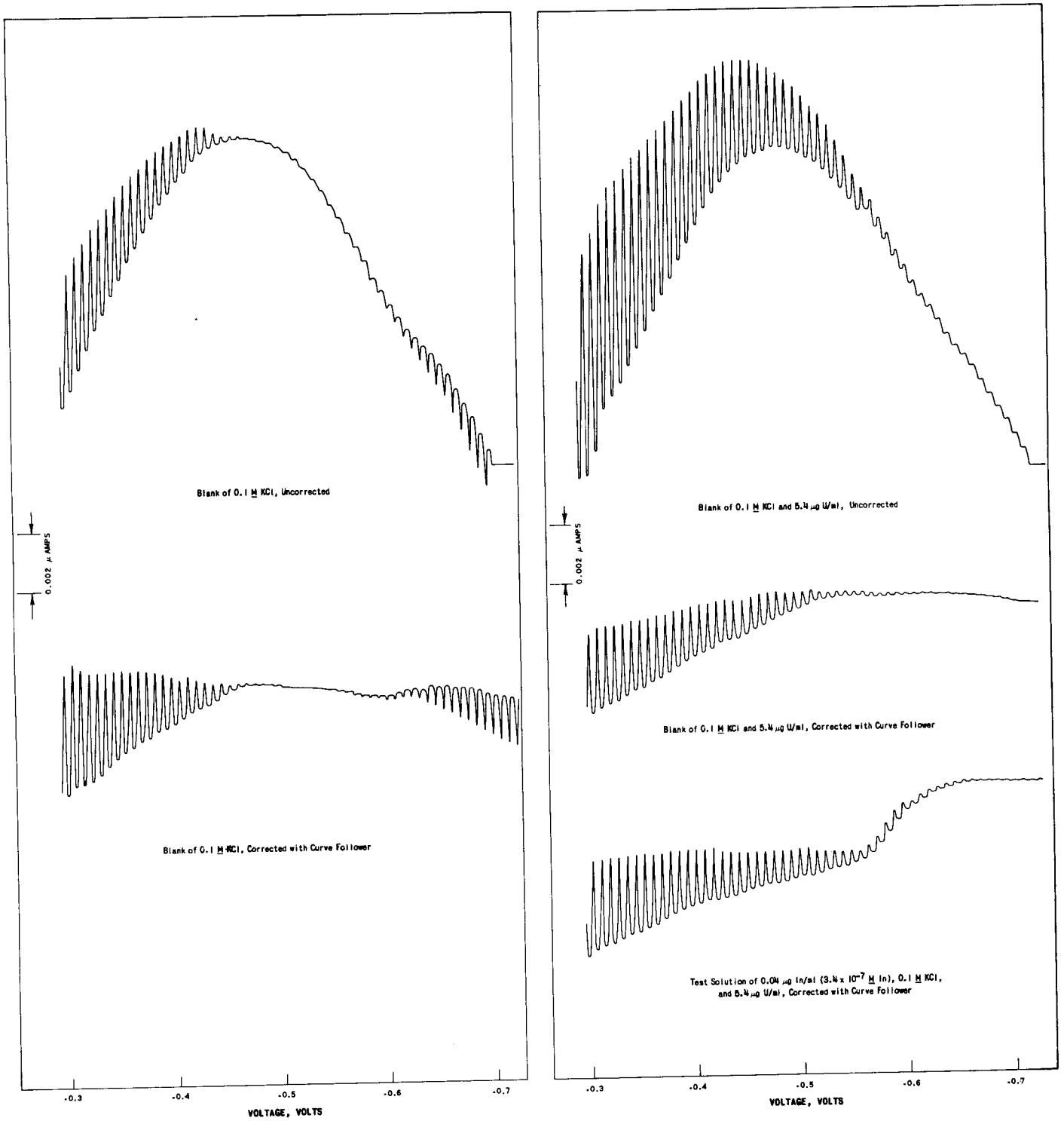


Fig. 8 - Polarograms of 0.1 M KCl and of 0.04 μg In(III)/ml Using the Curve Follower

ethanol and centrifuged, and the wash liquid is decanted. The precipitate is dissolved in enough 13 *M* hydrochloric acid and diluted to the desired polarographic volume with enough dilute pyridine to make the test solution of cobalt 0.1 *M* in pyridine and 0.1 *M* in chloride. This is the electrolyte recommended by Kolthoff[28] for cobalt which is being determined polarographically.

A few determinations have been attempted using sodium cobaltinitrite prepared according to Hillebrand.[29] Ethanol, 95%, was used to wash the precipitate, since it was reported by Seidell[30] that potassium cobaltinitrite was least soluble in this medium. However, a conference with H. H. Willard[31] established that water had been used in clinical methods with this precipitate, and it was recommended as satisfactory.

The results obtained by this method have been inconclusive. Recovery of potassium has generally been incomplete. Experimental work is in the early stages, and further work is necessary to establish the amount of sodium cobaltinitrite required, the minimum time required for complete precipitation, the type and amount of wash solution, and the proper composition of the polarographic electrolyte.

SPECIAL HOOD FOR AUTOMATIC TITRATION OF PLUTONIUM

F. J. Miller

To facilitate plutonium titrations by providing protection for analytical personnel a "dry box" type hood has been installed. The placement of the elements described below is shown in Fig. 9.

The hood is equipped with a Plexiglas front, permitting direct observation of all operations. Two portholes at the front are equipped with rubber gloves to permit necessary manual operations. A door at one end and an air-lock

(28) I. M. Kolthoff and J. J. Lingane, *Polarography*, rev. ed., p. 285, Interscience, New York, 1946.

(29) W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, p. 530, Wiley, New York, 1929.

(30) A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, Van Nostrand, New York, 1940.

(31) Conference with H. H. Willard, Secret Notebook No. 442, Mar. 2, 1951.

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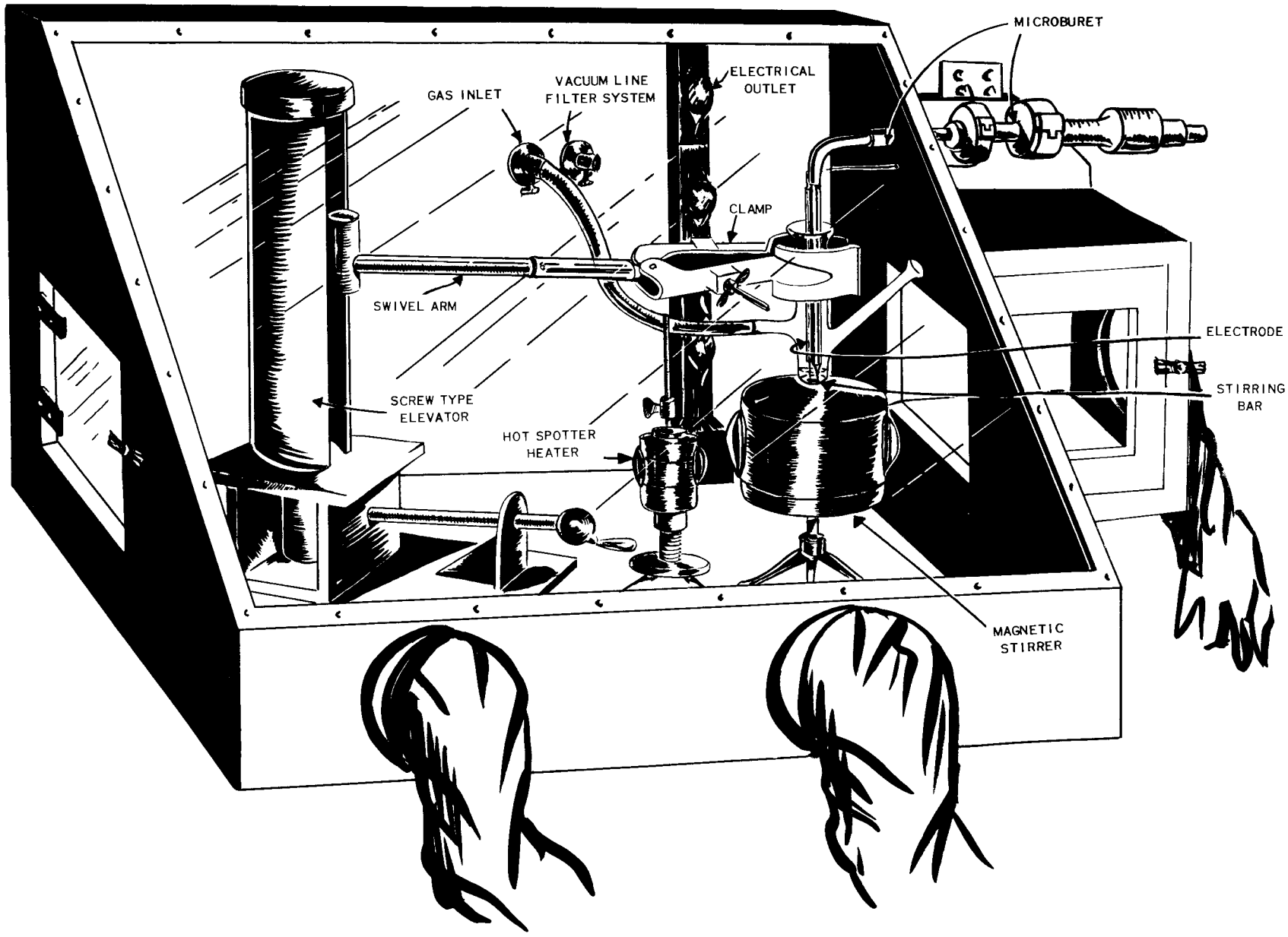

Fig. 9 - Special Hood for Automatic Titration of Plutonium

opening at the other permit easy access to the interior of the hood. The hood is serviced on the back wall with gases, electricity, and vacuum. The gas inlet tube may be connected externally to either N_2 or CO_2 cylinders for supplying an inert atmosphere.

The complete procedure for the micro titration of plutonium as previously described[32] may be carried out in the hood. The apparatus required in the hood consists of a Fisher "Hot-spotter" heater and a magnetic stirrer, each mounted on a movable tripod, and a titrating vessel. The titrating vessel is clamped onto a swivel arm which rides on a screw type elevator. The movable mounting enables the analyst to bring the vessel into easy reach in order to pipet aliquots into it, to place it on the heater for fuming operations, or to raise it until the buret tip and indicating electrode are immersed in solution. The microburet is mounted externally with only the glass delivery tube projecting through the hood wall. The drive portion of the buret and both components of the automatic titrator are thus removed from the zone of contamination.

(32) F. J. Miller "Automatic Micro Titrations" ORNL-686, p. [illegible], p. 9.

2. RADIOCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT

NUCLEAR PROPERTIES

This work is part of a continuing program begun in 1948 which has as its goal the elucidation of unknown or uncertain radioactive decay transitions of nuclides which are processed and shipped by the Operations Division of ORNL. Aside from the obvious scientific value of such a program, i.e., the accumulation of physical data concerning radioactive decay processes, this work has a significant economic aspect also, since, before the cost of production and hence the price charged for any radionuclide can be determined, the amount of radioactivity must be capable of accurate measurement. Only through the thorough and exact knowledge of the decay scheme can such measurements be made.

Disintegration of Cr^{51} (W. S. Lyon). Spectrometer studies made by previous investigators have established that Cr^{51} decays entirely by orbital electron capture accompanied partially by 2 quanta of gamma radiation. Kern *et al.*[1] list the gamma-ray energies as 0.32 and 0.267 Mev. Bradt *et al.*[2] find the gamma energies to be 0.320 and 0.237 Mev, and in addition suggest that the decay proceeds 97% directly to the ground state, 3% through the 0.32-Mev excited state, and about 1% through the 0.237-Mev level. By use of Cr^{51}, supplied by the Operations Division of the Oak Ridge National Laboratory, the branching ratio of this nuclide has recently been investigated by means of coincidence counting, X-ray counting, and ion chamber measurement.

In agreement with the data of Bradt *et al.*[2] we have found very little β^- or e^- associated with the decay. Using a helium-alcohol-filled tube as an electron detector we find 5.0×10^{-3} β^- per X-ray disintegration. The X rays observed are therefore essentially all from orbital capture, and no interference from a conversion process is encountered. A measured aliquot of Cr^{51} was coincidence-counted using a krypton-methane-filled thin-end-window proportional counter as an X-ray detector and a gold-coated argon-methane proportional counter as a gamma detector. X-ray and coincidence data were taken as a function of beryllium absorber placed before the X-ray counter. The disintegration rate of the source so measured was calculated and found to be constant and independent of beryllium absorber.

(1) B. D. Kern, A. B. C. Mitchell, and D. J. Zaffarano, "The Nuclear Spectra of Sb^{125}, Te^{125*}, Cr^{51}, and I^{131}," *Phys. Rev.* 76, 94 (1949).

(2) H. Bradt, P. C. Gugelot, O. Huber, H. Medicus, P. Preiswerk, and P. Scherrer, "Radioactive Transformation of Cr^{51}," *Helv. Phys. Acta* 18, 259 (1945).

A source of Mn^{54}, the disintegration rate of which was known through coincidence counting and ion chamber measurements, was used to determine the efficiency of a krypton-methane counter for Cr K X-rays (2.29 A). A measured aliquot of Cr^{51} (V X-rays, 2.50 A) was then counted on this krypton-methane counter, and, using the previously determined efficiency, the disintegration rate of the Cr^{51} was obtained. Agreement between this value and that obtained by coincidence counting was within 3%. An absorption curve in lead was obtained on an aliquot of the sample, using a calibrated high-pressure ion chamber similar to that described by Jones and Overman.[3] These data show the presence of two gamma rays, 0.33 and 0.27 Mev in the ratio of 3 to 1. Gamma radiation accompanies 15% of the total disintegration, and the decay would thus appear to be 11.3% through 0.33 Mev, 3.8% through 0.27 Mev, and 85% directly to the ground state.

Decay on a Cr^{51} source has been followed for four months on both a Geiger-Mueller counter and ion chamber. A value for the half-life of 27 ± 0.4 days is indicated.

Disintegration of Sr^{85} (W. S. Lyon and D. J. Coombe). Ter-Pogossian,[4] who used a 180° spectrometer, reports, in the only published study of Sr^{85}, this nuclide to decay by K-electron capture accompanied by gamma radiation of 0.510 Mev energy. Using coincidence counting and ion chamber measurements, we have confirmed these results and in addition have determined the fraction of the decay accompanied by the gamma radiation.

Sr^{85} was produced by the reaction $Rb^{85}(d, 2n)Sr^{85}$ using 15.8-Mev deuterons on Rb which had previously been freed from Sr. After a two-month cooling period the activity appeared to be greater than 99% Sr^{85}, with radiochemical analysis indicating only a trace of P^{32} as contaminant.

Aliquots of the Sr^{85} solution were evaporated and used in obtaining aluminum and lead absorption data. These data indicate the radiation to be composed entirely of Rb X-rays and electromagnetic radiation of 0.52 Mev, in agreement with the results of Ter-Pogossian.[4] The amount of activity due to conversion of electrons appears to be of the order of 0.2%. X-gamma coincidences were obtained using a beta proportional counter as the X-ray

(3) J. W. Jones and R. T. Overman, *The Use and Calibration of a 100% Geometry Ion Chamber*, AECD-2367 (Mar. 20, 1948).

(4) M. Ter-Pogossian, "On the Disintegration of Sr^{85}," *Phys. Rev.* 77, 743 (1950).

detector and an anthracene crystal with photomultiplier as the gamma counter. X-gamma coincidence data were obtained as a function of aluminum absorbers placed before the X-ray detector. The disintegration rate obtained from these data was constant and independent of absorber thickness. The disintegration rate was also independent of position of the gamma detector when the counter was varied through 90°, indicating no positron emission or angular correlation.

Using the above-determined disintegration rate and data obtained from a calibrated high-pressure gamma ionization chamber, it was found that the decay of Sr^{85} occurs 77% directly to the ground state and 23% accompanied by the 0.5-Mev gamma ray.

Cross-Sections for Pile Production of Fe^{55} and Fe^{59} (W. S. Lyon). Work is in progress which will lead to an accurate evaluation of thermal cross-sections for Fe^{55} and Fe^{59} production. At present enriched Fe samples are in the Hanford Reactor for activation.

MEASUREMENT OF RADIOACTIVITY

Geometry for Low-Energy Beta Counting (W. S. Lyon and S. A. Reynolds). By use of Na^{24}, Co^{60}, and Nb^{95}, geometries[5] have been obtained on five different Geiger-Mueller counters. While the Na^{24} geometry was essentially the same on all counters, some variance was observed in the Co and Nb geometry. The ratio G(Co)/G(Nb) remained the same (within experimental error), and it thus seemed practical to determine the geometry for low-energy beta emitters by applying a "factor" to the Co geometry.

The experimentally determined ratio G(Co)/G(Nb) = 1.08. Thus the Nb^{95} geometry may be determined from the equation G(Nb) = G(Co)/1.08.

The Nb geometry may be used for S^{35} since the energy (0.17 Mev) is quite close to that of Nb^{95} (0.15 Mev). In all cases, the sample should be free of solids and mounted on polystyrene. Absorption data in aluminum should be taken, and extrapolation to true zero should be made in the usual manner.

Low-Level Waste Activity (W. A. Brooksbank and S. A. Reynolds). The Analytical Division has been requested by W. K. Eister of the Chemical Technology Division and by members of the Measurements Subcommittee of the Wastes

(5) W. S. Lyon and S. A. Reynolds, "Assay of Low-Energy Beta Emitters," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955, p. 24 (Mar. 28, 1951).

Processing Group to develop a method for the routine assay of low-level liquid wastes (10^{-8} to 10^{-5} μc/ml). There appear to be two methods of approach to this problem. The first, the method outlined by J. W. Healy of Hanford,[6] would entail a large amount of experimental work at each site to determine such factors as geometry, back-scattering, self-absorption, etc. for each individual counting arrangement. It would still suffer from lack of interrelations between the sites, depending on the accuracy of determining these correction factors. The other method, which appears more promising, is to establish a standard activity having approximately the same beta characteristics as typical waste, i.e., the same average beta energy, and measured in the same form. Something similar to this has been done by Cowan and coworkers[7] at Brookhaven National Laboratory for a specific case. In the proposed method the analyst could measure the standard either in solution, dried, or as a "spike," in his own equipment; then, by comparison with the microcurie-per-milliliter figure for the standard, the activity of the waste could be expressed on the same basis.

The two radionuclides which seem applicable are 127-day Tm^{170} and 2.7-year Tl^{204}, either of which could be prepared, standardized, and distributed by ORNL. For special cases of low-energy activity, other standards of different energies could be distributed to all sites for intercomparison. The unit of activity concentration might be "μc/cc as Tm^{170}," for example. This procedure would at once eliminate the difficulties of corrections for back-scattering, self-absorption, yield, etc. involved in determining "absolute" disintegration rates. The following have expressed interest in the use of the standard: E. Orban, Mound; G. Swope, Argonne; W. K. Eister, R. Morton, R. A. Lauderdale, and A. H. Emmons, ORNL; J. W. Healy, Hanford; and F. P. Cowan, Brookhaven.

A bibliography has been compiled on counting methods for liquid wastes and low-level counting in general. This will be issued as a separate report.

A sample of liquid waste was submitted by Dr. Edward Orban of Mound Laboratory. He was interested in a comparison of the counting rate as determined here with that obtained in his own laboratory.

