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ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director
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for Period Ending January 10, 1951

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ANALYTICAL CHEMISTRY DIVISION — X-10 SITE

Ionic Analyses — Research and Development. The applicability of an automatic titration method for determination of iodides and chlorides in the presence of their oxyhalide salts was investigated. Automatic titration was found to permit fairly accurate determination of iodide, bromide, and chloride in a mixture of the three which is approximately 0.002 *M* in each. A brief description of the newly designed ORNL automatic titrator (Model #Q-945, Series #1) is included.

A polarographic method for the determination of U(IV) and U(VI) in the presence of large concentrations of copper and hydrogen fluoride has been developed. The U(IV) was separated by the lanthanum fluoride carrier method and determined polarographically. The separation of copper and fluoride from the U(VI) were effected, respectively, by electrolytic deposition and by fuming with perchloric or sulfuric acid; the U(VI) was then determined polarographically.

Radiochemical Analyses — Research and Development. The Cd ratios of Ag^{110} and Mn^{56} have been determined and used to estimate the importance of resonance capture in the capture process $Ag^{109}(n,\gamma)Ag^{110}$. Methods of calibration of end-window counters for assay of low-energy beta emitters are described.

The procedure for determining lithium and for determining the isotopic composition of lithium samples by activation analysis has been developed to the point of adaptability for routine use. The activity of the ORNL pile unit for Cu^{64} has been verified. Procedures for assay and purity estimation of Ca^{45} products are given. A study of the self-absorption of Ca^{45} oxalate precipitates has been made.

A method for the assay of Tl^{204} is given. A procedure for the determination of Mn^{52} and Mn^{56} is included. A solvent extraction procedure for polonium analysis has been tested. A scheme for identification of nuclides is given.

A method for the determination of Cs^{137} in waste solutions is proposed. The extraction of various radioactive elements with *n*-tributyl phosphate is being studied. The determination of zirconium-hafnium ratios with *p*-bromomandelic acid is being investigated.

The agreement between X-10 and K-25 groups in the determination of uranium and beta and gamma radiations from samples of recovered uranium has been

checked. The self-absorption of the weak gamma component in concentrated uranium solutions has been studied and found to be of importance.

Spectrochemical Analyses — Research and Development. A list of the spectrochemical methods which were developed this quarter for performing analyses by the porous cup technique is included.

Service Analyses. During this quarter 36,717 analyses have been completed.

Inorganic Preparations. The preparation of compounds for the Thorium Breeder Salts Program has been started. Cobaltous fluosilicate has been prepared and a fairly large but irregular crystal has been grown. A method for the preparation of calcium fluosilicate is described.

Analytical Chemical Control of Homogeneous Reactor Solution. A summary of the progress on the analytical chemical control of the reactor solution is given.

Optical and Electron Microscopy. An investigation has been made of the micro characteristics of multilayer films found on pretreated stainless steel samples before and after immersion in 0.17 *M* uranyl sulfate solution containing 0.1 *M* nitric acid at 250°C. Distinct differences in the surface characteristics of the formed films were found and the nature of the differences was studied.

ANALYTICAL CHEMISTRY DIVISION — Y-12 SITE

Ionic Analyses — Research and Development. The Pepkowitz and Judd method for the determination of oxygen in sodium is under investigation. Consideration is being given to improvement of the accuracy and precision of the method and to possible substitutes for the mercury used in the Pepkowitz and Judd apparatus. A microanalytical procedure for the determination of silicon carbide is proposed. A colorimetric method for turpentine assay is being considered.

A method based on ultraviolet absorption has been investigated for ammonium phthalate determination in recycle liquors. A method has been devised for determining excess ammonium hydroxide in ammonium phthalate solutions.

An investigation of the stability of Dow Corning Silicone Oil (DC 550) in the presence of sodium at elevated temperatures indicates that the oil is stable in the presence of sodium at 400 to 700°F for short periods and therefore can be safely employed as a pressure-transmitting agent.

Service Analyses. During this quarter 7,446 analyses have been completed.

PROJECT LITERATURE AND PUBLICATIONS

October, 1950 — December, 1950

Y-B31-213	*Analysis of Zirconium Hydride*, by C. D. Susano (Nov. 15, 1950).
Y-B31-217	*Corrosion Resistance of Zirconium Metal and Stainless Steels on Exposure to Concentrated Solutions of Uranyl Fluoride*, by C. D. Susano (Nov. 30, 1950).
ORNL-841	*Tantalum Phosphate — A New Compound*, by R. B. Hahn (Dec. 13, 1950).
ORNL-816	*A Preliminary Survey of Radioactive Constituents in Rainwater at ORNL*, by W. A. Brooksbank, S. A. Reynolds, A. H. Emmons, and J. W. Gost (Dec. 4, 1950).

ANALYTICAL CHEMISTRY DIVISION — X-10 SITE

1. IONIC ANALYSES — RESEARCH AND DEVELOPMENT

AUTOMATIC POTENTIOMETRIC TITRATION OF HALIDES

P. F. Thomason

An automatic titration method for the determination of bromide in sodium bromate has been reported.(1) The applicability of this method to the determination of iodides and chlorides in the presence of their oxyhalide salts was investigated this quarter.

For this investigation, the automatic titration apparatus previously described(2) was used. A silver wire which had been cleaned with emery cloth and then HNO_3(3) was used as the indicating electrode. A saturated calomel electrode connected with a KNO_3-agar bridge served as the reference electrode.

A 0.01 *M* solution of purified KI was prepared and microliter aliquots were titrated with 0.01 *M* $AgNO_3$ at room temperature. Excellent breaks in the curves of the order of 400 millivolts were obtained and several 100-λ aliquots of the 0.01 *M* KI solution were titrated with a precision of ±2%.

One-gram samples of reagent grade KIO_3 were dissolved in 10 ml of distilled water by warming, cooled to room temperature, and titrated. Ten micrograms of iodide per gram of KIO_3 was found. One-gram samples of KIO_3 were then spiked with 100 λ of 0.01 *M* KI and titrated. The spike of 127 γ of iodide plus the 10 γ of iodide originally present in the KIO_3 were recovered. Figure 1 shows the typical titration curves that were obtained.

It is to be noted that in the titration of the iodide in the presence of the oxyiodide salt, the break in potential is never as great as when the iodide is titrated alone. This is probably due to the fact that there is less difference between the solubilities of the silver iodate salt and the silver iodide that is formed under the experimental conditions than there is between the solubilities of silver iodate and silver iodide in distilled water.

Sodium chloride solutions were titrated in the presence of $KClO_3$ in the same manner. However, in this case, the solutions were made acidic with

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(1) Thomason, P. F., "Determination of Bromide and Bromine in Sodium Bromate," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-788, p. 11 (Oct. 4, 1950).

(2) Miller, F. J., "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).

(3) Clark, W., "The Electrometric Titration of Halides," *J. Chem. Soc. London*, 1926, 749.

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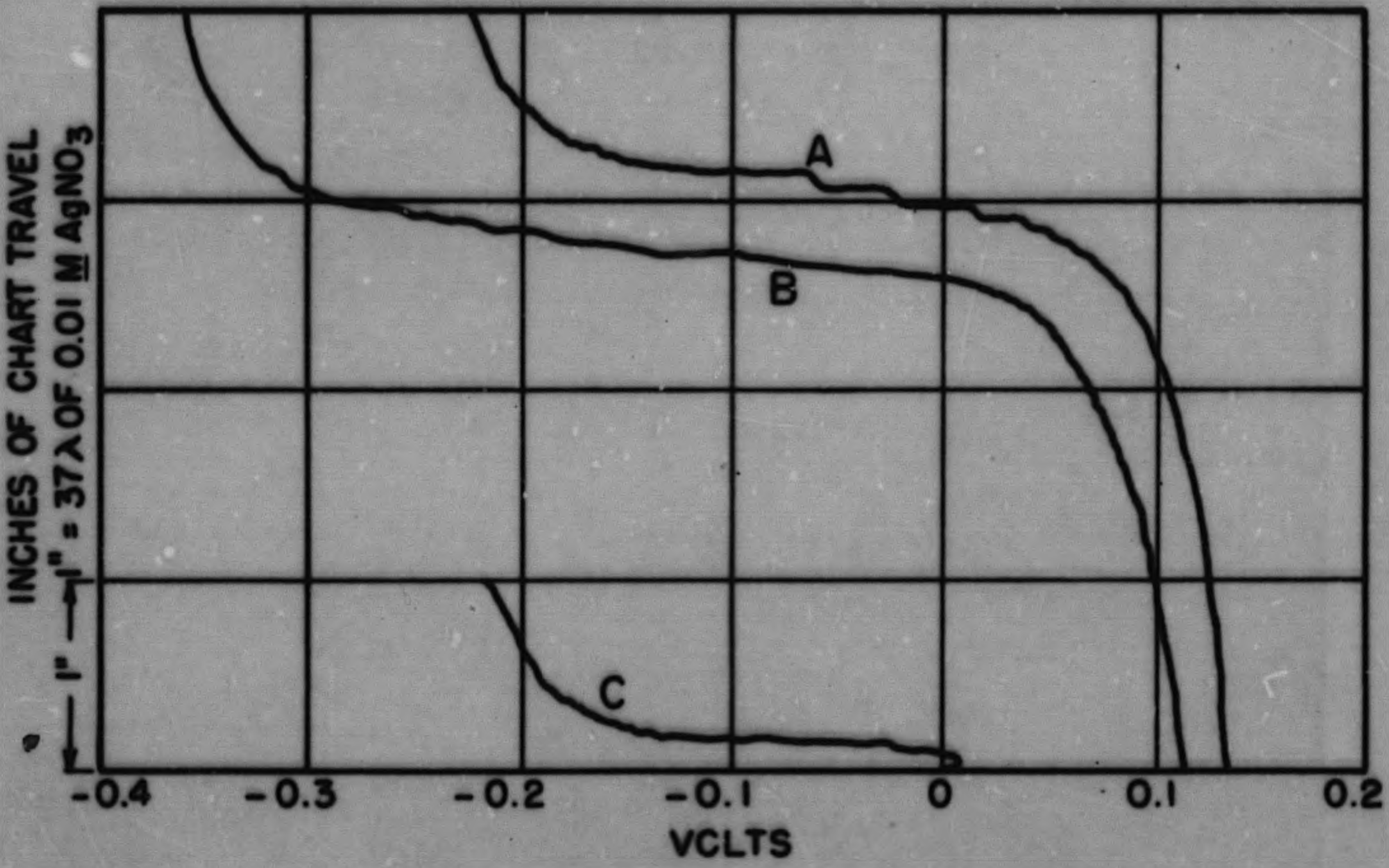

A - 1 g. OF KIO_3 + 127 γ I^- SPIKE
B - 127 γ OF IODINE AS KI
C - 1 g. OF KIO_3

FIG. 1
TITRATION OF IODIDE IN POTASSIUM IODATE WITH 0.01 M $AgNO_3$

HNO_3. Samples were also titrated at 4°C with a dry ice—methanol bath. Since AgCl is more soluble than AgI, the break in potential was only about 50 millivolts and was not nearly so sharp as that obtained in the iodide titration. Twelve micrograms of chloride was found per gram of reagent grade $KClO_3$.