(6) J. W. Healy, L. C. Schwendiman, and R. C. Thorburn, *Counter Calibrations in the Health Instrument Methods Group,* Hanford Report HW-18258 (July 1, 1950).

(7) F. P. Cowan and J. V. Nehemias, "Sensitivity of the Evaporation Method of Liquid-waste Monitoring," *Nucleonics* 7, No. 5, 39 (1950).

Two methods of assay were used:

1. The standard technique of drying an aliquot on a 1-in watch glass and counting on an end-window Geiger-Mueller counter (approximately 2.5 mg/cm^2 window), with about 8% geometry. No corrections for absorption or back-scatter were made.

2. Samples of various sizes evaporated on stainless steel disks, and counted on a Borkowski type proportional beta counter (50% geometry). After plotting sample volume against counts per minute per milliliter, extrapolation was made to zero volume (i.e., zero self-absorption). No correction was made for back-scatter. Errors refer to the 95% confidence level.

A sample was also counted by means of the proportional alpha counter. No alpha counts were found. Data are given in Table 4.

TABLE 4

Counting Data on Mound Laboratory Sample

METHOD	ACTIVITY (c/m/ml)
1	222 ± 5
2	(1.7 ± 0.1) × 10^3

Experimental Dishes for Sample Mounting (T. H. Handley). Copper and stainless steel dishes of various designs have been tested for use as sample mounts for gross beta counts with the object of replacing 1-in. watch glasses (Fig. 10*e*) now in use in routine work. Since neither of these metals is resistant to all acids, Teflon paint was sprayed on them to make them more acid resistant. The results on the various dishes were as follows:

1. With the design shown in Fig. 10*a* the vertical walls caused solids to be deposited in a ring around the base of the wall, thus causing maximum self-absorption.

2. With the design shown in Fig. 10*b* solids were deposited fairly evenly over the sides and bottom of the dish. When the dish was covered with Teflon paint, however, solids were deposited in one large mass near one side. This would cause distortion of the geometry and increase self-absorption. Teflon paint is resistant to HCl, HNO_3, and certain other acids but is not wet by water, thus causing solids to be unevenly deposited. Wetting agents do not seem to prevent this.

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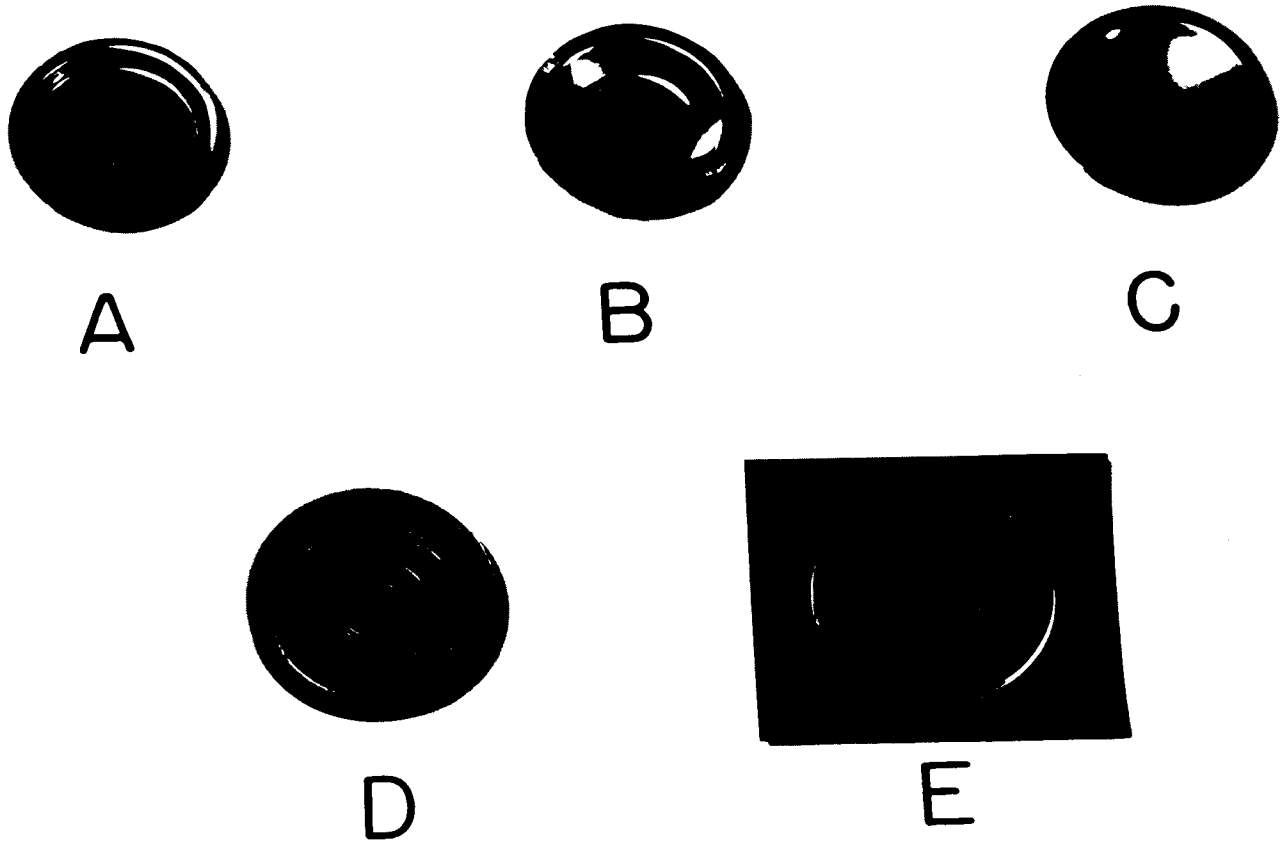

Fig. 10 - Dishes for Sample Mounting

3. With the design shown in Fig. 10*c* solids were deposited in fairly even concentric rings over this dish. However, painting with Teflon paint gave the same result as for design *b*.

4. With the design shown in Fig. 10*d* the concentric rings in the base of these dishes caused solids to be deposited in concentric rings of fairly even proportions, thus preventing solids from being deposited in one large mass. Since copper is not resistant to nitric and some other acids, if this design is accepted some other material will be necessary for a dish of general use. Some samples of stainless steel dishes of the same design have been received and are being tested.

None of the designs 1 through 3 can be recommended for general use in routine analysis for reasons previously stated. Design 4 is suggested and will be investigated further.

ANALYSIS FOR HEAVY ELEMENTS

Np^{237} (F. L. Moore). F. L. Moore's report, *A Solvent Extraction Method for Neptunium (237) Analysis,* ORNL-961, is being issued.

Transuranics in Radioisotope Preparations (W. A. Brooksbank and F. L. Moore). *Solvent Extraction.* A rapid method is needed for the separation of alpha-emitting americium and curium from the highly active beta- and gamma-emitting rare earths, the latter also giving counts on ordinary alpha chambers. The rapid separation is especially needed for the Chalk River type dissolver solutions in which as much as 10% of the activity may be from americium and curium. If a sharp separation can be effected the health hazard of the counting procedure, originating from the high beta and gamma activity, will be decreased. If a solvent extraction should prove effective in the laboratory, it would be advantageous for plant use.

The use of fluosilicic acid has been described[8] as effective for the separation of americium and curium from lanthanum but less satisfactory for their separation from rare earth elements. Some time has been spent performing scouting experiments using a "selective stripping" technique. This consists in extracting the rare earths, americium, and curium from an aqueous phase of *p*H 5 with 0.5 *M* TTA-xylene and then "stripping" the organic phase with a suitable complexing agent for americium and curium. The best complexing agent found to date was Versene, ethylenediamine tetraacetic acid. Table 5 indicates

(8) S. G. Thompson, L. O. Morgan, R. A. James, and I. Perlman, *The Tracer Chemistry of Americium and Curium in Aqueous Solutions,* Chicago Report CC-3874 (May 18, 1948).

the effect of *p*H on the selectivity of the stripping of americium. In these scouting experiments americium tracer (7639 c/m) and yttrium tracer (4630 c/m) were stripped for 5 min with an equal volume of Versene (3%) solution at various *p*H's.

TABLE 5

The Effect of *p*H on the Stripping of Americium and Yttrium from 0.5 *M* TTA-Xylene

*p*H	(% ACTIVITY STRIPPED)	
	Am	Y
4.11	99.7	~ 100
4.45	99.6	99.5
5.18	95.0	32.0
6.29	28.3	0
7.38	17.2	0

An experiment using the above technique and a second stripping of the organic phase with Versene solution at a *p*H of 6.47 yielded an aqueous phase containing 74% of the original americium with no detectable yttrium. It is felt that the separation of americium and curium from the "light rare earth group" (Ce group) should be better than the separation from yttrium. Work is being carried on now to determine the optimum conditions for the separation. Obvious advantages of this technique are the rapidity and the tolerability of high salt concentrations.

Ion Exchange. Most of the work this quarter on this subject dealt with the instrumentation for the column runs. A proportional tube was mounted on a pipet counter so that the 0.001-in. polystyrene window bounding the liquid is also the window to the chamber of the proportional counter (Fig. 11). This assembly was designed with the assistance of D. Knowles of the Instrument Department. It is hoped that it will be capable of counting the alpha particles from the activities in this separation. The chemical procedure will follow that of Thompson *et al.*[9]

(9) S. G. Thompson, A. Ghiorso, and G. T. Seaborg, *The New Element Berkelium (Atomic Number 97)* UCRL-669 (Apr. 26, 1950).

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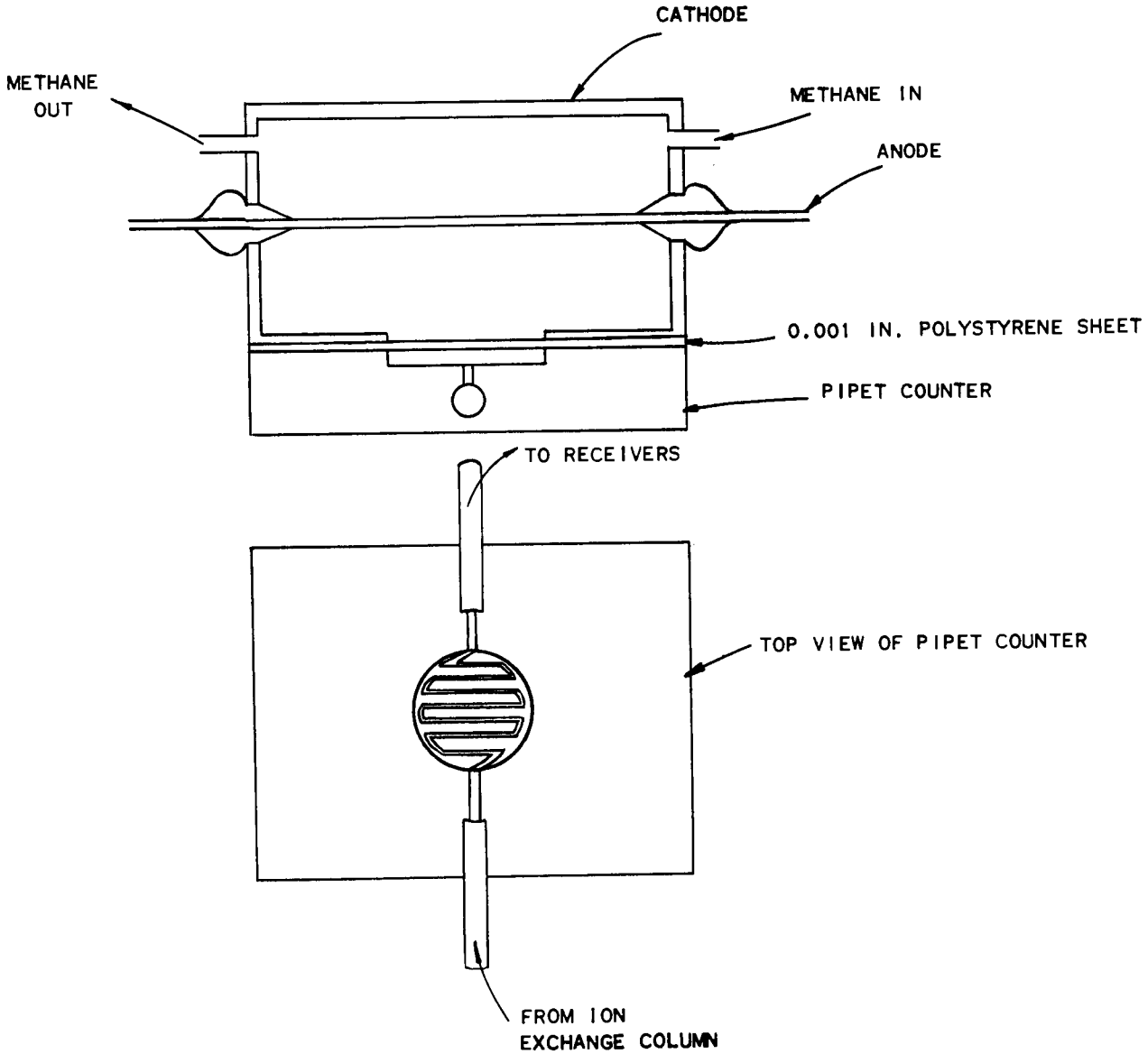

Fig. 11 - Proportional Alpha-Beta Monitor

ION EXCHANGE AND CHROMATOGRAPHY

Ion Exchange (W. A. Brooksbank). *Alkali Metals.* In connection with the investigation of Rb_2CO_3 as a target material for isotope production, a sample of Rb_2CO_3 has been prepared for irradiation and subsequent ion-exchange analysis for potassium according to the method given in ORNL-867.[10] The activation results will be compared with the data of the Spectrochemical Analyses Group.

Rare Earths. In the investigation of rare earth separation methods for production a second steam-heated column has been fabricated and installed. It is identical with that previously reported.[11] This second column is a necessary part of the activation analysis program of all 14 rare earths planned for the immediate future. The rare earth oxides will be furnished by G. E. Boyd.

In each case the irradiated oxide sample will be divided into two parts and placed on the two columns. Citrate complex elution at two *p*H values will shorten the time required for analysis. At a *p*H of 3.2 the yttrium group is well separated, but the time necessary to elute cerium group impurities is excessively long. With the other column at a *p*H of 3.4, the yttrium group will elute rapidly, with poor separation, but the cerium group will be well separated.[11]

Six preliminary runs were made on each column using Tm^{170}, Tb^{160}, and Ce^{141}. Good results were obtained.

A request from the Chemical Technology Division for some pure Gd tracer was fulfilled. The analysis by the citrate elution technique showed a trace of Sm^{153} and a Tb^{161} decay product of 3.6-min Gd^{161}. The elution curve is shown (Fig. 12).

Cobalt in Nickel Metal. A request for a method of pretreatment of a nickel sample to concentrate the cobalt and remove most of the nickel was received from G. W. Leddicotte, of the Activation Analyses Group. This was necessary to reduce the extent of $Ni^{60}(n,p)Co^{60}$ reaction in determining traces of cobalt. It was decided to use ion exchange to make the separation.

(10) W. A. Brooksbank, "Alkali Metals Separations," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950,* ORNL-867, p. 52 (Dec. 28, 1950).

(11) 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).

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NOT CLASSIFIED

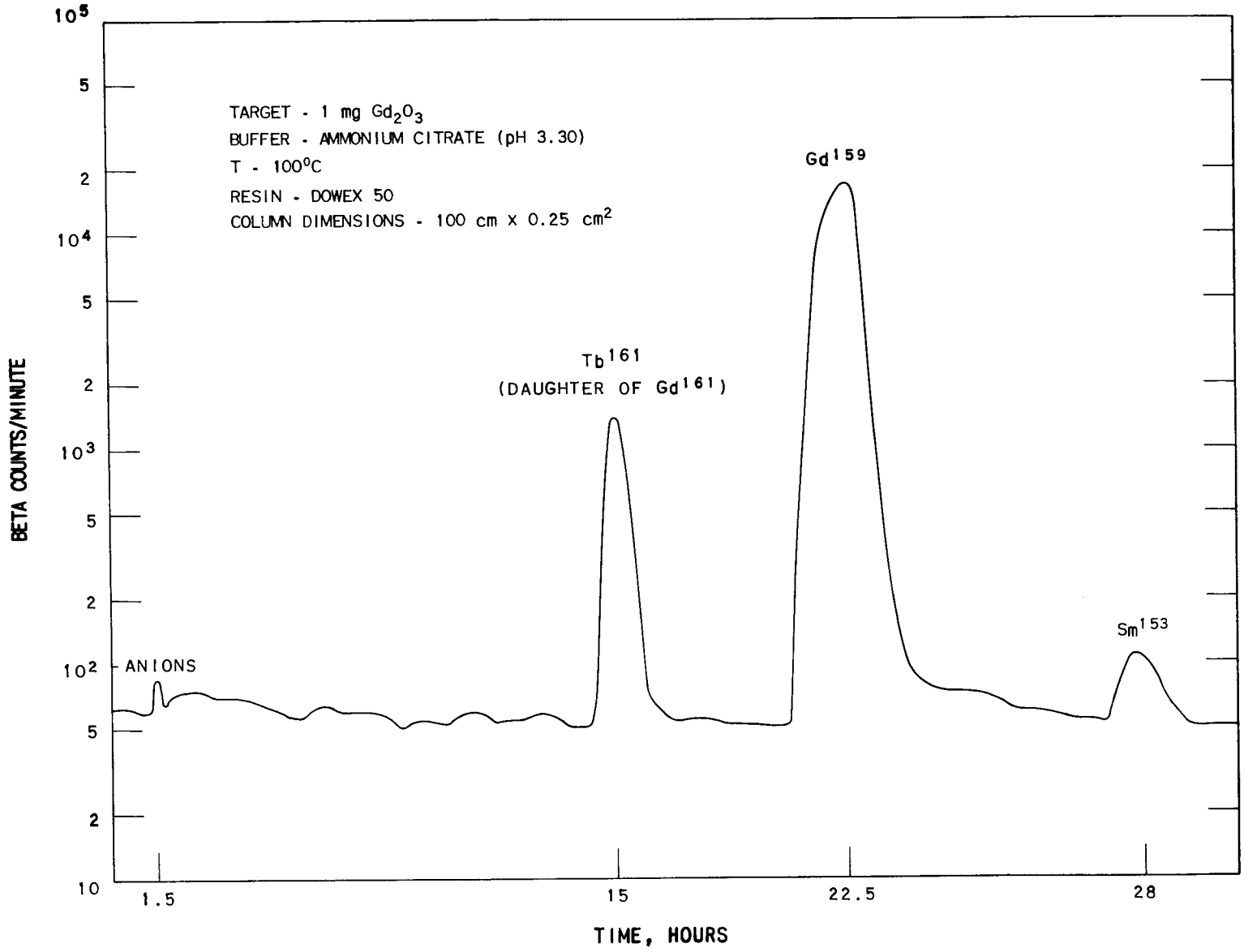

Fig. 12 - Elution Curve on Gadolinium Target

Cobalt forms a strong chloride complex in 10 *N* HCl which may be adsorbed on Dowex A-1 anion exchanger.[12] The method used is to dissolve the nickel in HCl, make the solution greater than 9 *N* in HCl and stir with 500 mg of Dowex A-1 in the chloride form in a round-bottomed centrifuge cone, filter the resin, and wash with 9 *N* HCl. The resin is stripped by stirring with distilled water and is refiltered. Preliminary experiments show that 97.2% of the cobalt (0.0094 mg) may be removed from 500 mg of nickel. One wash of the resin with distilled water strips 99.9%. The strip can then be evaporated, dried, and bombarded as usual for cobalt determination.

Chromatography (W. S. Lyon). By use of the method and technique described in the last quarterly report[13] attempts have been made to reproduce paper chromatography data recently reported by Pollard *et al.*[14] The solvent used was a mixture of 50% butanol, 10% acetic acid, 5% acetoacetic ester, and 35% water. Data have been obtained for R_f values using various radioactivities as tracers. The amount of inactive ion has in general been between 10 and 100 γ. Agreement between our values and those of Pollard are shown in Table 6.

TABLE 6

R_f Values for Various Ions

Whatman No. 1 paper; room temperature

ION	ORNL	POLLARD
Co	0.24	0.23
Zn	0.21	0.27
Hg	0.81	0.85
Cl	0.23	
Fe	0.56	0.70
Na	0.31	0.20
Sb	0.92	0.10
Cs	0.28	
Ni	0.27	0.23
Fe	0.30	
Cr	0.21	0.63
Y	0.27	

(12) G. E. Moore and R. W. Atteberry, private communications, Mar. 13, 1951.

(13) W. S. Lyon, "Chromatography," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955, p. 54 (Mar. 28, 1951).

(14) F. H. Pollard, J. F. W. McOmie, and I. I. M. Elbeih, "Inorganic Paper Chromatography and Detection of Cations by Fluorescence," *Nature* 163, 292 (1949).

Separations were, in general, quite sharp and the method is felt to have some promise for qualitative identification. Its great virtue lies in its simplicity and its rapidity of completion.

SPECIAL PROBLEMS

Decontamination of Platinum Dishes (T. H. Handley). Attempts to decontaminate platinum fluorophotometer dishes by chemical means have failed. Previous experience has shown that materials can often be decontaminated only by removal of the surface. Therefore buffing with carborundum (100 grain), which will remove a thin layer from the surface, has been tried. After buffing for 2 to 3 min, decontamination factors of 10 to 15 have been obtained; repeated buffing continued to lower the contamination although complete decontamination was not attained. Practically, a limit would be set on the contamination permissible.

General appearance of the dishes was also improved by this process, scratches were removed, and a polish was given to the metal even greater than that of new platinum.

Radioisotope Stack Filters (D. J. Coombe, W. S. Lyon, and S. A. Reynolds). Samples of filters from the Radioisotope Area stack are being received for determination of the nature of the activities being removed by the filters. Radioautographs show some particles, with a background of homogeneously distributed material.[15] The isotopes 2.4-hr I^{132} and 8-day I^{131} have been identified. Results of further work will be given in the next quarterly report.

(15) T. E. Willmarth, private communication, March, 1951.

3. SPECTROCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT

A. Estepp J. Gillespie
C. Feldman M. Murray

Working curves and procedures were developed for the spectrographic determination of the following metals in the concentration ranges and media indicated:

METAL	CONCENTRATION RANGE (ppm)	MEDIUM
Cr	1.5 - 25	Dilute H_2SO_4
K	125 - 2000	1% sodium solution
Li	60 - 1000	Dilute H_2SO_4
Na	90 - 1500	Dilute H_2SO_4
Ni	6 - 100	Dilute H_2SO_4
Sr	0.08 - 0.3	0.5% barium solution
Zr	1 - 70	Dilute H_2SO_4

Investigation of the spectrographic line-width method was continued in connection with the determination of small amounts of lithium in the presence of 500 to 1000 times as much sodium by weight. The porous cup method was used to excite the solutions, 1860 ppm of lanthanum being used as an internal standard. Moving-plate exposures showed that this method of measuring spectral lines is more sensitive to changes taking place in the first minute of the discharge than is the intensity ratio method. If the electrodes are rendered more porous by presparking dry and if the first 90 to 120 sec of the discharge are not photographed, good precision of line width can be obtained. The sensitivity of line-width measurements to spectrographic slit width indicates that fixed slits should be used for this work. Although this technique places greater demands on precision of light source, spectrograph, and densitometer than does the intensity ratio method, work is being continued because of indications that line widths may be less sensitive to the presence of other alkalies than intensity ratios.

A study of the use of TBP in analysis of uranium solutions for traces of molybdenum showed that when 5 ml of a solution of uranyl nitrate hexahydrate which is 5 *N* in HNO_3 is shaken for 1 min with three successive 5-ml portions of a mixture of 1 part of TBP + 4 parts of hexane, 15% of the molybdenum present (at the 20-ppm level) is lost from the aqueous layer. The same amount of molybdenum is lost when uranium is absent.

The presence of 1% lead in solution was found to have essentially no foreign-element effect on the Ni/Co ratio used in determining traces of nickel in H_2SO_4. The lead was present in HNO_3 solution.

4. SERVICE ANALYSES

IONIC ANALYSES — DEVELOPMENT GROUP

P. F. Thomason

The number of samples for the HRE increased this quarter because M. Lietzke and J. Griess submitted corrosion study samples in addition to the regular samples submitted by J. W. Boyle and coworkers. The types of analyses requested were the same as reported in the previous quarterly report.[1]

The analyses for the Chemical Technology Division included the determination of capacity of various cation- and anion-exchange resins of alkyl phosphates in aqueous solutions and the assay of plutonium solutions.

Analyses for the Operations Division included ionic analyses for cadmium, cobalt, tellurium, and manganese. The cadmium, cobalt, and tellurium were determined polarographically, and manganese was estimated colorimetrically.

The automatic electrometric titration of chlorides reported in a previous quarterly report[2] has been used to analyze solutions for J. H. Gross who is studying the separation of lithium and sodium chlorides. It has been found possible to titrate as little as 200 γ of chloride with an accuracy of ±1%.

RADIOCHEMICAL ANALYSES — DEVELOPMENT GROUP

S. A. Reynolds

Activation analyses comprised most of the work done for the Chemistry and Physics Divisions. Assays of radioisotope products and determinations of impurities were made for the Operations Division. Analyses of material caught on stack gas filters were made for Chemical Technology personnel.

ACTIVATION ANALYSES

G. W. Leddicotte

Determination of Lithium, Barium, Sodium, and Gold (G. W. Leddicotte and H. W. Wright). These determinations have been made in effecting the plant-site program of work, including work for Y-12.

(1) P. F. Thomason, "Ionic Analyses — Development Group," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955, p. 65 (Mar. 28, 1951).

(2) F. J. Miller, "Determination of Chloride with the Automatic Titrator," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1949*, ORNL-607, p. 187 (Mar. 7, 1950).

Li^6. The apparatus and procedures for Li^6 determination by activation analysis have been described in earlier reports.[3,4] The proposed apparatus has been put into operation, and a series of runs with samples of known lithium content has been made. The data obtained have not yet been fully correlated.

A series of samples has also been analyzed for the Materials Chemistry Division at Y-12. In Table 7 these results are compared with results obtained in the Mass Spectrometer Laboratory at Y-12.

TABLE 7

Comparison of Activation and Mass Spectrometer Methods for Determining Li^6

SAMPLE	Li^6 IN SAMPLE (%) BY ACTIVATION ANALYSIS	BY MASS SPECTROMETRIC ANALYSIS
1	93.6	93.4
2	92.8	93.3
3	94.5	94.6

A group of samples of mixed lithium-sodium sulfates submitted by the Chemistry Division is also being analyzed for lithium content. The work is incomplete.

Sodium. The sodium content of samples of mixed lithium-sodium sulfates is also being determined by radioactivation. The concentration of sodium in these samples ranges from 0.01 to 32.5%. Sodium is being determined by bombarding portions of the unknown samples together with standard samples (as Na_2CO_3) under the same reactor conditions for 1 hr. Sufficient Na^{24} activity is produced in this time to permit a rapid analysis. After discharge from the reactor, the samples and the standards, following dilution and aliquoting, are placed in contamination-free containers, and the gamma radiations are read directly on the high-pressure ionization chamber. Decay is followed through at least one half-life (Na^{24}, $t_{1/2}$ = 14.8 hr). Results were accurate to ±3%. In Table 8 the results are compared with those obtained by spectrographic analysis.

(3) W. A. Brooksbank, G. W. Leddicotte, T. H. Handley, N. D. Lee, and C. W. Keenon, "Activation Analyses," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*, ORNL-867, p. 30 (Dec. 28, 1950).

(4) G. W. Leddicotte and N. D. Lee, "Activation Analyses — Lithium," ORNL-955, *op. cit.*, p. 30.

TABLE 8

Comparison of Activation and Spectrographic Methods for Determining Sodium

SAMPLE*	Na IN SAMPLE (%)	
	BY ACTIVATION ANALYSIS	BY SPECTROGRAPHIC ANALYSIS
1	12.60	13.70
2-a	9.81	10.30
2-b	9.90	11.10
3-a	16.20	15.00
3-b	16.29	16.10

*Samples 2-a and 2-b, and 3-a and 3-b were sets of duplicates.

Barium. A series of samples from the RaLa Process (Chemical Technology Division, Mr. Blanco and associates) is being analyzed for barium content by radioactivation. The samples and standards are subjected to a 30-min bombardment in the reactor. They are discharged from the reactor and the radioactivity produced, Ba^{139} ($t_{½}$ = 84 min), is isolated by a chemical separation in which standardized barium carrier and suitable holdback carriers (strontium, copper, iron, sodium) are added to a solution of the sample. The separation is effected by precipitation of barium and strontium with fuming HNO_3. Barium is separated from strontium by sodium dichromate and is ultimately precipitated as $BaCl_2 \cdot 2H_2O$ using an HCl-ether mixture. It has been possible to determine barium in the range of 0.016 to 3.80 mg/ml with an accuracy of ±2%. Selected data are reported in Table 9.

TABLE 9

Comparison of Activation and Spectrographic Methods for Determining Barium

SAMPLE	BARIUM CONTENT OF SAMPLES (mg/ml)	
	BY ACTIVATION ANALYSIS	BY SPECTROGRAPHIC ANALYSIS
1	0.33	0.32
2	0.98	1.05
3	0.24	0.21
4	0.25	0.20
5	3.80	3.30

Gold. Macro amounts of gold plated on 2S aluminum bars are being determined by activation analysis. The concentration range of the "plate" is of the order of 0.20 to 8.00 mg of total gold. In this analysis the plate, the aluminum bar, and standard samples of gold foil are bombarded in the reactor for a maximum time of 30 min. This bombardment time is sufficient to produce enough Au^{198} ($t_{½}$ = 2.69 days) activity for determination. After discharge from the reactor the sample and standards are read in the high-pressure ionization chamber. After a decay period of at least 150 hr, the activity due to the Au^{198} ($t_{½}$ = 2.69 days) is followed through at least one half-life, and the amount of gold in the plate is computed on data obtained at that time. The decay period of 150 hr is necessary to minimize effects of the major contaminants of the aluminum. These contaminants have been qualitatively identified as Cu^{64} ($t_{½}$ = 12.8 hr) and Na^{24} ($t_{½}$ = 14.8 hr). These analyses were made with an accuracy of ±5%.

Exploratory Work on Neutron Activation (G. W. Leddicotte). A brief summary of the analyses of some of the materials submitted in this program follows. No attempt is made to outline the procedures used in this work, since a complete summary of the procedures and of the decontamination experiments is planned for a separate report at some future date.

The results of these analyses have been obtained either by a chemical separation or by a direct reading method using the high-pressure ionization chamber. In most cases our data have been substantiated by either aluminum absorption curves or decay studies.

The data are given in Tables 10 and 11.

TABLE 10

Beryllium Samples from AEC New Brunswick Laboratory

SAMPLE	CONCENTRATION OF INDICATED METAL* (ppm)				
	Cd	Co	Ag	Mn	Zn
1	1	1	39	14	1
2	2	5	19	156	230
3	6	7	1	462	1240
4	5	8	4	123	376
5	1	7	3	28	26

*Cadmium, cobalt, silver, and zinc determined by chemical seaparation; manganese by direct reading on ionization chamber.

TABLE 11

Stainless Steel Samples from Union Carbide and Carbon Research Laboratories

SAMPLE	TANTALUM (%)	
	BY ACTIVATION ANALYSIS*	BY SPECTROGRAPHIC ANALYSIS**
1	0.09	0.08
2	0.12	0.11
3	0.23	0.23
4	0.11	0.13
5	0.20	0.20
6	0.16	0.17
7	0.31	0.29
8	0.29	0.29
9	0.19	0.18

*By direct reading on ionization chamber.

**Data supplied by Union Carbide and Carbon research laboratories.

Nuclear Reactions Encountered in Neutron Activation Analysis (G. W. Leddicotte). In order to anticipate more completely the problems that could arise from fast-neutron reactions on certain elements in the ORNL reactor, general information relative to neutron activation analysis is being organized for issue in report form. The general equations for the four types of neutron interactions (both slow and fast) will be discussed. A table will be presented to indicate the possible products from the four types of nuclear reactions. It will include the half-life of the radioisotope produced, the type of radiation emitted, and the element or elements producing the radioisotope and the type of reaction by which production is achieved. A major part of the information will be adapted from that given by Kamen[5] and by Seaborg and Perlman.[6]

New Applications of Activation Analysis (G. W. Leddicotte). The recent publication by Leddicotte and Reynolds[7] has led to inquiries regarding use of the method of activation analysis for determining trace elements in carious and noncarious teeth and also in metal ingots and foil. A group of the latter samples has been received and work on these is progressing.

(5) M. D. Kamen, *Radioactive Tracers in Biology*, Academic Press, New York, 1947.

(6) G. T. Seaborg and I. Perlman, "Table of Isotopes," *Revs. Mod. Phys.* 20, 585 (1948).

(7) G. W. Leddicotte and S. A. Reynolds, "Activation Analysis with the Oak Ridge Reactor," *Nucleonics* 8, No. 3, 62 (1951).

GENERAL RADIOCHEMICAL ANALYSES

C. L. Burros

Active-constituent assays were made for the Chemical Technology Division on samples derived from studies of (1) decontamination steps of the Purex Process, (2) decontamination of Homogeneous Reactor fuel, (3) uranium purification by fluorination procedures, (4) extent of contamination of the water in the settling basin and White Oak Dam reservoir, and (5) the ecology of the Clinch River.

Cerium determination as outlined in CN-2815[8] requires 1.5 to 2 hr. Because of the frequency of cerium analyses a shorter procedure is desirable. In two procedures now being studied, the CN-2815 method was modified (1) to initially precipitate the cerium with oxalate instead of the rare earth fluorides and (2) to shorten the procedure for purifying the cerium precipitate. The procedures have been compared using both a regular feed solution and one containing total rare earths amounting to approximately fourteen times, and strontium approximately five times, the cerium concentration. Also, decontamination from zirconium was checked using a zirconium tracer having 11,000 c/m/ml of zirconium. The possibility of shortening the procedure without sacrifice of accuracy or of extent of decontamination is indicated. The study is being continued to check the decontamination from Nb^{95}, Ru^{106}, Sr^{89}, and La^{140}. A complete report will be issued later.

WATER ANALYSIS LABORATORY

J. H. Edgerton

Thorium breeder salts submitted by the Chemistry Division were assayed for silica, thorium, phosphorus, fluoride, and chloride. The separation of fluoride and chloride required operations new to this laboratory. The samples were dissolved in 12 *N* nitric acid. Fluoride was separated by steam distillation as hydrofluosilicic acid and titrated with thorium nitrate, using alizarin sulfonate as indicator. Chloride was determined by precipitation from 0.5 *N* nitric acid solution with silver nitrate, the phosphorus remaining in solution

(8) D. N. Hume, N. E. Ballou, and L. E. Glendenin, *A Manual of the Radiochemical Determination of Fission Product Activities*, CN-2815, p. 52 (June 30, 1945).

at this acid concentration. Silica, thorium, and phosphorus were determined as described in earlier quarterly reports (see p. 3 for numbers of previous quarterly reports).

Aqueous samples from the high-temperature corrosion studies by the Naval Reactor Division of Argonne National Laboratory were analyzed before and after irradiation for iron, nickel, chromium, calcium, and magnesium.

Analysis of blood and urine samples from the Health Physics Division for lead required the polarographic technique because of the small lead concentrations (less than 1 ppm). To reduce the interfering ferric iron to noninterfering ferrous in the presence of phosphates, samples were treated with hydroxylamine hydrochloride and orthophenanthroline after destruction of the organic matter by acid oxidation.[9]

The Metallurgy Division is interested in the corrosion of pure metals, stainless steels, and other high-temperature alloys by baths of liquid sodium, lithium, and lead. Aqueous test samples from these studies were analyzed for silica, beryllium, nickel, chromium, iron, molybdenum, niobium, thorium, and uranium. Beryllium was determined in an acetate—acetic acid buffer solution at a *p*H of 5.5 using aurintricarboxylate (Aluminon) as the color reagent.

Metallurgy Division samples of uranium and thorium which had been heated to 1000°C for 4 hr in lead baths were assayed for uranium or thorium as well as lead and iron. After solution of the sample in 6 *N* nitric acid, lead was removed without interference by electrodeposition as PbO_2 at a current of 1 to 2 amp, a potential of 2 to 2.5 volts, and a temperature of 25°C. Iron was separated from the uranium samples by ammonium carbonate precipitation, ignited and weighed as Fe_2O_3, redissolved, and determined colorimetrically with orthophenanthroline. Uranium was determined gravimetrically as U_3O_8. In the thorium samples iron was determined colorimetrically with orthophenanthroline after oxalate precipitation of the thorium, which was determined by ignition of the oxalate to ThO_2.

Uranium-beryllium and copper-nickel-zinc alloys were analyzed for the Metallurgy Division by the use of special separation techniques.

(9) H. H. Miller, "Polarographic Determination of Lead in Blood, Urine, and Air Samples," this report p. 35.

Uranium-aluminum and aluminum-copper alloys under study by the Chemical Technology Division and the Physics of Solids Institute, respectively, were analyzed, the former for traces of barium and strontium and the latter for aluminum, copper, magnesium, and manganese.

Additional work is reported in Table 12.

LABORATORY AND SEMI-WORKS CONTROL

L. T. Corbin

The Chemical Technology Division study of the Purex Process required the analysis of samples from hot runs for uranium, plutonium, nitric acid, gross beta, gross gamma, tributyl phosphate, sulfurous acid, and oxalate. The last two determinations were new to the laboratory. Sulfurous acid was determined by the iodometric method. The sulfurous acid solution was added to an iodine solution, and excess iodine was titrated with sodium thiosulfate, using starch as an indicator. Oxalate was determined by adding an excess of standard ceric sulfate solution and back-titrating excess ceric ion with standard ferrous sulfate solution.

Slug-dissolving solutions from the U^{235} process were submitted by the Chemical Technology Division for determination of uranium, nitric acid, aluminum, and nitrites. Nitrites were determined by the dimethylaniline method. Nitrous acid reacts with dimethylaniline to give the yellow color of *p*-nitrosodimethylaniline which is used for the colorimetric estimation. The training program for the Du Pont personnel has increased the total number of analyses for the Chemical Technology Division.

Some work has been done during the past quarter on the use of an induction heater rather than open flame for the NaF fusion of samples on platinum plates for fluorometric determination of uranium in the presence of plutonium. A more detailed report of this will be in the next quarterly report.

Work is progressing on the Manual of Analytical Procedures for the U^{235} Recovery Process for use by American Cyanamid personnel at Arco.