Several papers on the titration of the halides in the presence of each other with silver nitrate have been published. Behrend,(4) who first applied the silver electrode to the titration of the halides, was able to determine iodide in the presence of bromide but not bromide in the presence of chloride. Too much $AgNO_3$ was required before the bromide break in potential was reached. Kolthoff and Furman(5) attribute this to the adsorbent action of the silver halides which are formed during the titration of the halide ion. Several investigators tried various measures to correct this difficulty. Liebich(6) added 5% $Ba(NO_3)_2$. Pinkhof(7) used $(NH_4)_2CO_3$. These salts aided the titration by shortening the time required to establish the equilibrium potential close to the end-point but did not entirely eliminate the adsorbent effect.

Since the automatic titrator records the potential continuously during the titration, it was felt that it would have obvious advantages over manual methods in attempting to solve this problem. Also, microliter volumes of titrant could be used. Therefore a number of titrations of the halides in the presence of each other with silver nitrate were run under varying conditions.

It was found that on titrating mixtures of 200 λ of 0.01 *M* KI, 200 λ of 0.01 *M* KBr, and 200 λ of 0.01 *M* KCl diluted to 5 ml with 0.2 *N* HNO_3 at room temperature with 0.01 *M* $AgNO_3$, too much bromide (about 10%) was found and no break in potential was obtained for chloride. The iodide was only about 2% high. The addition of 5% $Ba(NO_3)_2$ slightly improved the values for both iodide and bromide, but again no break for chloride appeared.

When the temperature of the mixed halides was lowered to 4°C, a break in potential was obtained for chloride. However, the value for bromide was still about 8% high and the chloride correspondingly 8% low. It was thought that the

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(4) Behrend, R., "Elektrometrische Analyse," *Z. physik. Chem.* 11, 466 (1893).

(5) Kolthoff, I. M., and Furman, N. H., *Potentiometric Titrations*, p. 146, Wiley, New York, 1931.

(6) Liebich, C., *Die potentiometric Bestimmung von Chlor, Brom und Jod*, dissertation, Dresden, 1920.

(7) Pinkhof, *Over de toepassing der Elektrometrische Titraties*, dissertation, p. 17, Amsterdam, 1919.

addition of some organic solvent would permit lower temperatures for the titration and thus improve the breaks and perhaps differentiate the solubilities of the Ag halides. Several organic liquids miscible with water were tested. Ethanol, methanol, and dioxane gave some improvement. Twenty-five percent methanol mixtures of the halides permitted the titration to be carried out at -5°C, and the addition of $Ba(NO_3)_2$ to this solution did not further improve the titration.

A typical automatic titration curve of a mixture consisting of 200 λ of each of the 0.01 *M* halide solutions in 25% methanol at a temperature of -4°C is shown in Fig. 2. This shows that the bromide value is high at the expense of both iodide and chloride although only about 2.5% low in the case of iodide and about 4% low for the chloride. This titration was repeated many times with only slight variation in the results.

The tip of the buret was drawn to a fine capillary to lessen the diffusion of the titrant and this limited the delivery of titrant to a small volume per unit time. The speed of addition of the titrant had to be kept to about 50 λ per minute in order for the titrator to record the curve properly. This titration speed seems to allow sufficient time for the potential to reach equilibrium at the equivalence points. It was also found that the rate of stirring did not greatly influence the titration.

These results show that it is possible to obtain fairly accurate values by automatic titration for mixtures of halides in the vicinity of 0.002 mole of iodide, bromide, and chloride. However, the value for bromide seems to be inherently high, and some means must be found to eliminate the absorption error before precise results can be obtained.

MICRO AUTOMATIC TITRATIONS

F. J. Miller

Work has been continued on the automatic titration of uranium and plutonium in concentrations usually of the order of 100 to 200 γ in 0.2- to 0.5-ml volumes.