Miscellaneous analyses requested by other groups are summarized in Table 12.

TABLE 12

Summary of Analytical Service Work for Period January 11 Through March 26, 1951

GROUP MAKING ANALYSES	NO. OF PERSONNEL		ANP	CHEMISTRY	CHEMICAL TECHNOLOGY	ENGINEERING AND MAINTENANCE	HEALTH	HEALTH PHYSICS	METALLURGY	OPERATIONS	PHYSICS	REACTOR TECHNOLOGY	MISCEL-LANEOUS	TOTAL
	TECH.	NONTECH.												
Radiochemical Development	6	0		60	92					66	8			226
Ionic Development	4	1		438	199					5				642
Spectrochemical	4	0	8	126	178		14		111	9	9		10	465
General Radio-chemical	4	6			3,865			468						4,333
Water Analysis	2	8		66	1,768	123		75	479	11	46	1,041	109*	3,718
Laboratory and Semi-Works Control	3	10		187	17,735			5	6					17,933
Pilot Plant	9	15			16,193									16,193
Radioisotope Production Control	6	18		262	3,839					6,410				10,511
TOTAL	38	58	8	1,139	43,869	123	14	548	596	6,501	63	1,041	119	54,021

*For Argonne National Laboratory.

PILOT PLANT CONTROL

E. J. Frederick

An intensive study is underway to compare the uranium saturation, dielectric constant, and specific gravity methods for the estimation of the percent tributyl phosphate in Amsco solvent. Table 13 shows the results obtained on analysis of 10 synthetic samples submitted by the Chemical Technology Division. Each sample was saturated with water to simulate process streams and centrifuged before analysis. Hydrocarbon content, determined by change in volume resulting from solubility of the TBP in 85% sulfuric acid, is also reported. This method is used only as a rough check because of its limited accuracy, ±1% TBP by volume.

TABLE 13

Comparison of Methods for Determining Percent TBP in Amsco Solvent

SAMPLE	TBP (%)				HYDROCARBON CONTENT (by solubility in 85% H_2SO_4) (%)
	ACTUAL (by preparation)	BY URANIUM SATURATION*	BY DIELECTRIC CONSTANT	BY SPECIFIC GRAVITY	
1	23.7	25.5	24.0	24.0	23.9
2	34.5	33.3	35.0	34.9	35.9
3	25.0	25.1	25.0	26.0	26.0
4	34.0	33.4	34.8	34.6	36.7
5	29.5	28.7	30.0	30.0	30.7
6	30.9	30.9	31.2	32.2	33.0
7	28.1	25.0	28.2	28.8	29.0
8	26.1	25.3	26.5	26.4	26.2
9	30.2	29.5	30.5	30.8	30.8
10	32.0	30.7	32.2	32.6	32.7

*Formula used in calculating % TBP from uranium saturation:

$$\% \text{ TBP} = \frac{\text{U saturation}}{4.38 - (0.002 \times \text{U saturation})}$$

The above data indicate the dielectric constant method to be the most reliable, followed by the specific gravity and the uranium saturation, in that order. It is felt that the accuracy of the specific gravity method can be increased considerably by the use of a better specific gravity balance. However, some recent tests show different shipments of Amsco solvent to vary as much as ±0.01 in specific gravity with no apparent change in dielectric constant.

Another series of samples containing varying amounts of TBP as well as trace amounts of uranium and monobutyl and dibutyl phosphate are being prepared for further study. Each of these samples will be given a 1% ammonium carbonate wash followed by three water washes and centrifugation before analysis. This is the proposed clean-up step to be used on all solvent samples before analysis.

Four different batches of sodium fluoride (analytical reagent grade) have been tested in order to find a suitable low-blank flux for use in the fluorometric method for uranium. The results follow:

1. Baker and Adamson, reagent stock item. Excellent white melts of approximately 3.5 mγ of uranium when measured against a blank hole.
2. Eimer and Amend, supplied by K-25. Gives sufficiently low readings, but all melts have a definite blue color.
3. Baker's Analyzed. Too crystalline and does not form a pellet very readily. When heated the NaF spatters, causing loss of sample and melt. Readings taken on the fused melts indicated 23 to 35 mγ of uranium.
4. Mallinckrodt. Too crystalline and does not form a pellet. Like Baker's, it spatters when heated.

RADIOISOTOPE ANALYSES

E. I. Wyatt

Technetium (Tc^{99}) has been determined in solutions with a relative error of ±10% by using a known amount of rhenium as a carrier. A weighed precipitate of tetraphenylarsonium pertechnetate-perrhenate was counted at geometries of about 5%. Corrections were then made for yield, dilution, self-absorption, air gap, window thickness, and geometry. A specific activity of 1.5×10^7 d/m/mg was used for all calculations.

The general chemical procedure as recommended by G. W. Parker of the Chemistry Division is as follows: The technetium and rhenium are precipitated from the sample by adding tetraphenylarsonium chloride, the precipitate is dissolved with sulfuric acid, and the solution is then colored with bromine water and treated with hydrogen sulfide. The resultant sulfides are dissolved with hydrogen peroxide—ammonium hydroxide mixture and distilled from concentrated sulfuric acid. The distillate is colored with bromine water and treated

with hydrogen sulfide. This precipitate of sulfides is also dissolved with hydrogen peroxide—ammonium hydroxide mixture. Tetraphenylarsonium chloride is added to precipitate the tetraphenylarsonium pertechnetate—perrhenate, which is weighed and counted. An absorption study is run with aluminum absorbers. The corrections mentioned above are then made.

A solution known to contain about 6 mg of Tc^{99} per liter was found to have 6.2, 6.4, and 6.7 mg of Tc^{99} per liter. Approximately seventy-five determinations have been made on various samples within ±10% error.

The $C^{14}O_2$ apparatus has been remodeled to provide caustic scrubbers in series to trap the $C^{14}O_2$. The scrubber solutions may then be diluted to known volumes and aliquots taken for subsequent $C^{14}O_2$ evolutions and determinations in a conventional ionization chamber. Standardizations have not yet been made with the new equipment.

5. INORGANIC PREPARATIONS

D. E. LaValle and R. H. Sampley

THORIUM FLUOPHOSPHATES

D. E. LaValle

A number of reactions aimed chiefly at producing anhydrous thorium fluophosphates were studied in connection with the Thorium Breeder Salts Program. These may be summarized as follows:

1. ThF_4 + $Th(PO_3)_4$, heated together at temperatures up to 700°C in an argon atmosphere
2. $Th(OH)_4$ (freshly precipitated) + H_2PO_3F (anhydrous)
3. $Th(OH)_4$ + HPF_6 (conc.)
4. H_2PO_3F (in acetone) + $ThCl_4$ (in acetone)
5. KPF_6 (in acetone) + $ThCl_4$ (in acetone)
6. Benzyl trimethylammonium hexafluophosphate (in acetone) + $ThCl_4$ (in acetone)
7. NH_4PF_6* (solid) + $ThCl_4$ (solid) heated to 500°C in argon

Reactions 3, 4, and 6 showed promise according to the analyses of the products and are being studied further. Analytical results from some of the other reactions have not yet been obtained.

Mn_2Sb

D. E. LaValle

The last preparation of this intermetallic compound, described in the previous quarterly report, proved, upon X-ray examination, to be the pure product. However, larger amounts were required than could be produced using a clay boat sealed under vacuum in a quartz tube, and a recently obtained tube furnace of large bore was therefore employed. A large opaque quartz tube sealed off at the bottom was used, it and the furnace were set up on end, and the starting material contained in a large alundum crucible was rested in the

*Prepared in the laboratory of the Inorganic Preparations Group of the Analytical Chemistry Division.

bottom of the quartz tube. An arrangement of valves at the top allowed for evacuation and the introduction of argon which was passed through during the run. The furnace was brought to temperature as described previously (ORNL-955) and the tube with attachments and contents was then lowered into the hot zone. The run was successful and analysis of the product showed it to be pure.

FERROUS OXIDE

D. E. LaValle

Another attempt was made to produce FeO by a modification of the method of Günther and Rehaag[1] in which ferrous oxalate is dropped into a zone at 850°C in a vacuum. The gases of decomposition are pumped off immediately. The objection to this method is the small quantity of FeO obtainable because of the explosive nature of the decomposition under these conditions. It was proposed to set up a continuous process whereby small quantities of FeC_2O_4 are gradually fed down through an evacuated hot zone.

Two tube furnaces were set on end, one above the other, providing a hot zone of 26 in. A long quartz tube was suspended in this zone, extending out at the bottom and top. The material was contained in a bent upper arm of special design, being introduced into it after evacuation. When this upper arm was tapped a fine stream of oxalate was caused to fall down through the hot zone. After completion of the run, however, it was found that not all the FeC_2O_4 had decomposed during its descent. The experiment was discontinued until some means could be devised for slowing the passage of the material through the hot zone, yet ensuring that none of it remained there for more than 30 sec.

NEODYMIUM ETHYL SULFATE

D. E. LaValle

This compound was desired for study by the Nuclear Physics and Low Temperature Group of the Physics Division. Compounds of this type are generally prepared by the action of ethylsulfuric acid on the oxide of the metal.

(1) P. L. Günther and H. Rehaag, "Über die thermische Zersetzung von Oxalaten. II. Darstellung von reinem Ferrooxyd," *Z. anorg. u. allgem. Chem.* 243, 60 (1939).

The ethylsulfuric acid, $H(C_2H_5SO_4)$, was prepared by reacting concentrated H_2SO_4 with absolute ethyl alcohol. The excess H_2SO_4 was removed by neutralizing the solution with $BaCO_3$ and centrifuging off the $BaSO_4$. The $Ba(C_2H_5SO_4)_2$ was then crystallized out of the filtrate and filtered off. To an aqueous solution of the $Ba(C_2H_5SO_4)_2$ was added the requisite amount of H_2SO_4, thus precipitating $BaSO_4$ again and leaving in solution the ethylsulfuric acid. After removal of the $BaSO_4$ by centrifuging, the acid was concentrated by evaporation under vacuum to about 0.5 *M*, and, after a determination of its exact strength, the stoichiometric amount of Nd_2O_3 was added to it. The mixture was then agitated to effect solution of the oxide. However, since $Nd(OH)_3$ begins to precipitate at a *p*H of about 5.5, complete neutrality of the solution is not attained.

The $Nd(C_2H_5SO_4)_3$ could now be crystallized out, but several recrystallizations from absolute ethyl alcohol were necessary if the last traces of acid were to be removed to ensure future stability of the compound.

PHOSPHORS

R. H. Sampley

Phosphors of interest to Mr. James Schenck of the Physics Division were prepared. The following reagents used in the preparations received special purification:

1. Distilled water, laboratory
2. Nitric acid, c.p.
3. Hydrochloric acid, c.p.
4. Lithium chloride, c.p.
5. Sodium tungstate, c.p.

The following phosphors, some of questionable formula, were prepared:

1. Li_2CaSiO_4 plus 15% excess Si and 1% Pb as activators
2. Li_2CaSiO_4 plus 15% excess Si and 0.1% Pb as activators
3. Li_2CaSiO_4 activated with 1% Pb
4. Li_2CaSiO_4 activated with 0.1% Pb
5. Li_4ZrO_4
6. Li_4ZrO_4 activated with 5% Ti

7. Li_2ZrO_3
8. Li_2ZrO_3 activated with 5% Ti
9. $Li_2Zr_2O_5$
10. $Li_2Zr_2O_5$ activated with 5% Ti
11. $Li_8Ti_5Zr_3O_{20}$
12. Li_2WO_4
13. $CaWO_4$
14. Li_2CO_3
15. Li_2CaSiO_4 activated with 1% Ce^{3+}
16. $Li_2Si_2O_5$
17. $Li_2Ti_2O_5$
18. $Li_8Si_5Zr_3O_{20}$
19. $Li_8Si_5Zr_3O_{20}$ activated with 1% Sn
20. $Li_8Si_5Zr_3O_{20}$ activated with 1% Ti
21. $Li_8Si_5Zr_3O_{20}$ activated with 0.5% Pb
22. $Li_8Si_5Zr_3O_{20}$ activated with 1% Mn
23. Li_2CaSiO_4 activated with 3.2% Ce^{3+}
24. Li_2CaSiO_4 activated with 0.32% Ce^{3+}
25. $Li_2Sn_5Zr_3O_{20}$
26. $Li_2Sn_5Zr_3O_{20}$ activated with 1% Ti
27. $Li_8Ge_5Zr_3O_{20}$
28. $Li_8Ge_5Zr_3O_{20}$ activated with 1% Ti
29. $Li_8Ti_7ZrO_{20}$
30 Li_2CaSiO_4 activated with 5% Ce^{3+}
31. LiF
32. $Li_2MgW_2O_8$
33. Li_4SiO_4 activated with 1% Ce^{3+}
34. Li_2SiO_3 activated with 1% Ce^{3+}
35. Li_2SnO_3
36. Li_4SnO_4

37. $Li_2Sn_2O_5$

38. $Li_2Sn_3O_7$

The existence of some of these is doubtful since little if any information is found in the literature regarding their molecular structure. In the absence of this knowledge proof of their existence is lacking. Those compounds which are practical as phosphors will receive further study.

6. ANALYTICAL CHEMICAL CONTROL OF THE HOMOGENEOUS REACTOR SOLUTION

W. H. Davenport, Jr. and R. H. Powell

Full details of recent analytical work on the continuous control of the HRE soup solution appeared in the HRE quarterly report.[1]

The emphasis on methods and apparatus for continuous measurement of HRE solutions has shifted from the previously reported apparatus, the electromagnetic densitometer and the high-frequency coil for Q measurement, to another density-measuring device, a modification of the Princo Densitrol, which is being fabricated by the Precision Thermometer and Instrument Co., Philadelphia, Pa. The work on the former methods is being continued; however, these methods will require much more development before the apparatus can be recommended for incorporation in the homogeneous reactor. Since each of these three methods represents a different approach to the problem, any or all of them may prove to have a definite applicability.

Reactor irradiation tests are continuing on cadmium borofluorosilicate glasses which were developed for the purpose of being neutron absorbing. Chemical-stability tests of these glasses under high temperature and pressure with and without radiation are contemplated.

PRINCO DENSITROL

This instrument operates on the hydrometer principle. A submerged plummet attached by chains to a fixed reference point acts as a density-sensitive device. The position of the plummet is translated through the plummet core and electrical measuring devices to a recording chart. The chains, acting on the principle of a chainomatic balance, distribute their weight between the plummet and the reference point depending upon the position of the plummet at a given density. This results in an increase in density range over the conventional hydrometer. Interchangeable chain-plummet assemblies permit the use of the instrument at various ranges.

(1) W. H. Davenport and R. H. Powell, "Analytical Chemical Control," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 115 (May 18, 1951).

The instrument is being modified with respect to welds, material of construction, electrical installation, and plummet construction to best meet the homogeneous reactor conditions. Three instruments have been ordered, one for 250°C and 1000-psi conditions and two similar instruments for 110°C and 1000 psi. The lower temperature units would have to be installed after a heat exchanger if the reactor is operated at 250°C. All instruments are designed to operate at flow rates of 0.1 to 0.5 gpm and at viscosities less than 50 centipoises. Chain-plummet assemblies were ordered for the density range 0.83 to 0.85 g/ml for the high-temperature unit and 0.99 to 1.01 g/ml for the low-temperature units. These units are equipped with automatic temperature compensation over a limited range. The Princo Densitrol offers the advantage of continuous measurement as contrasted to the discontinuous measurement of the electromagnetic densitometer. Pressure, temperature, and operational testing of the Princo Densitrol using a dynamic test loop will be required. The best approach to this problem is now being determined.

ELECTROMAGNETIC DENSITOMETER

The component parts which will be required for the first water testing of the densitometer have been assembled.

Temperature and coil current will be measured and recorded using potentiometers and Brown recorders. The response of a recently acquired Microformer[1] to the movement of the float containing an iron core will be measured through the 1/8-in. wall of a specially constructed stainless steel bomb. The temperature will be controlled by a resistance heater to temperatures over the range 25 to 300°C. The pressures will be those of the various equilibrium steam pressures. If the water test proves satisfactory, the bomb and float will be passivated, then studies will be made of uranyl sulfate solutions. Precautions will be taken to avoid precipitation by local overheating.

Q COIL

E. S. Cantrell of the Research Shops has furnished several types of ceramic-insulated coils for *Q* measurement. The platinum coils embedded in Lava Grade A described in ORNL-925[2] could not be satisfactorily glazed by

(2) Davenport and Powell, *op. cit.*, p. 266.

the American Lava Corporation. At its suggestion, Cantrell has utilized compressed powdered Lava Grade M and has succeeded in embedding copper coils in a variety of forms. Three of these embedded copper coils have been glazed by using the technique and glaze supplied by the American Lava Corporation, and the other two by a glaze selected and applied by Cantrell. Radiographs of these forms indicate that the coils remained intact during fabrication. Satisfactory Q values for the coils in air were obtained.

The mechanical strength of the glaze under gasketing pressure as well as the technique of inserting the ceramic into a high-pressure, high-temperature liquid medium will be tested upon receipt of a specially designed bomb now being fabricated by the Research Shops. At present nothing is known of the chemical or radiation stability of the glazes. It is obvious that a glaze stable to radiation will be required.

RADIATION-PROTECTED GLASSES

Gamma- and neutron-absorbing glasses have been cut and polished. Spectrophotometric measurements prior to irradiation have been made. Similar measurements will be made after completion of pile exposure. A glass having chemical and optical stability under homogeneous reactor conditions is being sought.

7. OPTICAL AND ELECTRON MICROSCOPY

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

AN IMPROVED METHOD OF REMOVING DEPOSITED LAYERS FROM STAINLESS STEEL

A more rapid method of removing deposited oxide layers or films from stainless steel was developed. The surface of the steel was crosshatched into 1/8-in. squares with a sharp cutting edge. The steel was then made the anode of a cell having a platinum cathode and an electrolyte of 20% hydrobromic acid in methanol. Electrolysis was carried out at 20 volts and a current density of 2 amp. Free bromine was released at the anode which attacked the underlying metal and thus loosened the film. The film was shaken free for collection in a methanol bath. Five to ten minutes, depending on the thickness of the layer, was usually adequate to loosen sufficient material for optical and electron microscopy inspection.

FILM PACK ADAPTER FOR VICKERS MICROSCOPE

A film pack adapter for the Vickers microscope was designed and fabricated to allow the more rapid taking of sequence pictures using films with a higher speed rating.

SUMMARY OF SERVICE WORK

Work related to the HRE is included with the report from the Reactor Technology Division.

Lectures were given by Mr. Willmarth at the annual Oak Ridge High School vocational conference and to the Visual Education Department of the Oak Ridge Teachers' Workshop.

Most of the work of the period has been of a service nature, the results being reported elsewhere. A summary of the service work follows:

Samples received		151
Pictures taken		821
Electron micrographs	525	
Electron diffraction patterns	108	
Photomicrographs	90	
Metallographs	38	
Radioautographs	10	
Lantern slides	47	
Copy	3	

ANALYTICAL CHEMISTRY DIVISION — Y-12 SITE

8. RESEARCH AND DEVELOPMENT

AIRCRAFT NUCLEAR PROPULSION

Determination of Oxygen in Sodium (J. C. White and W. J. Ross). As previously reported,[1] efforts are being made to develop a method for the determination of oxygen in sodium which will permit the making of spectrographic analyses on the same sample. It is anticipated, also, that any new method will have certain other advantages over the presently used Pepkowitz and Judd procedure.[2]

During the initial phases of this study a large number of organic compounds were investigated in a search for a reagent that would take sodium into solution without dissolving or reacting with sodium oxide. All these materials proved to be unsuitable for one or more reasons. Ethylacetoacetate and acetonylacetone, at first appeared promising but were later discarded because of excessive reactivity with sodium oxide, as well as for other reasons.