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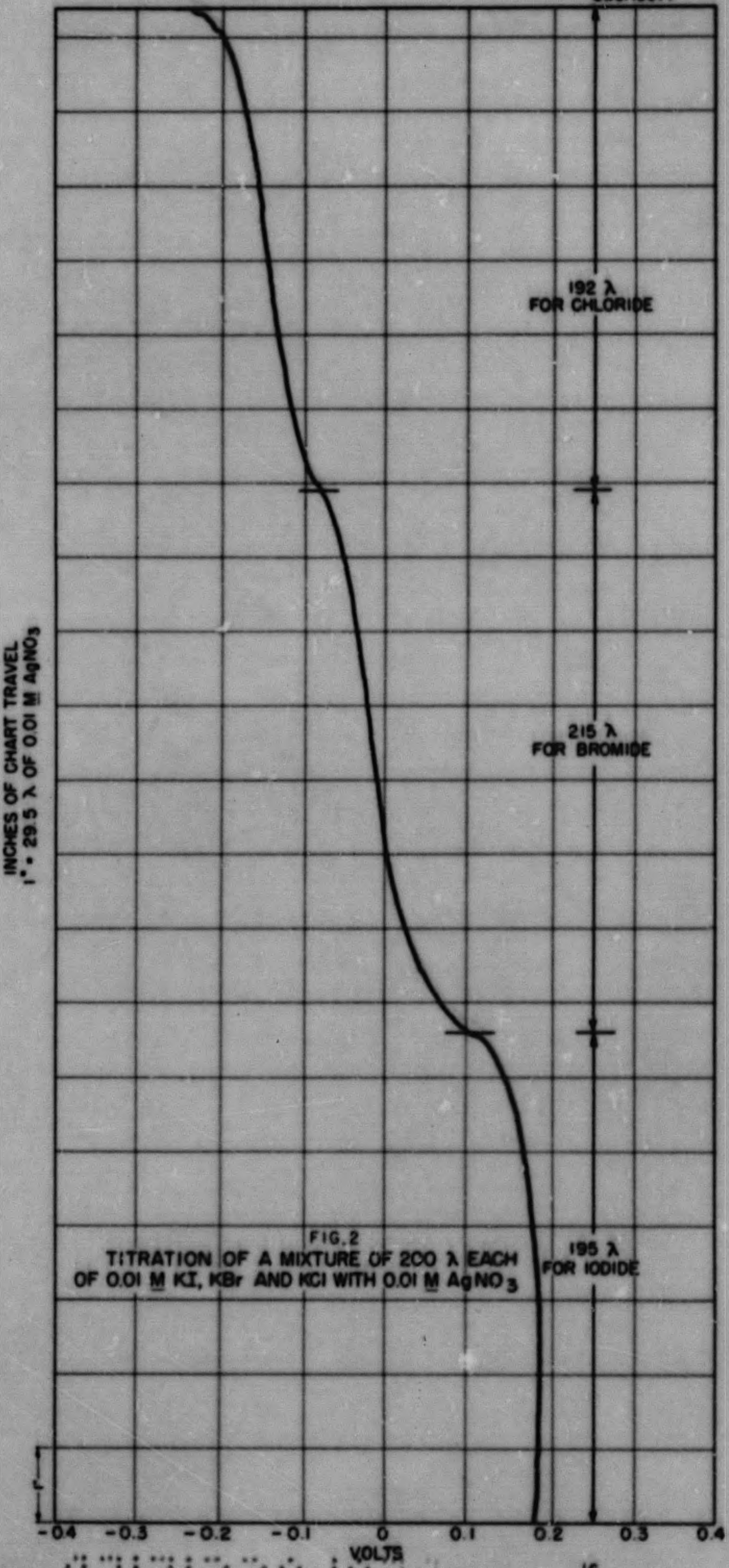

FIG. 2
TITRATION OF A MIXTURE OF 200 λ EACH OF 0.01 M KI, KBr AND KCl WITH 0.01 M AgNO$_3$

This work has been performed using the Oak Ridge National Laboratory model recording titrator, known as "Automatic Titrator, Model #Q-945, Serial #1," and the positive-feed microburet also developed here.

The automatic titrator will be described more fully in a separate report, which is now being prepared, but some of the main features of its construction will be described here.

The recording section of the titrator uses a Brown Recorder equipped with a preamplifier whose input impedance is 300 megohms, thus making it possible to use it with a high-resistance electrode system such as a glass electrode. The recorder chart is driven by a selsyn coupled to the solution-feed mechanism so that the chart travel is directly proportional to the volume of solution fed. For work on a macro scale the solution can be fed from a syringe buret; for micro work the positive-feed microburet mentioned above can be used. With the microburet the chart travels 1 in. for 0.18 λ of solution added. The drive mechanism for the solution feed contains a magnetic clutch actuated by the Brown recorder in such a way that when solution addition produces a rapid change in potential the feed is cut off until the recorder is able to establish equilibrium at the new potential.

Several modifications of the originally designed apparatus were necessary to obtain satisfactory performance. The initial curves recorded by the titrator showed that some diffusion from the buret was occurring. The size of the opening of the buret tip was reduced to approximately 40 μ. This small aperture makes it more difficult to fill the buret, but there has been no evidence of diffusion since this change was made.

A platinum wire fastened to the glass tip of the buret was initially used as one electrode. It was noticed that a film of solution would build up between the electrode and the buret. This solution build-up changed the potential at the electrode. To obviate this difficulty, the platinum electrode was sealed in a glass tube and then was fastened to the buret tip with plastic fasteners. The fasteners provided a space of approximately 1/8 in. between the buret tip and the glass tubing containing the electrode. This spacing allowed complete washing and drying of the buret tip and the electrode.

As yet, it has not been found possible to titrate a series of aliquots of a standard uranium solution within the narrow margin of precision required (1%). Further efforts are being made to bring the precision obtainable within the desired limits.

DETERMINATION OF Sb IN Mg-Sb ALLOYS

R. B. Hahn and H. H. Miller

The standard polarographic method for the determination of antimony was considered for determination of antimony concentrations in magnesium-antimony alloys submitted by the Metallurgy Division. This procedure requires solution of the sample in acid, reduction to the antimonous state with KI, and dilution to a suitable volume in a background electrolyte of 1 *N* NaOH.

When antimony is alloyed with an active metal like magnesium which evolves hydrogen when dissolved in an acid, it can be readily volatilized as SbH_3 gas. During dissolution of the sample, a great excess of bromine water was kept over the alloy to avoid this loss. On dilution with 1 *N* NaOH, $Mg(OH)_2$ precipitated. The polarograms obtained when the supernatant was analyzed were low, indicating that some of the Sb was carried with the $Mg(OH)_2$ precipitate. These results, although low, indicated that the concentration of antimony present was high and a chemical method could be used.

The following procedure was, therefore, used: After the alloy was dissolved in bromine water, Sb was precipitated as the sulfide from a 1 *N* HCl solution using thioacetamide.(8) The SbS_3 was caught on a fritted glass disk, washed with H_2O, and dissolved in hot concentrated HCl. This solution was diluted with H_2O, and the H_2S was destroyed by adding a slight excess of iodine solution. The excess iodine was titrated with thiosulfate. An excess of sodium carbonate was then added, and the antimony was determined by titration with standard iodine solution.

POLAROGRAPHIC DETERMINATION OF U(IV) AND U(VI) IN THE PRESENCE OF LARGE AMOUNTS OF COPPER AND HYDROGEN FLUORIDE

A. D. Horton

The Chemical Technology Division is attempting to produce UF_6 by anodic oxidation of uranium metal to the VI state in a molten bath of NaF·HF or KF·HF.

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(8) Flaschka, H., and Jakobljevich, H., "The Use of Thioacetamide in Quantitative Analysis. I. The Determination of Antimony." *Anal. Chim. Acta.* 4. 247 (1950).

The process is carried out in a copper vessel. The samples submitted to this laboratory for U(IV) and U(VI) analyses were cold trap receiver washings and were expected to contain $UF_6(UO_2F_2)$, NaF·HF, Cu, and other corrosion products.

Uranium(IV) was separated by the lanthanum fluoride carrier method and determined polarographically by the method previously described.(9)

It has been observed that the presence of large quantities of fluorides enhance the polarographic uranium wave and tend to produce maxima which may be confused with the true limiting current of the wave. The copper wave which normally begins at zero potential interferes because a well-defined diffusion current is not obtained for the more easily reduced copper before reduction of the uranium begins.(10)

Several attempts were made to determine uranium polarographically after complexing the fluorides with $AlCl_3$. However, copper interference was appreciable and several maxima were noted in the waves. The results obtained by analyzing various dilutions of a sample solution which contained 10 mg of solid sample per milliliter of solution were erratic.

An attempt was made to electrolyze the copper in a mercury cathode cell with an applied potential of 2 volts and a current of 0.5 amp. The sample solution was first freed of fluoride by fuming with H_2SO_4, and then was diluted to 20 ml with 5% H_2SO_4 and electrolyzed for 1 hr. The solution was filtered through glass wool and the filtrate was examined for visible particles of mercury. None were found. The solution was then boiled to dryness and diluted to a suitable polarographic volume with 0.2 *N* HNO_3. The very high diffusion current obtained at zero potential indicated the presence of some mercury in the solution. For this reason the method was abandoned.

The use of 2% sodium potassium tartrate in 0.1 *N* H_2SO_4(11) for shifting the uranium to a more negative potential produced a diffusion current for copper at a half-wave potential of approximately 0.2 volt and for uranium at about 0.4 volt. This shift to a more negative potential allowed the recording of well-defined waves for both copper and uranium which were sufficiently

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(9) Horton, A. D., Miller, F. J., and Thomason, P. F., "Separation of U(IV) from U(VI) by the Lanthanum Fluoride—Carrier Method," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*, ORNL-867, p. 16 (Dec. 28, 1950).

(10) Kolthoff, I. M., and Lingane, J. J., *Polarography*, p. 58, Interscience, New York, 1946.

(11) Marshall, E. D., personal communication.

separated so that there was no interference. This method is successful without modification only when the copper concentration is less than or equal to the uranium concentration. If the copper concentration is very high, it must be removed by electrolytic deposition before the polarographic determination of uranium is attempted.

The following procedure is recommended for the polarographic determination of total uranium in the presence of fluorides and copper using a mercury anode type cell developed by Heyrovsky:(12)

Oxidize all lower valence states of uranium to the VI form by fuming with perchloric or sulfuric acid. Boil the solution to dryness. Dissolve the residue in a solution containing 2% sodium potassium tartrate in 0.1 *N* H_2SO_4. Use the standard addition method to determine the uranium content polarographically.

POLAROGRAPHY OF DILUTE SOLUTIONS

H. H. Miller

In previous work on the polarography of very dilute solutions, the diffusion coefficient for Pb^{++} calculated from the Ilkovic equation seemed to be markedly different at 10^{-6} *M* than at 10^{-3} to 10^{-4} *M*. It was thought desirable to extend this study to other ions, especially to those in which the number of electrons transferred in the reduction was different than in the case of lead. Since not all ions give well-defined waves in very dilute solutions, much of the work this quarter has been devoted to finding suitable cases for study.

In order to obtain a good polarographic wave in the concentrations of 10^{-6} to 10^{-7} *M* using the curve follower, it is necessary that the solution have the following characteristics: (1) that the reducible ion give a well-defined curve in normal polarographic concentrations, 10^{-3} to 10^{-4} *M*, and (2) that the supporting electrolyte be one that can be compensated and corrected for with the instrument, i.e., that the residual current of the supporting electrolyte due to minute impurities be low.

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(12) Kolthoff and Lingane, *op. cit.*, p. 243.

Since the height and the slope of the polarographic wave are functions of the number of electron changes in the reduction as well as the concentration of the reducible ion, it should be possible to obtain a more readily measurable wave from a three-electron reduction than from a one- or two-electron change. For this reason bismuth, antimony, and indium were considered for polarographic study in very low concentrations as examples of a three-electron change.

Preliminary experimental work indicated that the further consideration of antimony and bismuth for this study was not feasible. When the sensitivity was high, antimony in a supporting electrolyte of 1 *N* NaOH gave an erratic wave. The caustic also attacked the agar salt bridge which connected the cell to the reference electrode.. A well-defined wave also could not be obtained for bismuth in a background electrolyte of 10% Rochelle salt.