Recently a more fruitful approach to this problem has been discovered which depends on the well-known Wurtz reaction. In the Wurtz synthesis the action of sodium on two alkyl halide molecules results in a coupling of the alkyl groups to form a hydrocarbon and the conversion of the sodium to sodium halide. It was believed that the general reaction,

$$RX + 2Na + R'X \longrightarrow R'-R + 2NaX \qquad (1)$$

might be useful as the basis for a method of determining oxygen in sodium if an excess of halide were employed, which is the reverse of the usual procedure. Sodium was found to react quantitatively, with almost explosive violence, with *n*-butyl bromide or iodide. *n*-Amyl bromide and iodide reacted with sodium in a similar manner. It was also found that the reaction rate could be controlled by the addition of an inert diluent to the reagent. A 1:1 mixture of *n*-butyl bromide and hexane was selected as optimum for preliminary tests.

(1) *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955 (Mar. 28, 1951).

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

The effect of *n*-butyl bromide on sodium monoxide was then investigated. It seemed probable that an ether-forming reaction is the only one in which basicity can be lost (Na_2O consumed) in such a manner that it cannot be restored by hydrolysis and determined by titration.

A weighed amount of Na_2O was introduced into the reagent (1:1 *n*-butyl bromide—hexane), and the mixture was refluxed at 65 to 70°C for various periods of time. Water was then added to dissolve the monoxide, and the total basicity of the resulting two-phase system was determined by titration. The results of these experiments indicate that after 24 hr there is no loss of basicity, after 36 hr there is a barely detectable loss, and after 72 hr there is a slight loss, which is of questionable significance. In actual practice, however, a contact time of more than 24 hr is neither necessary nor desirable.

In the actual determination the sodium sample is placed in the reagent mixture, which rapidly attacks it as evidenced by formation of a blue salt. As fresh sodium is exposed, this reaction proceeds with greater vigor, especially when the temperature is raised to about 60°C. The reaction is generally complete in 2 to 4 hr, although it is usually more convenient to allow the mixture to stand overnight. After completion of the reaction, the insoluble sodium bromide and monoxide are dissolved in water, and the solution is titrated with weak acid to a potentiometric end point. A bromide titration on an aliquot of the water solution allows calculation of the sample weight (total sodium), and the rest of the solution is processed for spectrographic analysis.

Several sampling techniques have been employed in an effort to obtain standard samples. According to one procedure, sodium was melted under an atmosphere of argon, and the molten metal was drawn into evacuated glass bulbs. The oxygen content of sodium sampled in such a manner has been found to range between 0.02 and 0.05% as determined by the Pepkowitz and Judd method. The uniformity of such samples is usually questionable because of possible segregation of the Na_2O in the sodium. Representative test results are shown in Table 14.

Another technique of sampling which provides more uniform samples is the double distillation of sodium into glass bulbs under vacuum. The results of determinations on samples of this type are given in Table 15. In this table, groups A and B represent two separate distillations.

TABLE 14

Determination of Oxygen in Sodium Sampled From Pot of Molten Metal (*n*-Butyl Bromide Method)

PREPARATION	SODIUM (g)	OXYGEN (g x 10^4)	OXYGEN (%)
A	1.192	3.7	0.031
A	1.464	3.4	0.023
A	0.553	1.5	0.027
A	1.336	3.4	0.025
B	1.768	3.14	0.018
B	1.340	2.38	0.018
B	1.537	5.13	0.033
B	1.593	9.15	0.057
B	1.548	4.55	0.029
B	1.958	10.9	0.056
B	1.314	1.28	0.010
B	1.882	3.31	0.017
B*	1.48	3.11	0.021
B*	1.51	2.71	0.018
B*	1.13	1.14	0.010

*Pepkowitz and Judd method.

TABLE 15

Determination of Oxygen in Sodium Sampled by Double Distillation (*n*-Butyl Bromide Method)

GROUP	SODIUM (g)	OXYGEN (g x 10^4)	OXYGEN (%)
A	2.103	11.2	0.053
A	2.212	11.5	0.052
B	1.362	3.44	0.025
B	1.340	4.20	0.031
B	0.946	1.66	0.018
B	1.323	3.27	0.025
B	0.895	1.88	0.021

A "brick" of bulk sodium, furnished by the ANP Experimental Engineering Group, was sampled and analyzed for oxygen. Slices ¼ in. thick were cut from one end of the brick, and samples were taken from each slice. The results are given in Table 16.

TABLE 16

Determination of Oxygen in Bulk Sodium
(*n*-Butyl Bromide Method)

LAYER NO.	OXYGEN (%)					
	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6
1	0.033	0.034	0.033	0.033		
2	0.046	0.047	0.048	0.048		
3	0.055	0.048	0.053			
4	0.073	0.070	0.081			
5	0.055	0.056	0.064	0.047		
6	0.064	0.063	0.067	0.058		
7	0.050	0.060	0.050	0.042		
8	0.042	0.057	0.055			
9	0.033	0.067	0.059	0.070		
10	0.052	0.044	0.076	0.049		
11	0.065	0.093	0.076	0.070	0.072	0.073
12	0.063		0.052	0.052	0.049	0.055
13	0.038	0.036	0.037			
14	0.042	0.032	0.030			

A standard deviation value was calculated for each set of oxygen values pertaining to the individual layers. These values are given in Table 17. The average of all the standard deviations is an estimate of the standard deviation for the method. Actually, there are two factors which affect the calculated standard deviation in this case: (1) segregation of oxide within the individual layers, which tends to make it larger, and (2) the small number of samples, which tends to make it smaller. The effect of the latter factor can be estimated, but the effect of the former cannot. Since these factors work against each other, it seems fair to assume that the value obtained approximates the true standard deviation of the method, at least until data on more uniform samples are available.

The average standard deviation is 0.006%, but if the two largest values are disregarded (since both are larger by a factor of 2 than the overall

TABLE 17

Standard Deviation of *n*-Butyl Bromide Method for the Determination of Oxygen in Sodium

LAYER NO.	NO. OF DETERMINATIONS, N	AVERAGE (%)	STANDARD DEVIATION, S*
1	4	0.033	0.001
2	4	0.047	0.001
3	3	0.052	0.004
4	3	0.075	0.006
5	4	0.055	0.007
6	4	0.063	0.004
7	4	0.051	0.005
8	3	0.051	0.008
9	4	0.057	0.016
10	4	0.055	0.014
11	6	0.075	0.009
12	5	0.054	0.005
13	3	0.037	0.001
14	3	0.034	0.006

*Standard deviation = $S = \sqrt{d^2/(N - 1)}$, where d = deviation of individual determinations from the average.

average) the average becomes 0.005%. It seems highly probable, on the basis of this study, that an unusually high degree of segregation of oxide was encountered in layers 9 and 10. Statistically speaking, at a confidence level of 99.5%, any two determinations on identical samples should lie within ±0.01% of the true value.

Since it is contemplated that this method will replace the Pepkowitz and Judd method in this laboratory, a comparison of results on duplicate samples is being made. The results to date are given in Table 18.

Excellent agreement has been found in most instances with only two cases of more than 0.01% deviation. The average of three determinations by the Pepkowitz and Judd method on double-distilled sodium was 0.017% with a standard deviation of 0.006% while the *n*-butyl bromide method on the same lot of sodium gave an average of 0.024% oxygen with a standard deviation of 0.004%. No definite conclusion can be drawn as yet with respect to whether one method gives consistently higher or lower results than the other.

TABLE 18

Comparison of *n*-Butyl Bromide and Pepkowitz and Judd Methods for the Determination of Oxygen in Sodium

SAMPLE	OXYGEN (%)	
	PEPKOWITZ AND JUDD	*n*-BUTYL BROMIDE
A	0.034	0.043
B	0.011	0.012
C	0.025	0.019
D	0.043	0.047
E	0.038	0.022
F	0.010	0.024
G	0.022	0.017
H	0.018	0.029
I	0.025	0.020
J	0.018	0.028
K	0.010	0.025
K	0.018	0.031
K	0.021	0.018
K		0.025
K		0.021

The results so far indicate that the *n*-butyl bromide method is suitable for the determination of oxygen in sodium and that it possesses important advantages over the Pepkowitz and Judd method, among which are: (1) determination of oxygen and spectrographic analysis can both be made on the same sample; (2) less time per determination is required; (3) less skill and judgment are required on the part of the operator; (4) the apparatus is much simpler and less fragile; and (5) the precision is equally good, if not better.

A report covering this investigation is being prepared. It is considered that most of the necessary development work has been completed, although some refinements in technique and method may still be made.

Determination of Oxygen in Argon and Helium (J. C. White and J. R. Lund). The amount of oxygen in argon or helium is generally quite small. Some question has been raised, however, as to the uniformity of these gases from cylinder to cylinder with regard to purity. It is contemplated that these gases will be used as inert blankets in contact with liquid alkali metals, and, since it is known that as low as 10 ppm of oxygen will prove deleterious, it appears desirable to resort to some purification of the gases before use.

This purification, as planned by the ANP Experimental Engineering Group, consists in passing the gas through heated copper oxide, titanium turnings heated to 800°C, sodium-potassium alloy (Na-K), and finally through a liquid-air trap. Such drastic treatment will, presumably, reduce the oxygen content to far less than the minimum tolerable amount. The efficiency and service life of this train will be determined by testing the gas for oxygen after various intervals of time up to 1000 hr of operation.

A method described by L. J. Brady[3] for the determination of oxygen in gases, which is based on the oxidation of sodium anthraquinone-β-sulfonate from the red, reduced form to the colorless, oxidized form, has been applied to the analyses of helium and argon. The reduction in color intensity of the sodium anthraquinone-β-sulfonate solution, which is a function of the oxygen content of the gas, is measured spectrophotometrically. Investigations are underway to establish the lower limit of detection afforded by this method.

In Brady's method the gas to be analyzed is bubbled through a constant volume of reagent, the reagent is passed through a spectrophotometer, and the change in transmittancy of the solution is determined. The volume of gas is determined by means of a flowmeter. The total volume of oxygen consumed is read from a calibration curve on which the volume of oxygen is plotted against transmittancy. In order to obtain such a calibration curve, oxygen is generated in the apparatus by the electrolysis of water, the amount introduced being determined by calculations based on current flow, time, temperature, and pressure. It has been necessary to make several modifications in the specifications which Brady gives for his apparatus in order to adapt it to the particular type of spectrophotometer available for this work. In addition, it is anticipated that these changes will make the method more sensitive.

The first determinations were made directly on cylinders of argon and helium. The results are given in Table 19.

Helium No. 1 contained so much oxygen that there was instantaneous and marked discoloration of the reagent upon initial contact with the gas. Several checks confirmed this contamination to be above 0.3%. Although this is probably an isolated case, it is significant in that it demonstrates the wide variance from tank to tank with regard to oxygen content. The test results

(3) L. J. Brady, "Determination of Small Amounts of Oxygen in Gases," *Anal. Chem.* 20, 1033 (1948).

indicate that it will be necessary to purify these gases if they are to be used as protective atmospheres for liquid alkali metals.

TABLE 19

Oxygen Content of Commercial Helium and Argon

GAS	CYLINDER	OXYGEN (ppm)
Helium	1	3000
Helium	2	57
Argon	1	20
Argon	2	45
Argon	3	35

Plans are also underway to determine nitrogen in helium and argon by means of isotopic dilution analysis, using N^{15} as a tracer. This work will be carried out in cooperation with the Y-12 Assay Laboratory.

Flame Photometric Determination of Calcium in Sodium Metal (O. Menis). A limited study was made of the applicability of flame photometric methods in the determination of calcium in metallic sodium. A flame spectrophotometric method which utilized an oxygen—illuminating gas flame and the Beckman spectrophotometer was tested. The aim of the experiment was to establish the effect of the sodium emission background on the measurement of the calcium emission intensities. A very high flame background, of an intensity of about 90% of that emitted by 1 γ of calcium, decreased the sensitivity of the calcium readings. Only by relative enhancement of the calcium band emission or by reducing the background can a favorable ratio be attained. A higher temperature flame, such as an oxygen-acetylene source, may provide an enhancement of the calcium emission in the spectral region of least sodium emission interference. An oxygen-acetylene flame attachment for the Beckman spectrophotometer has been purchased and will be placed in operation in the near future.

Thermal Stability of Dow Corning Silicone Oil 550 (J. C. White). A study of the stability of Dow Corning Silicone Oil 550 at elevated temperatures, alone and when in contact with sodium, has been previously reported.[1,4]

(4) R. Rowan, Jr., *Stability of Dow Corning Silicone Fluid 550 in the Presence of Sodium*, ORNL, Y-12 Area, Report Y-B31-227 (Jan. 17, 1951).

The oil polymerized at 900 to 1050°F in the presence of sodium, but little change was noted at a temperature of 1000°F when sodium was not present.

Further tests were recently made to determine the thermal stability of the oil. In one case the oil was heated under helium and maintained at 1200°F for 15 min. Upon removal from the furnace it was found that about 20% of the liquid had been lost by evaporation and approximately 40% of the remaining fluid had polymerized into a dark-brown, hard, brittle mass. In a second trial, the oil, sealed in a quartz tube under argon and heated to 1200°F, was observed to undergo polymerization after 15 to 20 min at this temperature.

These results indicate that DC-550 is thermally unstable at temperatures above 1200°F because of polymerization, even when not in contact with sodium.

Determination of Carbon in Chlorinated Silanes (O. Menis and C. K. Talbott). A determination of carbon in samples of chlorinated silanes was requested in connection with the NEPA project.

After a search of the literature, it was decided that wet combustion was the method most likely to be successful for the analysis of these compounds. It was believed also that the development of the apparatus and method would strengthen the facilities of the laboratory by adding another technique to those already available.

The semimicro apparatus employed was patterned after that of McCready and Hassid.[5] It was modified by the insertion of a hydrazine scrubber before the drying tube to remove the liberated halogen gases. A combustion (oxidation) mixture, consisting of 20.0 g of phosphorus pentoxide, 85 ml of 95% sulfuric acid, 15 ml of 85% phosphoric acid, 10.0 g of chromic oxide, and 1.0 g of potassium iodate, was prepared according to procedures found in the literature.[6]

The apparatus and procedure were tested by analyzing several pure organic compounds of known composition. Inasmuch as the silanes are quite volatile, particular attention was paid to the analysis of volatile compounds. The test results are given in Table 20.

(5) R. M. McCready and W. Z. Hassid, "Semimicrodetermination of Carbon Using the Van Slyke-Folch Oxidation Mixture," *Ind. Eng. Chem. Anal. Ed.* 14, 525 (1942).

(6) P. S. Farrington, C. Niemann, and E. H. Swift, "Determination of Carbon by Wet Combustion," *Anal. Chem.* 21, 1423 (1949).

TABLE 20

Determination of Carbon by Wet-Combustion Method

EXPERIMENT NO.	SAMPLE	VOLUME OF COMBUSTION MIXTURE (ml)	TEMPERATURE (°C)	CARBON FOUND (%)	RECOVERY (%)
1	Ethyl alcohol	10	Open flame	34.5	66
2	Ethyl alcohol	10	Open flame	30.5	58.
3	Benzoic acid	10	Open flame	67.1	97.4
4	Ethyl alcohol	10	Open flame	15.2	29
5	Ethyl alcohol	10	185 - 195	21.7	41.6
6	Ethyl alcohol	15	185 - 195	52.6	100.8
7	Ethyl alcohol	15	185 - 195	44.2	84.7
8	Ethyl alcohol	15	185 - 195	37.9	72.6
9	Ethyl alcohol	15	210 - 220	45.4	87
10	Ethyl alcohol	15	210 - 220	44.2	84.7
11	Ethyl alcohol	15	210 - 220	46.3	88.7
12	Ethyl alcohol	15	210 - 220	44.0	84.3
13	Glacial acetic acid (commercial)	15	210 - 220	39.6	99
14	Glacial acetic acid (commercial)	15	210 - 220	39.3	98.3
15	Ethyl alcohol	15	210 - 220	42.8	82
16	Ethyl alcohol	15	210 - 220	45.9	87.9
17	Acetone	15	210 - 220	56.2	90.5

Remarks: In experiments 1 through 11 samples were delivered through the reagent inlet. To test for any losses in experiments 12 through 17, the samples were weighed directly into the flask.

For better control of combustion temperature, an oil bath was used in experiments 5 through 17.

In experiments 15 through 17, glass wool was inserted into the reaction flask to increase the area of contact between the combustion mixture and volatile oxidation products of the sample.

The data presented in Table 20 show that, in the case of volatile compounds, the results were low by about 10%. It is possible that in the case of alcohol the oxidation does not go to completion and a volatile intermediate oxidation product is lost.

To test whether the size of the apparatus was partially responsible for low results obtained, a micro procedure was adopted. A simplified micro combustion apparatus was constructed which consisted of a 15-ml reaction flask equipped with an air inlet tube protected by a CO_2 absorption tube and connected to a small condenser, sulfuric acid bubbler, an absorber filled with

zinc granules and anhydrous calcium sulfate, and a Pregl type CO_2 absorption tube connected to another absorption tube filled with Ascarite and Anhydrone. All connections consisted of standard-taper joints or ball joints. The samples were weighed in sealed glass capillaries. To overcome the difficulty in sealing capillaries containing the highly volatile silane compounds, a smaller capillary containing the sample was sealed in a larger capillary. The capillaries were introduced into the reaction flask and broken. Ten milliliters of the oxidizing mixture was introduced through the dropping funnel, and the combustion was carried out for 10 min at 210°C. The results are shown in Table 21.

TABLE 21

Determination of Carbon by Micro Wet-Combustion Analysis

SAMPLE NO.	COMPOUND	SAMPLE WEIGHT (mg)	CARBON (%)	RECOVERY (%)
1	Ethyl alcohol	18.570	52.5	100.6
2	Ethyl alcohol	6.311	52.2	100.0
3	Carbon tetrachloride (com.)	7.068	7.4	94.9
NEPA 0978 (1)	Si_2Cl_6	22.759	16.83	
NEPA 0978 (2)	Si_2Cl_6	13.029	16.43	
NEPA 0979 (1)	$SiHCl_3$	2.377	16.70	
	$SiHCl_3$	4.085	18.93	

These results indicate that, of the methods tried, the micro apparatus and procedure give the most complete combustion and recovery of carbon for the known compounds analyzed (ethyl alcohol and carbon tetrachloride). It cannot be said with certainty that the same will hold true for the chlorinated silanes, since no standards are available, but this may be a fair assumption. The precision of the test results for the unknown compounds is not unusual for an analysis of this type.

Micro Determination of Carbon Dioxide and Sulfur in Thallium Carbonate (O. Menis and C. K. Talbott). Approximately 100 mg of impure thallous carbonate was submitted, in connection with the NEPA program, for the determination of carbonate and sulfur.

Because of the small size of the sample, it was necessary to work on a micro scale. A small all-glass carbonate analysis train was designed and constructed. In order to test the apparatus, carbonate determinations were made on Bureau of Standards Na_2CO_3; the results checked with the Bureau's value within 1.5% (relative error). The analysis of the unknown was carried out under similar conditions.