Indium, however, gives well-defined waves in a background electrolyte of 0.1 *N* KCl. It has been found that KCl is a good medium for work at high sensitivities. Indium will be studied further for testing the applicability of the Ilkovic equation to solutions containing low concentrations of a reducible ion.

POLAROGRAPHIC DETERMINATION OF URANIUM IN PITCHBLENDE SOLUTIONS

H. H. Miller

Solutions of pitchblende material were submitted by the Chemical Technology Division for uranium assay. An attempt to analyze these samples using the standard colorimetric method was not successful because foreign ions present in the solutions interfered with the color development. When the standard polarographic method was used, a wave was obtained at zero applied potential which interfered with the uranium wave.

Two methods of eliminating this interference were tried. The first method made use of a complexing agent which would shift the deposition potentials of the interfering ions and leave the uranium wave at its normal position. Sodium citrate and sodium potassium tartrate were tested, but in neither case was the interference completely removed. Since the wave which came at zero potential was due to copper, an attempt was made to extract copper with a dithizone-chloroform solution at *p*H 1 to 2. This method showed promise but was not perfected because the Chemical Technology Division abandoned work on the extraction of uranium from ores.

The procedure of Lewis and Overton,(13) using a background electrolyte of 2% sodium potassium tartrate in 0.1 *N* H_2SO_4, was considered but not investigated. In this solution the uranium potential is shifted so that uranium and copper as well as some other ions may be determined simultaneously.

POLAROGRAPHIC DETERMINATION OF CADMIUM IN VINYLITE RESIN

H. H. Miller

Because the previously reported polarographic results(14) did not agree too closely with the results obtained by activation analysis, some of the samples were rerun. The polarographic results, as well as the activation analysis results are given in Table 4, "Cadmium Analyses in Vinylite Resin," on p. 35.

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(13) Lewis, J. A., and Overton, E. C., *A New Method for the Polarographic Determination of Uranium in the Presence of Other Metals*, Montreal Report CRL-AE-41 (October, 1949).

(14) Miller, H. H., "Polarographic Determination of Cadmium in Vinylite," ORNL-867, *op. cit.*, *p*. 21.

2. RADIOCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT

NUCLEAR PROPERTIES

Cd Ratios for Pile Neutron Capture to Produce 225d Ag^{110} (W. S. Lyon). Cadmium, which has a resonance peak from 0.18 to 0.30 ev, attenuates neutrons of energy below 0.3 ev; using cadmium as shielding is thus an effectual way of observing only fast neutrons. Goldhaber(1) found that the Ag^{110} activity was strongly induced by Cd-filtered neutrons, indicating a resonance in the fast-neutron region. The following experiment was run to obtain an indication of the amount of resonance capture in the capture process $Ag^{109}(n,\gamma)Ag^{110}$: Two weighed samples of pure Ag metal together with Mn monitors were placed in "rabbits," one with and one without Cd shielding, and exposed in the reactor for 8 hr. Two runs were made. The induced activities (Ag^{110} and Mn^{56}, identified by absorption study and decay study, respectively) were read on the high-pressure ion chamber, and the activity per unit weight was calculated.

According to H. Pomerance of the Physics Division, manganese is a perfect $1/v$ absorber and, therefore, the Cd ratio of Mn when compared with the Cd ratio of Ag should be an indication of the amount of resonance capture in Ag. The results are given in Table 1.

TABLE 1

Cd Ratios of Ag^{110} and Mn^{56}

RUN	R^*	R_{Ag}/R_{Mn}
Ag 1	7.79	0.44
Mn 1	17.7	
Ag 2	8.40	0.43
Mn 2	19.7	

*R is the cadmium ratio, defined as:

$$\frac{\text{activity per g unshielded}}{\text{activity per g Cd-shielded}}$$

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(1) Goldhaber, M., "Activation of Ag (225d) by Resonance Neutrons," *Phys. Rev.* 70, 89 (1946).

The data listed in Table 1 support Goldhaber's observation; the Cd ratio of Mn^{56} represents the *R* value of true $1/v$ (i.e., no resonance) neutron absorption since in Mn^{56} the cross-section for capture is inversely proportional to neutron velocity. An increase over this Cd ratio value would have indicated an absorption resonance in the thermal region (increase of activity produced while unshielded); a decrease below the Mn-Cd ratio value would have indicated a resonance in the fast (above 0.3 ev) neutron region. The data on Ag^{110} indicate a decrease in the *R* value of about ½. Apparently, then, resonance capture is of considerable importance in the capture process $Ag^{109}(n,\gamma)Ag^{110}$.

MEASUREMENT OF RADIOACTIVITY

Assay of Low-energy Beta Emitters (W. S. Lyon and S. A. Reynolds). Over a period of time data have been accumulated which indicate that "absolute beta counting" involving simple extrapolation of an absorption curve to zero absorber does not give an accurate result when a low-energy beta emitter is measured on a counter which has been calibrated with a high-energy beta emitter. This was predicted for Co^{60} (0.31-Mev beta) by Zumwalt.(2) Emmons of the Health Physics Division has reported similar observations.(3) The fact that the Co^{60} absorption curve shows a rapid initial drop was reported by Ketelle,(4) who explained the phenomenon in terms of the presence of a large fraction of low-energy electrons in the spectra of beta emitters of decay energy less than m_0c^2 (0.51 Mev).