With the aid of standards whose concentration ranges were close to those of the unknown with respect to the major constituents, the determination of sulfate was made turbidimetrically.

Determination of Water Formed in the Reaction Between Sodium Hydroxide and Uranium Trioxide (W. K. Miller and S. A. McKinnon). When sodium hydroxide reacts with uranium trioxide at about 500°C, water is evolved. In order to assign a definite formula to the product of the reaction, it was necessary that the amount of water given off in the reaction be determined. The two proposed reactions between which it was desired to distinguish are

$$2NaOH + UO_3 \longrightarrow Na_2UO_4 + H_2O$$

$$NaOH + UO_3 \longrightarrow \tfrac{1}{2}Na_2U_2O_7 + \tfrac{1}{2}H_2O$$

The first reaction, in which one molecule of water is formed per molecule of uranium trioxide, seems more likely at 500°C than does the second, in which only half as much water is formed.

Sodium hydroxide, 15 g, in a silver crucible was placed in a pyrex container fitted with a delivery and an outlet tube. The apparatus was placed in a pot furnace and the system was heated at 550°C for 1 hr with a stream of dry argon passing through the reaction vessel. The outlet tube was fitted with a U tube containing Dehydrite, and this, in turn, was protected from the atmosphere on the outlet end of the train by a guard tube containing Drierite. After the heating the sodium hydroxide was assumed to be dry, the system was cooled, and the U tube was weighed. The container was opened momentarily while a weighed amount of dry UO_3 was added, and the system was again heated to 550°C for 1 hr while argon was flowing through the train. The gain in weight of the U tube in the latter heating was assumed to represent the amount of water evolved during the reaction. Two trials were made, in the second of which the heating period was increased to 2 hr. The quantity of water was

higher in both cases than the theoretical amount corresponding to either of the above equations. In the second trial more than two molecules of water were evolved per molecule of uranium trioxide added. It is believed that the sodium hydroxide must not have been dried to an equilibrium state by the treatment to which it was subjected prior to reacting it with UO_3. Tests will be carried out to determine the conditions under which the reactants must be dried before making the determination.

Determination of Potassium in a Eutectic Mixture of Uranium and Alkali Fluorides (O. Menis and C. K. Talbott). In connection with phase studies of sodium-potassium-uranium fluoride systems, it was necessary that analytical methods be made available for the determination of sodium and potassium in eutectic mixtures of this type. The total alkali content was known fairly accurately, a circumstance which made it necessary to determine only sodium or potassium, but not both. The total alkali fluoride content was of the order of 25%.

As a first approach to this problem, the perchlorate method of separation and determination of potassium was tried. This method depends upon the fact that potassium perchlorate is insoluble in certain organic liquids, while practically all other perchlorates are appreciably soluble. In the present case the solvent used was anhydrous ethyl acetate. Briefly, the procedure consists in evaporating a mixture almost to dryness with perchloric acid and taking up the residue in anhydrous ethyl acetate. The insoluble portion is filtered off, washed, dried, and weighed as potassium perchlorate.

The method was tested on a synthetic solution of sodium, potassium, and uranium salts. A double precipitation of the perchlorates was found to be necessary for the quantitative separation of potassium from uranium. Under these conditions, potassium in the presence of a sevenfold concentration of uranium can be determined with a relative error of less than 1%.

The flame photometric determination of potassium in such mixtures was also studied briefly. The standards employed contained sodium and uranium in concentrations approximating those of the unknown solutions. A comparison of test results on three unknown solutions is given in Table 22.

A comparatively close agreement between the two methods was found. Since the gravimetric (perchlorate) method is quite satisfactory for this determination, further work on the flame photometric method has been temporarily suspended.

TABLE 22

Determination of Potassium in Solutions Containing Uranium and Sodium

SAMPLE	POTASSIUM (%)		DIFFERENCE
	A FLAME PHOTOMETRIC	B GRAVIMETRIC	A - B
C-1	7.10	7.13	-0.03
C-2	7.31	7.26	+0.05
C-5	6.60	6.80	-0.20

Determination of Uranium by Extraction Methods (J. C. White). The method for the semimicro determination of uranium in minerals and ores by Smith and Williams[7] is being checked for possible application in this laboratory. The procedure calls for the use of a cellulose-alumina column which retains all metals except uranium. The method offers a promising means of eliminating the interference of vanadium in the determination of uranium in low-grade uranium ores.

Detection of an Organic Binder in Graphite (W. K. Miller and J. R. Lund). A portion of a graphite bearing was submitted for tests to determine the possible presence of an organic binder.

It was believed that heating in an inert atmosphere at a high temperature would decompose any organic resin which might be present. The sample was ground in a diamond mortar, dried at 110°C, and placed over phosphorus pentoxide for 72 hr. On heating in a quartz boat at 750°C for 1 hr in an atmosphere of argon which had previously been passed over hot copper, the graphite showed a weight loss of 3.90%. A second heating at 975°C for 1 hr gave an additional loss of 0.23%. It was believed that the loss in weight might be due to desorption of water, so a second sample was weighed and heated to 250°C for 1 hr in the same train with a loss of only 0.83%. Continued heating of the second sample at 975°C for 1 hr produced an additional loss of 3.04%, or a total loss of 3.87%. Since the original heating probably drove off essentially all water, the loss in weight must have been due to some other

(7) G. H. Smith and A. F. Williams, *A Rapid Semimicro Procedure for the Determination of Uranium in Minerals and Ores by Extraction Methods*, Montreal Report CRL-AE-46 (January, 1950).

cause. A charred mass, which could not be removed by ordinary means, was found on the inside of the fused silica combustion tube after the high-temperature treatment. This, and also the loss in weight, might be attributed to mechanical loss of graphite, but this does not seem likely, particularly since the carbon seemed almost embedded in the quartz. A more likely explanation would be the high-temperature volatilization and charring of an organic constituent.

In order to determine the approximate temperature of the weight loss on heating and the effect of prolonged heating, a sample of the graphite was subjected to 2-hr periods of heating in an inert atmosphere at temperatures ranging from 110 to 950°C. About 80% of the weight loss occurred at 500°C. A very slight loss of weight occurred on prolonged heating at 950°C, but this was negligible. The temperature of maximum weight loss is approximately that which would be predicted for charring of organic adhesives.

An attempt was made to extract any suspected binder in a Soxhlet extractor. The extractor was operated for 8 hr at the rate of 12 extractions per hour, using a solvent of equal volumes of ethyl alcohol and benzene. A blank determination was made in a second extractor. No loss in weight was observed after drying and weighing the extracted samples. This is not evidence against the presence of a binder, since most resins are not dissolved by organic solvents. It does, however, prove the absence of oils and other soluble organic sustances whose presence might explain the black deposit previously described.

A combustion analysis of the graphite gave 93.3% carbon and 0.79% hydrogen. However, an unreacted residue remained after combustion. The presence of hydrogen could have been due to adsorbed water, but it is a coincidence, if not evidence, that a similar sample of graphite (see p. 108) known to contain an organic binder, gave an exactly equivalent value for hydrogen when subjected to combustion analysis.

Although it has not been definitely proved, it is considered likely, on the basis of the evidence, that the graphite in question does contain an organic binder.

Analysis of Fluorides by the Pyrohydrolysis Method (W. K. Miller and S. A. McKinnon). With certain fluorides, e.g., those of beryllium, zirconium, and uranium, the removal of fluoride as hydrofluosilic acid by steam distillation

(the Willard and Winter method[8]) has been found to require exceedingly long distillation, and even then removal of all the fluoride is sometimes questionable. An alternate method therefore appeared to be highly desirable. It is believed that the pyrohydrolysis method[9] furnishes the desired improvements. Briefly, the apparatus used in carrying out the pyrohydrolysis consists of a steam generator attached by means of a tapered glass joint to a platinum tube which terminates in a condenser whose inner tube is also made of platinum. This equipment was identical with that described on pp. 9ff. of reference 9 except that no superheater was used in the initial tests on heavy metal fluorides. A superheater was later added when it was found that beryllium fluoride could not be hydrolyzed at a practical rate without it, even in the presence of a catalyst (uranium oxide, U_3O_8). The tube containing the sample in a platinum boat is heated under an atmosphere of steam by means of a combustion furnace. When the superheater is used, the steam is preheated before it enters the pyrohydrolysis tube by passage through a fused silica tube surrounded by a combustion furnace. The method has been tested with samples of zirconium tetrafluoride, uranium tetrafluoride, thorium tetrafluoride, and hafnium tetrafluoride at 900°C. The test results are tabulated below, along with two values on beryllium fluoride, using the superheater at 1000°C (see Table 23).

TABLE 23

Determination of Fluoride by Pyrohydrolysis

COMPOUND	TIME OF HYDROLYSIS (min)	FLUORIDE (%)	
		THEORETICAL	FOUND
ZrF_4	60	45.45	43.19 43.89 43.70 43.74
UF_4	50	24.20	23.87 23.80 23.74
ThF_4	60	24.66	24.96 24.81
HfF_4	60	29.85	30.08 29.98
BeF_2*	60	80.73	80.6 79.5

*U_3O_8 was used to catalyze the hydrolysis.

(8) H. H. Willard and O. B. Winter, "Volumetric Method for Determination of Fluorine," *Ind. Eng. Chem. Anal. Ed.* 5, 7 (1933).

(9) J. C. Warf and W. D. Cline, *Pyrohydrolysis in the Analysis of Fluorides and Other Halides*, Report CC-2723 (June 30, 1945).

The precision of the method appears to be excellent. Although the test results sometimes differ from the theoretical values, it cannot be assumed for this reason that they are inaccurate because the degree of purity of the compounds is not known. It is believed, however, that the method presents an improvement over the steam distillation procedure for many materials in which fluoride can be determined only with difficulty, or not at all, by the Willard and Winter method.

The Identification of White Coating Inside a Fused Silica Tube (W. K. Miller and S. A. McKinnon). A sample of a fused silica tube, inside which had been fused a eutectic mixture of sodium fluoride and uranium tetrafluoride, was submitted to this laboratory with a request that a white coating, formed as a distinct layer between the clear quartz and the fused mass, be identified. A sample was also submitted to the Physics Section of the Stable Isotopes Division for X-ray diffraction analysis. Theoretical considerations led to the belief that the white coating was sodium fluosilicate, formed by a reaction between sodium fluoride and the tube. X-ray diffraction patterns, however, indicated that the coating was not sodium fluosilicate but silicon dioxide.

A portion of the tube, with a small amount of the adhered coating, was separated mechanically from the melt until no green salt was visible. A sample of the material containing an estimated 10 to 50 mg of the coating was boiled in distilled water for 1 hr and filtered. Most of the coating was unattacked by hot water; this insolubility furnished further evidence against sodium fluosilicate. The filtrate from the above treatment was diluted to 100 ml, and sodium was determined by flame photometry. A value of 2.1 γ of sodium per milliliter or a total of 0.21 mg of sodium was obtained. This value is only 2% of the estimated lower limit of 10 mg of white coating. Sodium represents 24.5% of the weight of sodium fluosilicate.

In another experiment all the tube fragments and a large portion of the sodium fluoride–uranium tetrafluoride melt were separated mechanically from the white coating so that the coating constituted an estimated 20 to 40% of the sample. The sample was ground, and duplicate portions were fused in platinum crucibles with a mixture of sodium and potassium carbonates. The melt was taken up with water, and the insoluble uranium oxide was filtered off. The silica was precipitated from the filtrate and determined according to the method of Berzelius.[10]

(10) W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, p. 800, Wiley, New York, 1929.

The uranium oxide, which was filtered off after the carbonate fusion, was dissolved in nitric acid and reprecipitated as hydrated uranium oxide by ammonium hydroxide. The precipitate was filtered, ignited to U_3O_8, and weighed. From the results of the silica determination and the uranium determination, and a knowledge of the ratio of uranium fluoride to sodium fluoride, it should be possible to calculate sodium fluoride and obtain a material balance. The precision of duplicate tests was good, but a value of only 17.5 mole % UF_4 in the melt was obtained; the eutectic mixture is supposed to contain 26 mole %. A small error in either the silica or uranium determination could account for a large error in the material balance, since sodium fluoride was obtained by difference. Another attempt will be made to obtain a material balance.

An attempt was also made to separate the melt from the white coating. Portions of the melt and adhered coating were refluxed with ammonium oxalate solution in order to dissolve the UF_4. Five 1-hr periods of refluxing with separate portions of the oxalate were required to dissolve all the UF_4. After the final refluxing, the white coating was filtered and washed. Only a trace of green color remained. The coating was filtered, ignited, weighed, treated with hydrofluoric and sulfuric acids, and reweighed. This treatment indicated that the isolated coating was 96.3% silica. The remainder could have been contamination from the uranium melt which could not be separated. This served as the most conclusive chemical evidence that the coating was silica, but does not prove that at least a small amount of sodium fluosilicate was not present.

A silica determination was made on the melt from which all the coating had been mechanically removed. The fact that no silica was found indicated that the coating had not contaminated the melt except on the walls of the tube.

On the basis of the results to date, it is considered highly probable that the white coating was not sodium fluosilicate but was crystalline silicon dioxide, formed by the crystallization of the fused silica tube. It is hoped that an accurate material balance can be obtained to support this belief.

Chlorination of Earth Acid Oxides (O. Menis and C. K. Talbott). On several recent occasions it has been necessary to make determinations of titanium in the presence of niobium, and the prospect is that such occasions

will recur. There is, therefore, a considerable need for a satisfactory method of separating titanium from niobium and tantalum. Present methods do not offer a sharp separation of these elements. Numerous reprecipitations are necessary, and the results are affected by the usual coprecipitation and adsorption errors.

Since titanic chloride boils at 137°C, while niobic chloride boils at 240.5°C and tantalic chloride at 242°C, it would appear that it should be possible to separate titanium from the earth acid elements by fractional distillation of the chlorides. An investigation of the chlorination of the oxides of these elements has been undertaken. Only one reference[11] dealing with chlorination methods for niobium and titanium for the purpose of separation was found. It was reported that octachloropropane is the most effective chlorinating agent, but no details of procedure were given, and it has been impossible to obtain further information. An investigation of the various chlorinating agents available has been made, essentially without benefit of assistance from the literature. The results of these experiments are summarized in Table 24. In each case 40 mg of niobic oxide (containing 3% tantalic oxide) was weighed out into a 250-ml standard-taper flask equipped with a reflux condenser and thermometer, and the reagent was added. In experiments 3, 6, and 9 a three-neck standard-taper flask, equipped with a mercury-sealed stirrer, reflux condenser, and a thermometer, was employed.

As shown in Table 24, the reaction with heptachloropropane is the most promising. In experiment 9 this reaction was repeated with more careful control of conditions. The oxide was crushed to a powder, and the reaction was much more rapid than in experiment 3 where crude oxide flakes were used.

On the basis of the first nine experiments, heptachloropropane was selected as the chlorinating agent for the niobium and titanium oxide mixture. Samples of the two oxides were weighed into the reflux flask, and the reaction was carried out as in the previous experiments for 16 hr at 230 to 245°C. At the end of the reflux period the solutions were fractionated through a short column. The two fractions collected were those boiling below 150°C and between 150 and 240°C. The residue was also digested with nitric and sulfuric acids. The two fractions and the residue were analyzed for titanium and niobium. The results are presented in Table 25.

(11) Polytechnic Institute of Brooklyn, *A Study of the Chemistry of Columbium, Tantalum, and Some Associated Transition Elements*, Final Report Covering Period January 1, 1948 to October 31, 1949, NP-1266 (no date).

TABLE 24

Chlorination of Nb_2O_5

EXPERIMENT NO.	CHLORINATING AGENT	AMOUNT OF REAGENT	TEMPERALTURE OF REACTION (°C)	TIME (hr)	REMARKS
1	Hexachloro-propene	100 ml	190 - 200	19.5	Reflux; no visible reaction
2	Heptachloro-propane	100 ml	235 - 240	21.5	Reflux; solution turned dark
3	Heptachloro-propane	100 ml	200 - 215	10	Stirring and reflux; complete solution
4	Hexachloro-ethane	10 g			Reagent sublimed; no reaction
5	Hexachloro-ethane, carbon tetra-chloride	10 g 50 ml	75	7	No reaction
6	Hexachloro-propene	100 ml	200	11	Stirring and reflux; no reaction
7	Hexachloro-phenol	10 g	220	1	Reflux; some reaction; most reagent sublimed
8	Hexachloro-phenol, carbon tetra-chloride	10 g 50 ml	75	15	Reflux; some reaction
9	Heptachloro-propane	100 ml	235 - 240	3	Stirring and reflux; complete solution

TABLE 25

Separation of Niobium and Titanium

EXPERIMENT NO.	WEIGHT OF OXIDE (mg) PRESENT Nb_2O_5	PRESENT TiO_2	FOUND Nb_2O_5	FOUND TiO_2	RECOVERY** (%)
10	8.4		7.8		92.9
		30.8		3.5	11.4
11*	5.6		5.2		92.9
		41.3		3.0	7.3

*Mercury present.

**Based on distillates only; residues not included.

A summary of the material balance figures obtained in experiments 10 and 11 is given in Table 26.

TABLE 26

Material Balance

EXPERIMENT NO.	WEIGHT OF MIXED OXIDES (mg)			
	ORIGINAL	IN DISTILLED FRACTIONS	IN RESIDUE	LOSS
10	39.2	11.3	23.5	4.4
11	46.9	8.2	23.6	15.1

The last two experiments indicate that niobium chloride is almost quantitatively recovered in the higher boiling fraction. The failure to achieve total overall recovery may be partly due to mechanical causes and partly to loss of volatile titanium tetrachloride. Further work will be necessary to establish the nature of the loss. The incompleteness of chlorination of titanium indicates the need for further modifications in the chlorination procedure, such as (1) more drastic chlorination with higher boiling chlorinating agents, (2) chlorination of the two elements after a chemical precipitation as the hydroxides from a single solution, and (3) use of catalysts. On the basis of the meager data obtained, the chloride fractionation method appears to be promising for the separation of niobium from titanium.

HOMOGENEOUS REACTOR PROJECT

Some Analytical Problems of the HRE Program (O. Menis and C. K. Talbott). Corrosion processes which occur during the operation of the HRE test rigs, often causing failure of the system, are being investigated through chemical analysis of samples of the solutions and residues withdrawn during trial runs. It is expected that from these analytical data an insight into the mechanism of the corrosion process can be obtained. It is hoped that a better understanding of this mechanism will lead to methods of preventing corrosion and of selecting the least troublesome system. A search is being made to find a reliable indicator by which the imminence of trouble due to corrosion can be detected so that corrective steps can be taken before complete failure occurs.

Of immediate interest is the composition of the uranyl sulfate solutions as they are sampled during the operation of the HRE test system. The elements of interest are the components of the stainless steel reactors and the decomposition products of the solutions. The determinations which are being considered include total uranium, uranium(IV), iron, chromium, nickel, manganese, silica, molybdenum, niobium, reduced sulfates, *p*H and free acid, and nitrates. Complete analyses of solid residues found in some of the samples will be made. In addition, determinations of free oxygen and of traces of fluorides and chlorides and miscellaneous tests, such as field tests for the identification of steel samples, are also contemplated.

In the first phase of the work, during a period covering a few weeks, over a hundred samples were received and about 80% of these were analyzed for total uranium, uranium(IV), iron, chromium, nickel, and *p*H. The total uranium was determined potentiometrically, while uranium(IV) was separated as the fluoride, using lanthanum fluoride as a carrier, then oxidized to uranium(VI) and determined colorimetrically or polarographically. Iron, nickel, and chromium also were determined colorimetrically, iron as the 2,2′-dipyridyl complex, nickel with dimethylglyoxime, and chromium with diphenylcarbazide. In the case of iron the 2,2′-dipyridyl method was found to be less subject to interference from uranium than the 1,10-orthophenanthroline method. The *p*H of the solutions was determined by means of a glass electrode. This work is still in progress and is expected to continue for some time.

Also under study is the stability of uranium(IV) in uranyl sulfate solutions. Duplicate samples, one of which contained added hydroxylamine, were analyzed for uranium(IV), and it was found that in the presence of hydroxylamine the uranium(IV) values were higher. This indicates that the hydroxylamine prevented the oxidation of uranium(IV).

Future development work will involve a continued study of the factors affecting the stability of trace quantities of uranium(IV) in uranyl sulfate solutions. Various inhibitors and complexing agents such as hydroquinone and cysteine will be tested.

A large part of future development work will deal with methods of separating the trace elements from uranium and determining a large number of these elements in a single solution by means of the polarograph. Extraction and chromatographic procedures using various common extracting agents such as TBP (tributyl phosphate) will be carried out and checked for complete recovery of trace elements.

Another phase of the development work includes various miscellaneous analyses, among them the polarographic determination of oxygen and the electrographic analysis of steel samples.

Y-12 TECHNOLOGY

Determination of Phthalate in Recycle Liquors (W. K. Miller and S. A. McKinnon). In the last quarterly progress report[1] details were given of the development of an ultraviolet absorption method for the determination of phthalate ion in recycle liquors from the zirconium refining process. A few test results by this method were reported and compared with results by the lead acetate method [12]. Determinations by the latter method have previously been made by the Normal Accountability Laboratory. In view of the need for a greater number of test results on which to base an evaluation of the method, however, a number of determinations by both methods have recently been made in this laboratory. The results are given in Table 27.

TABLE 27

Determination of Phthalate in Recycle Liquors

SAMPLE NO.	CONCENTRATION (moles/liter)		DIFFERENCE, A - B
	A SPECTROPHOTOMETRIC METHOD	B LEAD ACETATE METHOD	
1	1.28	1.28	0.00
2	0.955	1.06	-0.10
3	0.655	0.659	-0.004
4	0.660	0.663	-0.003
5	1.10	1.14	-0.04
6	0.57	0.64	-0.07
7	1.42	1.40*	+0.02
8	1.52	1.46	+0.06
9	0.190	0.194	-0.004
10	0.17	0.19	-0.02
11	1.00	1.05	-0.05
12	1.38	1.39	-0.01

*Chloride was removed before precipitation with lead acetate.

(12) L. G. Overholser and W. R. Grimes, *Chemical Determination of Phthalate Ion*, Oak Ridge National Laboratory, Y-12 Area, Report Y-602 (Apr. 17, 1950).

It will be observed that values obtained by the lead acetate method in this laboratory are usually higher than those by the spectrophotometric method. The results obtained by the Normal Accountability Laboratory have been both higher and lower than the spectrophotometric test results, and the precision has been poor. These discrepancies may be due to the interference of the chloride ion with the lead acetate method. An average value of 1.98 *M* was obtained by the lead acetate method in this laboratory on sample 7 (Table 27) without removing chloride. A value of 1.40 *M* was obtained after the chloride had been removed by precipitation with silver nitrate.

Standard samples of phthalate containing different amounts of chloride were submitted to this laboratory for spectrophotometric analyses and to the Normal Accountability Laboratory for gravimetric analyses. The results are shown in Table 28.

TABLE 28

Determination of Phthalate in Ammonium Phthalate Solution

SAMPLE NO.	CONCENTRATION* (moles/liter)			
	ACTUAL CHLORIDE	ACTUAL PHTHALATE	PHTHALATE FOUND	
			ULTRAVIOLET	LEAD ACETATE
A	0.000	0.196	0.200	0.170, 0.207
B	0.113	0.196	0.196	0.198, 0.171
C	0.282	0.196	0.196	0.146, 0.184
D	0.564	0.196	0.196	0.173, 0.135
E	1.128	0.196	0.197	0.191, 0.162

*Each value represents the average of two determinations.

It is obvious from these results that the lead acetate method does not serve as a good check on the spectrophotometric method. High results by the lead acetate method may be attributed to coprecipitation of lead chloride. Low results, however, are difficult to explain, even on the basis of the formation of $PbCl_4^{--}$, since the excess of lead acetate present is much more than sufficient to combine with all the chloride.

A likely source of error in the absorption method could be the side reactions between phthalic anhydride and ammonia when the ammonium phthalate solution is prepared. Since the standard absorption curve was based on

phthalic anhydride rather than on the phthalate ion, formation of phthalimide or ammonium phthalamidate could give rise to either a positive or negative error depending on the relative absorption of the phthalate ion and the impurity. It is hoped to investigate these possible sources of error.

The spectrophotometric method, however, has been shown to be sufficiently accurate for the use for which it was developed, and it is now being used in a routine manner.

Determination of Oxygen in Zirconium (W. K. Miller and S. A. McKinnon). As a consequence of analytical work on a sample of zirconium hydride (ZH-1) submitted by the MIT Metallurgical Project as a part of a cooperative analytical program, this laboratory reported higher values for the oxygen content of the sample than those found by other cooperating laboratories. The same method, that of Read and Zopatti,[13] was used by all the cooperating laboratories. According to this method, dry HCl is passed over a sample of zirconium metal (or zirconium hydride) in a closed system at 550°C, $ZrCl_4$ is formed and volatilized, and the ZrO_2 originally contained in the sample is left behind and can be weighed as such. The method prescribes the use of an HCl generator. In the analysis of zirconium hydride sample ZH-1, however, cylinder HCl was used.

In order to eliminate possible errors due to contamination of the cylinder gas with oxygen, it was decided, for all future determinations, to generate the hydrogen chloride in strict accordance with the method as outlined by Read and Zopatti. The only modifications in the apparatus and procedure were as follows: Instead of pushing the sample and boat into the hot portion of the tube after the stream of HCl had begun to flow, the sample was put in place in the combustion tube before heat had been applied to the furnace. The temperature of the furnace was gradually raised to the operating temperature, 550°C. An additional dry flask was used to trap the evolved zirconium tetrachloride, and all stopcocks beyond the combustion furnace (on the outlet side) were eliminated to prevent clogging the exit train with zirconium tetrachloride.

Recently, samples of both zirconium and zirconium hydride were submitted to the cooperating laboratories for analysis. Analysis of samples by the above method produced an average value of 0.25% oxygen in the metal. These values compare favorably with those obtained by the MIT Metallurgical Laboratory on the same samples.

(13) E. B. Read and L. P. Zopatti, *Determination of Oxygen in Zirconium Metal*, AECD-2798 (decl. Feb. 14, 1950).

Determination of Sulfur in Propane (J. C. White, W. K. Miller, O. Menis, and C. K. Talbott). The repeated failure, by embrittlement and cracking, of a number of large nickel reactor tubes used in a step of the zirconium refining process has been a matter of some concern. These tubes are operated at an elevated temperature and are heated directly by gas flame with propane as the fuel. It has been established by the manufacturer of the tubes that more than approximately 20 grains per 100 cu ft of sulfur in the gas can cause the type of failure encountered. It was, therefore, requested that a determination of total sulfur be made on the fuel gas.

A sample of about 35 liters of propane was collected at its point of use in Building 9211. It was later learned, however, that only one grade of propane is used in the Y-12 Area, and subsequent determinations were made on propane from the gas lines of the Analytical Chemistry Laboratory.

The referee method,[14] considered an official procedure by the Bureau of Standards, was used for the determination of total sulfur. According to this method, the gas is burned in the presence of excess ammonia in apparatus consisting of a chimney and a condenser tower filled with glass beads. Condensible products of combustion are collected at the bottom of the tower. The sulfur in the gas, converted to SO_2 by combustion, is collected as $(NH_4)_2SO_3$ in the condensate, converted to sulfate by treatment with H_2O_2, and determined gravimetrically as barium sulfate. Approximately 1 cu ft of gas was burned in each test.

Determinations were also made of the amount of sulfur present as hydrogen sulfide or sulfur dioxide. Approximately 0.3 cu ft of propane was bubbled through an ammoniacal cadmium chloride solution to absorb hydrogen sulfide. This solution was acidified and titrated with 0.01 *N* iodine solution.

Sulfur dioxide was determined by passing propane through a 5% potassium carbonate solution containing several drops of 30% hydrogen peroxide, the sulfur dioxide being absorbed to form sulfite which was oxidized to sulfate by the peroxide. A gravimetric sulfate determination was then made.

The results for hydrogen sulfide and sulfur dioxide (Table 29) indicate that roughly half the sulfur present in the propane supplied to Y-12 is organic in nature.

(14) L. M. Dennis and M. L. Nichols, *Gas Analysis*, p. 359, Macmillan, New York, 1929.

TABLE 29

Determination of Sulfur in Propane (Fuel Grade)

PROPANE LABORATORY NO.	SULFUR (grains per 100 cu ft)		
	AS H_2S	AS SO_2	TOTAL SULFUR
50587	0.09		
50588	0.13		
50589		0.58	
50590		0.82	
50591			1.3
50592			1.4

It is evident that the total sulfur content of the gas is far below 20 grains per 100 cu ft, which is the reported tolerance figure.

SPECIAL PROBLEMS

The Determination of Trace Elements in the Human Body (O. Menis and C. K. Talbott). In connection with an extensive study of trace elements in the human body which is being conducted by the Health Physics Division, samples of human bone and teeth were submitted for the determination of the following elements: nickel, chromium, molybdenum, manganese, silicon, copper, strontium, sulfur, rubidium, cobalt, aluminum, vanadium, lithium, boron, titanium, zinc, cadmium, lead, tin, gold, and others. A literature survey revealed very little previous work of this nature. However, Hill, Marshall, and Jacob,[15] in a study of phosphate rock, reported a single analysis of bone ash for the following elements: phosphorus, magnesium, sodium, potassium, titanium, manganese, chromium, vanadium, copper, and zinc. Results of the determination of major components of bone and teeth have also been published.[16,17]

On the basis of the information available, it was decided that the most promising approach to the problem would be by spectrographic analysis for most

(15) W. L. Hill, H. L. Marshall, and K. D. Jacob, "Minor Metallic Constituents of Phosphate Rock," *Ind. Eng. Chem., Ind. Ed.* 24, 1306 (1932).

(16) A. E. Sobel, M. Rochenmacher, and B. Kramer, "Microestimation of the Inorganic Constituents of Bone," *J. Biol. Chem.* 152, 255 (1944).

(17) M. L. LeFevre and H. C. Hodge, "Changes in the Composition of Teeth Due to Physiological Stimuli," *J. Dental Research* 16, 279 (1937).

of the trace elements. Consequently it was necessary to prepare standards in a matrix material of composition similar to that of the analyzed sample and free of these trace elements. The accuracy of the method is obviously dependent on the purity of the matrix.

A base material, free of spectroscopic traces of other elements and containing 30% calcium, 20% phosphorus, 1% sodium, and 1% magnesium, was prepared from spectroscopically tested reagents. Calcium metal, which was spectrographically pure except for 10 ppm of manganese, was dissolved in distilled water in a platinum dish. Phosphoric acid was added, and the precipitate was dissolved in nitric acid. To the clear solution calculated amounts of sodium acetate and magnesium carbonate were added. Ammonia gas was bubbled through the solution until the first precipitate appeared. The mixture was then digested at room temperature for 2 hr, and the mother liquor was decanted. Precipitation was completed by adding ammonia to the clear liquor to *p*H 6, and the precipitate was filtered and ignited at 500°C in a muffle furnace. It was expected that the first fractional precipitate would gather the trace impurities, leaving the second fraction spectroscopically pure. Spectrographic analysis of the two fractions proved this supposition to be true. The second fraction was used as the matrix for the spectrographic standards. The analyses of the various bone samples were reported by the spectrographic laboratory of the Stable Isotopes Division.

It is planned in the future to make chemical determinations of sulfur in bone and teeth.

The problem of analysis of various body tissues has been reviewed. Such a program will involve the preparation of corresponding spectrographically pure base materials, preparation of samples for spectrographic analysis, and chemical determinations of elements for which spectrographic methods are not applicable.

Determination of Phosphorus and Halogen in Tricresyl Phosphate (J. C. White and C. K. Talbott). Some difficulty has been encountered in the determination of phosphorus and halogen (present as an impurity) in tricresyl phosphate. Phosphorus test results were very erratic, and precision was rather poor for the halogen determination. The method employed was the combustion of the sample in a Parr bomb, determination of the phosphorus by the alkalimetric method (after a phosphomolybdate precipitation), and determination of the halogen volumetrically by the mercuric nitrate method.

A number of methods requiring solution of the sample were studied, including digestion with hydrogen peroxide (30%) and sulfuric acid, sulfuric and nitric acids, and extraction with sodium hydroxide. In each case in which an acid digesting reagent was used, the sample was taken into solution. A halogen determination on the same sample was impossible, however, because of the loss of halogen by evolution during digestion. Digestion with base saponified the phosphate ester with the result that cresol separated upon acidification. Extraction of the phosphate salt from the cresol salt with base was unsuccessful. These results indicate that, of the methods tried, a Parr bomb fusion is the best for taking the sample into solution.

By limiting the size of sample to approximately 50 mg, fusions were complete in 1 min. The phosphate in the resulting solution was precipitated as the phosphomolybdate, ignited to $P_2O_5 \cdot 24MoO_3$, and weighed. Satisfactory test results for phosphorus were obtained by this procedure. Typical results were 7.96, 7.96; 8.04, 7.89; and 8.10, 7.55%; the theoretical value was 8.0%. The total time per determination compared very favorably with that for the alkalimetric method, and elimination of the undesirable titration step and its significant error was possible.

When care was taken to reduce the bromate formed during combustion, no difficulty was encountered in the determination of bromine. Hydrazine sulfate, which introduces no extraneous ions, was used for this purpose.

No reduction was necessary when the halogen was chlorine, since chlorate is not formed under these conditions.

Determination of Hydrogen in Carbate (O. Menis and C. K. Talbott). In connection with bombardment experiments at X-10, a small block of bonded graphite (Carbate) was submitted for the determination of hydrogen. It was the object of the analysis to establish whether or not a change in hydrogen content had occurred in the bombarded portion of a sample of Carbate as a consequence of bombardment with electrons. It was assumed, in the absence of other information, that the differences in hydrogen content might be very small and that a larger than ordinary number of determinations, along with the highest possible precision, might be required. These considerations, together with the limited quantity of sample available, dictated that a micro method should be employed.

A micro combustion train was assembled as described in Niederl and Niederl,[18] and ordinary micro combustion techniques were used to perform the analysis. A so-called "simple" filling was used in the combustion tube. Apparatus and procedure were tested by analyzing a Bureau of Standards sample of benzoic acid. A blank determination was made at the beginning of each day.

Samples were prepared by carefully scraping the bombarded and unbombarded portions of the Carbate block with a razor blade. About 60 to 70% of the bombarded material was removed, as judged by the line of demarcation between the two portions. The scrapings were ground in an agate mortar and dried under vacuum over P_2O_5 for 24 to 48 hr.

In order to establish the technique and to ascertain the fact that the equipment was functioning properly on the Carbate material, five successive determinations were first made on the unbombarded portion, after which alternate determinations were made on the bombarded and unbombarded portions. The test results are given in Table 30.

TABLE 30

Determination of Hydrogen in Carbate

HYDROGEN (%)	
UNBOMBARDED PORTION	BOMBARDED PORTION
0.92	0.56
0.78	0.52
0.75	0.57
0.89	0.51
0.73	0.51
0.73	
0.81	
0.83	
0.68	
0.87	
0.72	
0.79 (avg.)	0.53 (avg.)

A statistical evaluation of the data indicates that the probability of the observed difference being due solely to random sample variations is less than 1 part in 10,000. It can therefore be concluded that the difference is real and that the bombardment has effected a decrease in hydrogen content.

(18) J. B. Niederl and V. Niederl, *Micromethods of Quantitative Organic Analysis*, Wiley, New York, 1942.

ORGANIC SYNTHESES

W. K. Miller

In connection with investigations of molecular rotational spectra, the following list of compounds was submitted by the Stable Isotopes Division with the request that they be either prepared or obtained commercially:

Iodoacetylene, $H-C\equiv C-I$

1-Chloropropyne, $CH_3-C\equiv C-Cl$

1-Cyanopropyne, $CH_3-C\equiv C-CN$

Vinyl iodide, $CH_2=CH-I$

Vinyl fluoride, $CH_2=CH-F$

The compounds are listed in the order of importance to the present project. Through correspondence with Armour Research Foundation it was learned that vinyl iodide and vinyl fluoride can be obtained commercially, but that the haloacetylenic compounds are explosive and sensitive to shock. Because of the hazards involved in shipping such materials, it would be necessary to prepare these compounds near the location where they are to be used.

A literature search revealed no previous work on 1-cyanopropyne and only one preparation of 1-chloropropyne, the latter having been obtained as an impure product in low yield. Since these two compounds are of secondary importance, it was decided to concentrate on the preparation of iodoacetylene.

Grignard and Tchéoufaki[19] reported a small yield of iodoacetylene along with a good yield of monoiododiacetylene by reacting the acetylenic Grignard reagent with iodine. No other preparations of iodoacetylene were reported in the literature, although the corresponding chloro and bromo derivatives, as well as diiodoacetylene, are well known. The latter compound is obtained along with acetylene when diiodoethylene is treated with alcoholic potassium hydroxide,[20] although monoiodoacetylene would be expected. This suggests

(19) V. Grignard and Tchéoufaki, "Sur les hydrocarbures α-diacétyléniques," *Compt. rend.* 188, 357 (1929).

(20) *Beilsteins Handbuch der organischen Chemie*, Band I, p. 194, Julius Springer, Berlin, 1918.

that iodoacetylene is unstable and that it disproportionates according to the equation:

$$2I{-}C{\equiv}C{-}H \longrightarrow I{-}C{\equiv}C{-}I + H{-}C{\equiv}C{-}H$$

In spite of this evidence, it was decided to attempt the preparation reported by Grignard and Tchéoufaki.

In order to obtain the acetylenic Grignard reagent, Br-Mg-C≡C-Mg-Br, the starting product in the reaction of Grignard and Tchéoufaki, ethyl magnesium bromide, was first prepared by the usual procedure. This was then converted to the acetylenic Grignard reagent by passing acetylene through the reaction mixture.

Ethyl ether is normally used as a solvent for the preparation of Grignard reagents. Di-*n*-butyl ether, however, was used as the solvent in the first attempt to prepare ethyl magnesium bromide, since the boiling point of the desired product is reported to be 32°C,[19] almost identical with that of ethyl ether. However, little or no reaction of ethyl bromide with magnesium was obtained in the butyl ether medium, and a second preparation was made in which ethyl ether was used as the solvent. The ethyl ether was later replaced by butyl ether.