In the present work, it was initially observed that high-energy beta rays are counted with about the same efficiency. Typical of those checked are RaE (1.17 Mev), Na^{24} (1.38 Mev), and P^{32} (1.7 Mev). The geometry of the second shelf of the standard tube support (Fig. 3) was found to be 7.6 to 7.8% by means of (1) National Bureau of standards RaDE sources, (2) similar sources prepared by Zumwalt and standardized by alpha counting of the daughter, RaF,(2) and (3) P^{32} whose disintegration rate was determined by calorimetry.(2)

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(2) Zumwalt, L. R., *Absolute Beta Counting Using End-window Geiger-Mueller Counters and Experimental Data on Beta-particle Scattering Effects* (MonC-397, 1949), AECU-567 (1950).

(3) Emmons, A. H., and Lauderdale, R. A., *Preliminary Report on the Dependence of Counting Efficiency on the Energy of Beta Emitters*, private communication, Mar. 30, 1950.

(4) Ketelle, B. H., *Recent Developments in Radiochemistry*, Modern Chemistry Symposium, Oak Ridge, Aug. 24, 1950.

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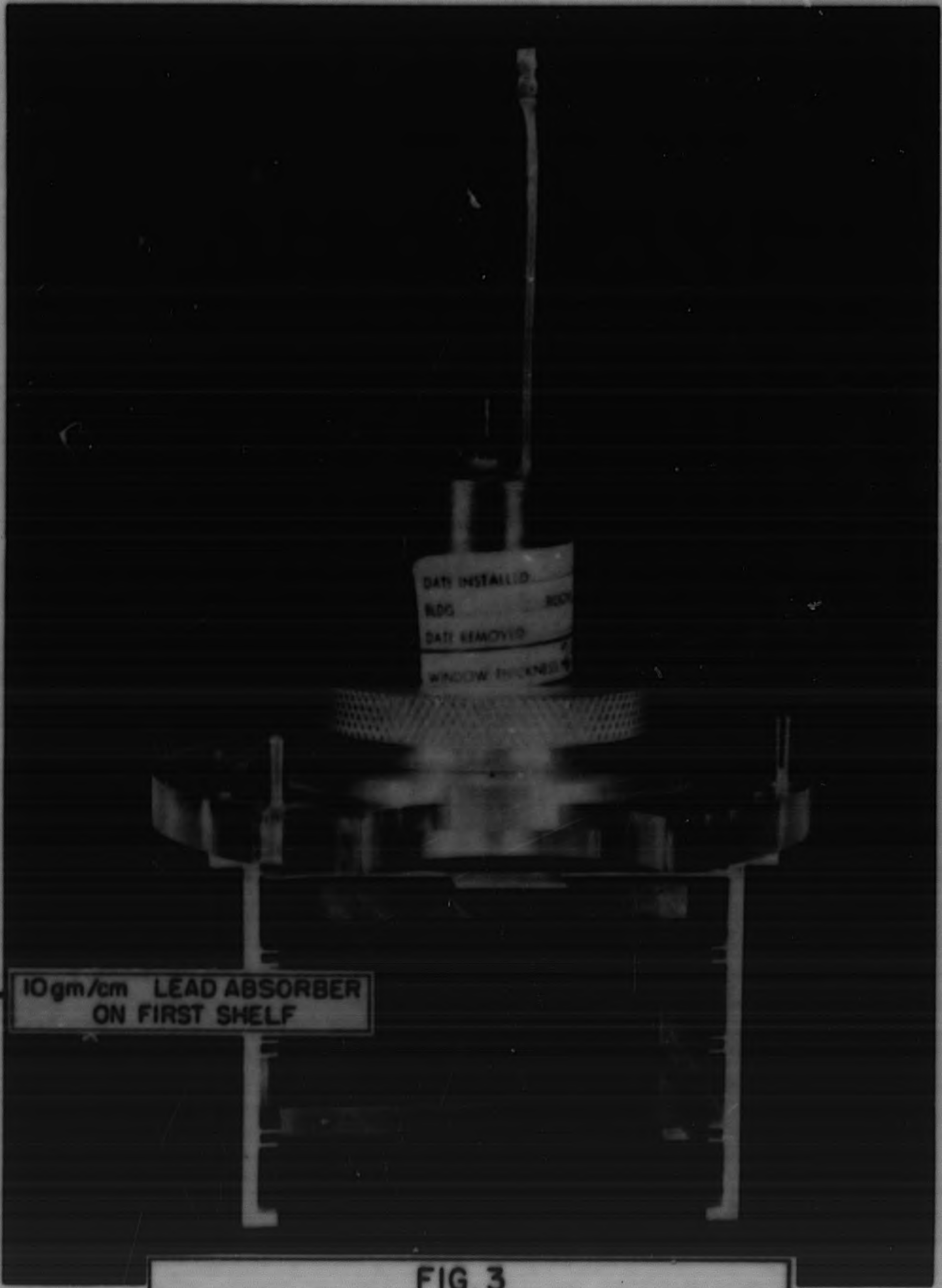

FIG. 3
CONSTANT GEOMETRY TUBE SUPPORT

With a Co^{60} source standardized by coincidence counting, the geometry was found to be 6.5 to 6.8% or about 1.2 times lower. Nb^{95} (0.15 Mev) gave a still lower geometry, approximately 6%. These observations have led to such procedures as the use of "Na^{24} geometry" for Sr^{89} (1.5-Mev beta) assay, "Co^{60} geometry" for Ca^{45} (0.25-Mev beta) determination, and "Nb^{95} geometry" for S^{35} (0.17-Mev beta) analysis.