The procedure was as follows: A 1-liter three-neck flask was fitted with a mercury stirrer, separatory funnel, reflux condenser, inlet tube for passing in acetylene, and outlet tube for distilling off the product. Six grams of magnesium turnings was placed in the flask, nitrogen was passed through the top of the reflux condenser, and the flask was heated with a flame to ensure dryness. When the flask had been cooled, 160 ml of anhydrous ethyl ether was added, followed by the slow addition of 19 ml of ethyl bromide in 100 ml of ether. The reaction was carried out under an atmosphere of nitrogen and the reaction vessel was cooled. When the reaction was complete, 260 ml of butyl ether was added, and the ethyl ether was distilled off in a stream of nitrogen. Acetylene was then passed through the solution until the reaction was complete, and 32 g of iodine in 200 ml of butyl ether was added dropwise. The resulting solution was hydrolyzed by the slow addition of ammonium chloride solution. The solution was then heated to 50°C on a water bath, and the distillate was collected in two U tubes in acetone—dry ice baths. The entire process was carried out in a nitrogen atmosphere.

The small amount of product obtained under these conditions was dried and submitted to the Physics Group of the Stable Isotopes Division so that a measurement of its microwave rotational absorption spectrum could be made. We have been advised that no spectrum of the product was found in the region which was calculated for iodoacetylene.

The remainder of the solution from the Grignard reaction will be worked over for monoiododiacetylene, but this product is not so desirable as monoiodoacetylene, since a study of its microwave absorption spectrum would yield only limited information on the structure of the molecule. It is not at present contemplated that a second attempt will be made to prepare the compound.

9. SERVICE ANALYSES

IONIC ANALYSES

J. W. Robinson

The work of the Ionic Analyses Group for this period is summarized in Tables 31, 32, and 33. The number of determinations made during this quarter exceeds by a substantial margin that of the preceding quarter. This increase is attributable principally to a rise in the number of uranium determinations.

Approximately 75% of the analyses were carried out for the Raw Materials Project, the remaining 25% for other groups on the area. The more important divisions of the analytical work are discussed briefly under their separate headings.

TABLE 31

Operational Summary

PERIOD	NO. OF SAMPLES RECEIVED	NO. OF SAMPLES REPORTED	BACKLOG	NO. OF DETERMINATIONS	AVG. NO. OF PERSONS
September, October, November	2169	2109	326	5800	15
December, January, February	2102	2029	399	7550	13

Raw Materials (E. C. Lynn and A. F. Roemer). Analyses of approximately 1500 samples were reported this quarter. Analyses of residues and leach solutions (Table 32) comprised the largest part of the work. In addition to making determinations for the commonly sought elements, i.e., uranium, vanadium, iron, and aluminum, complete analyses were made on numerous leach solutions and leached residues. Generally, when complete analyses were made, constituents

occurring in concentrations of 0.1% or greater were determined by gravimetric, colorimetric, and other methods, whereas a spectrographic examination was made for the purpose of estimating the constituents occurring in smaller amounts.

TABLE 32

Sample Types and Components Determined

TYPE OF MATERIAL	NO. OF SAMPLES REPORTED		PRINCIPAL DETERMINATIONS
Synthetic uranium solutions (eluates and related solutions)		330	U, Fe, V, Cl, SO_4, PO_4, F, CH_3COO
Uranium carbonate solutions		294	U, Na, CO_3, F
Leach solutions from:			
Carnotite ore	172		U, V, major constituents
Phosphate ore	268		U, PO_4, major constituents
Marysvale ore	169		U, Fe, major constituents
		609	
Ores and residues from:			
Phosphate ore	56		U, major constituents
Carnotite ore	63		U, V, major constituents
Marysvale ore	38		U, major constituents
		157	
Quality control samples		90	U, Na, CO_3
Transformer oil		72	Dielectric strength, acid number, H_2O
Alkali fusions of oxides and salts		70	U, Be, K, Na, F, CO_3
Sodium metal		65	O, spectrographic analysis
Miscellaneous uranium mixtures		60	U, others
Phthalate solutions and residues		43	Phthalate ion, C, H
Corrosion solutions		37	Si, Fe, Al, Ni, Cr, Ca, Mg, Li
Lithium materials		20	Li, K, O, N, spectrographic analysis
Alloys		15	Si, P, S, Cr, Ni, Mn, Fe, Nb, Mo
Gases		15	CO_2, CO, H
Zirconium materials		15	Zr, O, H, C, N
Standard solutions		15	Standardization
Miscellaneous		122	
Total no. of samples reported		2029	

The synthetic uranium solutions which originated from the experimental work with extraction columns constitute the second major group of samples that were analyzed for the Raw Materials Project. With some of the synthetic solutions, as well as in several of the leach solutions from ores, it was found that unduly high results were obtained for uranium when the ascorbic acid—colorimetric method was used. A preliminary investigation indicated that

such high results are probably attributable to the presence of organic material, since it was found that oxidation of the sample with perchloric acid prior to the ether extraction eliminated the interference. It has been observed that such organic material may occur in the ore as humus. An investigation is continuing to further elucidate the effect of organic material on the accuracy of this determination.

The third large group of samples is that derived from phase studies of uranium carbonate complexes. Analyses of materials from this source have proceeded satisfactorily; no difficulties requiring drastic modifications of methods have been encountered.

TABLE 33

Classification of Determinations by Components

DETERMINATION	NO. OF DETERMINATIONS
U	4580
V	530
Fe	200
Al	100
Cr	130
Na	340
Mg	70
F	90
SO_4	90
PO_4	230
CO_3	170
SiO_2	70
Water	110
Dielectric strength	80
Neutralization number	80
Others	680
Total	7550

Analyses for the Liquid Metals Chemistry Section (E. C. Lynn and J. H. Hackney). By far the greater number of samples that were analyzed consisted of mixtures and fusion products containing salts and oxides of sodium, potassium, uranium, and beryllium. In addition, compounds of uranium and beryllium were analyzed.

Potentiometric, gravimetric, and colorimetric methods were used for the determination of uranium. The choice of method was governed by the range of uranium concentration and by the accuracy required.

In mixtures and fusion products beryllium was determined as follows: The total oxides (BeO plus U_3O_8) were determined as well as the uranium. The difference between total oxides and uranium (calculated as U_3O_8) was assumed to be BeO, from which the beryllium content was calculated. Obviously, when the U/Be ratio is high, the accuracy of the beryllium determination will be of a low order. To improve this accuracy, it is planned to separate the uranium and beryllium by one of the following methods: (1) beryllium carbonate precipitation, (2) diethyl ether extraction of the uranium, or (3) peroxide precipitation of the uranium.

Fluorides were separated from interfering elements by the Willard and Winter distillation method,[1] or by the pyrohydrolysis method.[2] The fluoride was precipitated from the condensate as PbClF, the chloride was determined volumetrically, and the fluoride was calculated from the F/Cl ratio. As was noted in a preceding section of this report (p. 94), it was found that the usual Willard and Winter distillation procedure for the separation of fluorides, when applied to beryllium fluoride, yielded low results unless an exceedingly long distillation period was used. Even then the results were erratic. The pyrohydrolytic procedure, whereby beryllium fluoride is hydrolyzed at 1000°C by superheated steam and the resulting hydrogen fluoride is collected for analysis, was found to yield quite satisfactory results in much less time.

Two points of further interest were observed in connection with the pyrohydrolytic method: (1) a single furnace, 8 in. in length, would not suffice to superheat the steam and the sample; rather, it was necessary to

(1) H. H. Willard and O. B. Winter, "Volumetric Method for Determination of Fluorine," *Ind. Eng. Chem., Anal. Ed.* 5, 7 (1933).

(2) J. C. Warf and W. D. Cline, *Pyrohydrolysis in the Analysis of Fluorides and Other Halides*, Report CC-2723 (June 30, 1945).

superheat the steam by passing it through a separate furnace of similar design; and (2) the oxide resulting from such pyrohydrolytic separation could not be used for beryllium determination since milligram quantities of beryllium are generally found in the distillate.

Cooperative Analysis of Zirconium Samples (E. C. Lynn, A. F. Roemer, Jr., S. R. Buxton, and J. M. Rogers). This laboratory, together with several other cooperating laboratories, is carrying out extensive analytical work on zirconium, zirconium hydride, and zirconium-uranium alloys. The purpose of this cooperative effort, which is being coordinated by E. B. Read, of the Massachusetts Institute of Technology Metallurgical Project, is to develop a supply of standard samples of zirconium and zirconium compounds and alloys of known purity and to evaluate different methods of analysis. Components determined by methods other than spectrographic, together with the methods used for the determinations, are as follows:

COMPONENTS	METHODS OF ANALYSIS
Si, Fe, Cr, Ni, Mn, Pb, Cu, U	Colorimetric
Na, Ti, K, Ca	Flame photometric
N	Micro-Kjeldahl
U	Potentiometric titration
C, H	Combustion

ANALYTICAL SERVICES FOR NEPA AND ANP

L. J. Brady

Spectrographic Analyses (J. M. Peele and John A. Norris*). *Sodium Metal.* Corrosion studies with sodium metal served as the source of most of the samples analyzed for the NEPA plant during this period. Approximately 70% of all samples submitted for analysis were derived from this source.

The methods employed for determining the concentration of minor impurities have been outlined in previous progress reports (see p. 3 for numbers) and were applied without significant change during this period. A somewhat wider variety of determinations was requested during this quarter, and spectrographic standards containing such elements as lead, copper, cobalt, and uranium were required more frequently than in the past.

*Isotope Analysis Methods Laboratory.

One problem which presented itself during the analysis of a series of sodium samples was a marked reduction in the intensity of the platinum reference line. An investigation of this difficulty revealed that the concentration of sulfuric acid in the samples which gave trouble was higher than that found in samples which did not show this effect. When the amount of sulfuric acid was adjusted to fall within a range of 15 to 20%, the solution flowed through the electrode at a normal rate and no further difficulty was encountered.

A series of preliminary tests was conducted in which elements other than platinum were employed as an internal standard. Vanadium, which is more closely related to the elements being determined, appears to offer some advantages over platinum as a standard. Accordingly, further tests will be made with standards containing known quantities of this metal.

Sodium Hydroxide. Spectrographic examination of a series of samples of sodium hydroxide for nickel revealed that this element was absent, or essentially so. More recent examination of two series of samples of this compound have been made, and the concentrations of some of the impurities were found to be in excess of those of the spectrographic standards. Consequently, these elements were determined by chemical methods.

Bismuth Samples. Nine bismuth samples were analyzed during the period. In general, these samples were relatively highly contaminated and required some dilution in order to bring the concentration of the impurities into the range of the spectrographic standards. These samples were analyzed without separating the bismuth from the impurities.

Metals, Alloys, and Miscellaneous Samples. In addition to the analyses by the porous cup technique, spectrographic methods were also employed in classifying a number of alloys, and specification tests were made on samples of relatively pure materials such as graphite.

Semiquantitative spectrographic tests of a number of materials of unknown composition, which can be made in a relatively short time, continue to prove most helpful in eliminating the necessity for making time-consuming preliminary chemical tests before carrying out quantitative chemical analyses of these materials.

Chemical Analyses (L. H. Jenkins). *Oxygen Content of Sodium.* Although efforts of the Development Group are being directed toward developing a more adequate method for the determination of the oxide content of sodium metal (see p. 80), the method developed by Pepkowitz and Judd[3] has continued to be applied in determining the concentration of this component in samples of sodium submitted during this quarter. In addition to the regular samples of sodium which were analyzed, a number of comparative tests were made on "standard" samples which were also analyzed in the laboratory at NEPA and at the University of Chattanooga. Samples of sodium were also analyzed in order to compare the results obtained by this method with those found by proposed methods involving the reaction of the sodium with *n*-butyl bromide. This program of comparative tests will be extended in the future.

Metals and Alloys. Approximately forty samples of metals and alloys were analyzed during the period. These samples were of various types, including samples of the more common stainless steels and other ferrous alloys, brasses, nickel and nickel alloys, copper alloys, and alloys of manganese and copper. Information concerning the concentration of a few of the major components for the purpose of classifying metals as to type was requested for a number of the samples, especially the ferrous alloys. Rather complete analyses were required for other samples. The results of preliminary spectrographic analyses of a semiquantitative nature were employed in outlining a procedure for making these determinations and in ascertaining which elements were present in the sample in sufficient quantity to be determined by chemical methods. In general, chemical methods were employed where maximum accuracy in estimating the concentration of the major components of the alloy was required.

Uranium Compounds. Samples of uranium oxides, fluorides, and carbides were analyzed during this period. The concentration of uranium in these samples was sufficiently high to permit the use of gravimetric or volumetric methods.

Since the carbide of uranium is pyrophoric, special precautions were taken to minimize the possibility of oxidation of the material prior to analysis. This material does not readily dissolve in acids, and a carbon residue remains after repeated treatments of the sample with nitric acid and

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

evaporation to fumes with sulfuric acid. This residue was filtered from the solution, ignited, fused with potassium bisulfate, dissolved in dilute acid, and added to the original filtrate. It then became necessary to remove silicon dioxide from the solution prior to the estimation of uranium gravimetrically, or to remove all the nitrate ions if volumetric methods were to be employed.

The fluoride samples consisted of mixtures of uranium fluoride with sodium fluoride. Sodium was determined flame-photometrically, uranium by potentiometric titration with ferric sulfate, and the fluoride by fusion of the sample with sodium carbonate, separation of the fluoride by distillation, and determination of this ion by the lead chlorofluoride method.

Miscellaneous Samples. A wide variety of miscellaneous samples was analyzed. The quantity of some of these samples available for analysis was small and semimicro methods were required. One sample of thallium carbonate is an example of this type; about 200 mg of this sample was submitted for analysis with the information that no more of the material from the batch was available. Semimicro equipment was constructed, and the carbonate concentration was determined by treating the sample with acid and collecting and weighing the released carbon dioxide. Turbidimetric methods were employed to determine the sulfate ion concentration, and a semiquantitative spectrographic determination of the minor constituents, which required only a few milligrams of sample, was then made. The results of these tests indicated the presence of one or more anions other than the carbonate and sulfate. An X-ray diffraction pattern of the material revealed the presence of an oxide of thallium. By correlating the information thus obtained, it was possible to get a rather complete picture of the composition of the material even when the amount of sample available was limited.

The past experience of the Spectrographic Group in the estimation of hafnium in the presence of zirconium proved an asset in the determination of the ratio of hafnium to zirconium in a series of samples of zirconium salts.

Other determinations on miscellaneous samples included determination of the sodium peroxide content of a sample of sodium oxide; determination of traces of nitrogen in a rather pure titanium oxide sample; determination of tungsten, boron, and carbon in tungsten carbide; determination of the concentration of hydrogen, nitrogen, and titanium in titanium hydride; determination of hydrogen in a fused melt of lithium hydride and lithium and beryllium

fluorides; determination of water in barium hydroxide; and determination of traces of copper in magnesium perchlorate. This list, although not complete, indicates the diversity of the samples included in this category, and gives some indication of the variety of methods which must be employed to obtain the information desired.

Summary of Analytical Work for NEPA. A summary of the analytical work performed during this period for the NEPA plant is tabulated below.

	NO. OF SAMPLES
Backlog of samples, 12-1-50	79
Samples received, 12-1-50 to 2-28-51, inclusive	234
Total	313
Samples reported, 12-1-50 to 2-28-51, inclusive	234
Backlog as of 3-1-51	79

A total of 1695 determinations were made during the period. This number includes 1250 spectrographic and 445 chemical determinations.

10. QUALITY CONTROL

R. L. McCutchen

During this quarter, the following new quality control programs have been initiated:

1. Uranium by the colorimetric method (X-10 laboratories).
2. Uranium by the fluorometric method (X-10 laboratories).
3. Uranium in Marysvale raw ores.
4. Uranium in leached residues of Marysvale ores.
5. Uranium in carnotite raw ores.
6. Uranium in leached residues of carnotite ores.
7. Uranium in second acid leaches of carnotite ores.

A vanadium standard solution for the control of the colorimetric method of determining vanadium, along with a Marysvale leach and carnotite first-leach solutions, is now being prepared. The solutions will become part of the control program during the next quarter.

Since January 1, 1951 a total of 559 control samples have been analyzed. The types of analyses and the laboratory in which the samples were tested are given in Table 34.

TABLE 34

Quality Control Samples Analyzed in 1951

LABORATORY	MATERIAL	DETERMINATION	METHOD	NO. OF DETERMINATIONS	TOTAL
Y-12, analytical	Synthetic	Sodium	Flame photometer	19	
	Synthetic	Carbonate	Gas evolution	10	
	Synthetic	Uranium	Fluorometric	46	
	Synthetic	Uranium	Colorimetric	31	
	Snythetic	Uranium	Potentiometric	24	
	Leach solutions	Uranium	Fluorometric	10	
	Raw ores	Uranium	Fluorometric	5	
	Residues	Uranium	Fluorometric	7	152
X-10, analytical	Synthetic	Uranium	Fluorometric	142	
	Synthetic	Uranium	Colorimetric	169	311
Y-12, physics, spectrographic	Synthetic	Iron	Spectrographic*	24	
	Synthetic	Manganese	Spectrographic*	24	
	Synthetic	Chromium	Spectrographic*	24	
	Synthetic	Nickel	Spectrographic*	24	96
					559

*Porous cup technique.

The emphasis during this period has been on the determination of uranium by the fluorescence, the *l*-ascorbic acid and thiocyanate colorimetric, and the potentiometric titration methods of analysis. During this period the test results for each method were found, at times, to be "out of control." It was possible to apply corrective measures in each case to bring the test results back within the control limits.

During the periods in which the fluoresence test results were out of control, a persistent trend toward low results was noted. An investigation indicated that the following factors were affecting the results:

1. Inexperienced operators, or change of operators.
2. A loose light housing on the fluorometer.
3. Segregation or other variations in significant properties of the flux material used with the method.

The first two sources of error have been corrected, and the necessary steps are being taken to control the variation due to the flux.

The precision of the fluoresence test results was found to be about the same for the X-10 and Y-12 laboratories. A similar comparison of the X-10 and Y-12 colorimetric test results, however, indicates that the precision obtained by the X-10 laboratories is superior. The X-10 laboratories are using the ammonium thiocyanate colorimetric method[1] which, in contrast to the method used at Y-12, does not require either an ammonium hydroxide precipitation or an ether extraction purification process prior to the development of the color. The *l*-ascorbic acid colorimetric method now in use at the Y-12 laboratories is sensitive to small amounts of impurities, and this necessitates a rather complete separation of the uranium before the addition of the chromogenic reagent. The types of samples being processed by the two laboratories, however, differ so much that a comparison of the two colorimetric methods may not be justified.

A Recordomatic titrator (Precision-Dow) is now in operation in the laboratory for the determination of uranium by potentiometric titration with ferrous sulfate. The limited data available at this time indicate that the precision of the test results for control samples is not so good as previously

(1) J. E. Currah and F. E. Beamish, "Colorimetric Determination of Uranium with Thiocyanate," *Anal. Chem.* 19, 609 (1947).

obtained by the manually operated titrator. It is anticipated, however, that the precision will improve as more experience is gained and optimum conditions of operation are more closely approached.

With reference to the spectrographic control program, a study to determine the effect of the internal standard on the precision of the test results has been completed. Four elements — iron, nickel, chromium, and manganese — were each determined at three concentrations, using platinum as an internal standard. The second half of this program will consist in analyzing the same control solutions, using vanadium as the internal standard. It is believed that the precision of spectrographic test results by the porous cup method can be improved considerably when vanadium is used as the internal standard.