The above-mentioned observations led to some curiosity about the shape of low-energy beta absorption curves in the region of very low total absorber. For investigation of this region a windowless counter was used, which was designed by R. L. Butenhoff, formerly of the Chemistry Division.(5) This counter consists of an outer airtight cylinder, in which the sample is placed near a side-window type windowless Geiger tube. Absorbers of various sizes are mounted over holes in an inner cylinder which is located so that absorbers pass between the source and the tube. The whole system can be evacuated and filled with the desired gas or used as a proportional flow type counter. For this investigation, a continuous flow of a mixture of 17% methane in helium was passed through the counter. This mixture was chosen for its low density, since betas must traverse a small distance before entering the sensitive volume of the counter. The gas absorption was about 0.1 mg/cm². In the counters used, this mixture did not give a voltage-counting-rate plateau, but fairly reproducible counts were obtained at a given voltage setting. The scaler, Nuclear Instruments Model 162, furnished a stable high-voltage supply. The smallest aluminum absorber was 0.3 mg/cm². (No "open window" was provided because the field would be distorted.) The geometry was about 23%.

Absorption curves in the low-absorber region are given (Figs. 4, 5, and 6) for S^{35}, Ca^{45}, and Co^{60}. On each curve is posted the factor, F_e, by which the usual straight-line extrapolation must be increased to equal the value observed in these curves. The Co and S samples were mounted on various thicknesses of polystyrene to demonstrate the absence of any back-scattering effect. The extrapolation factor is uncertain for Ca^{45} because the source contained a little inactive Ca. It will be noted that the factors vary about as would be expected from the apparent geometries given by Co^{60} and Nb^{95} standards described earlier. The half-thicknesses of the straight portions of the curves have approximately the values observed for end-window counters.

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(5) Clinton Laboratories Drawings C-1333, D-1331, D-1332 and Q-466A.

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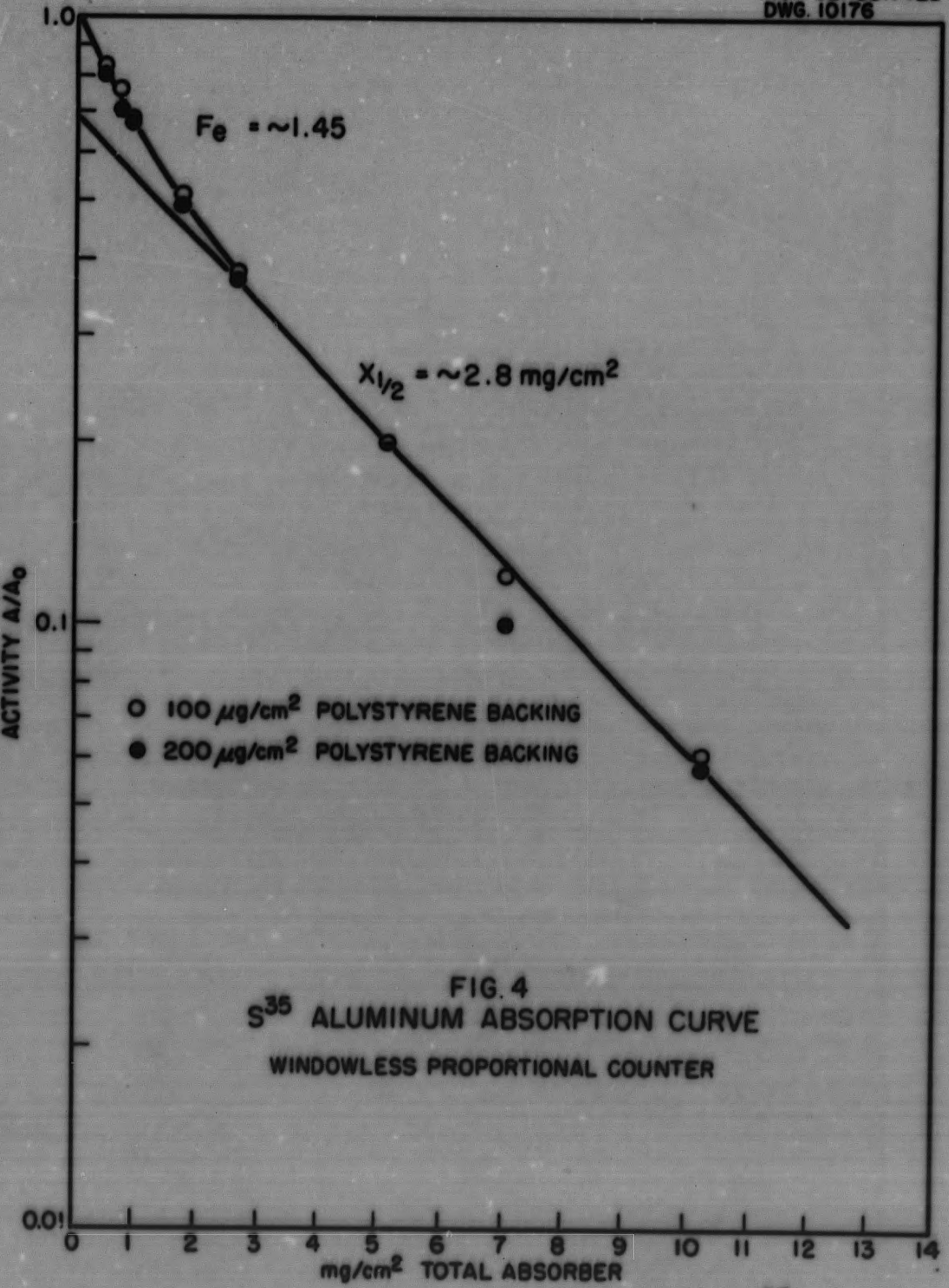

FIG. 4
S^{35} ALUMINUM ABSORPTION CURVE
WINDOWLESS PROPORTIONAL COUNTER

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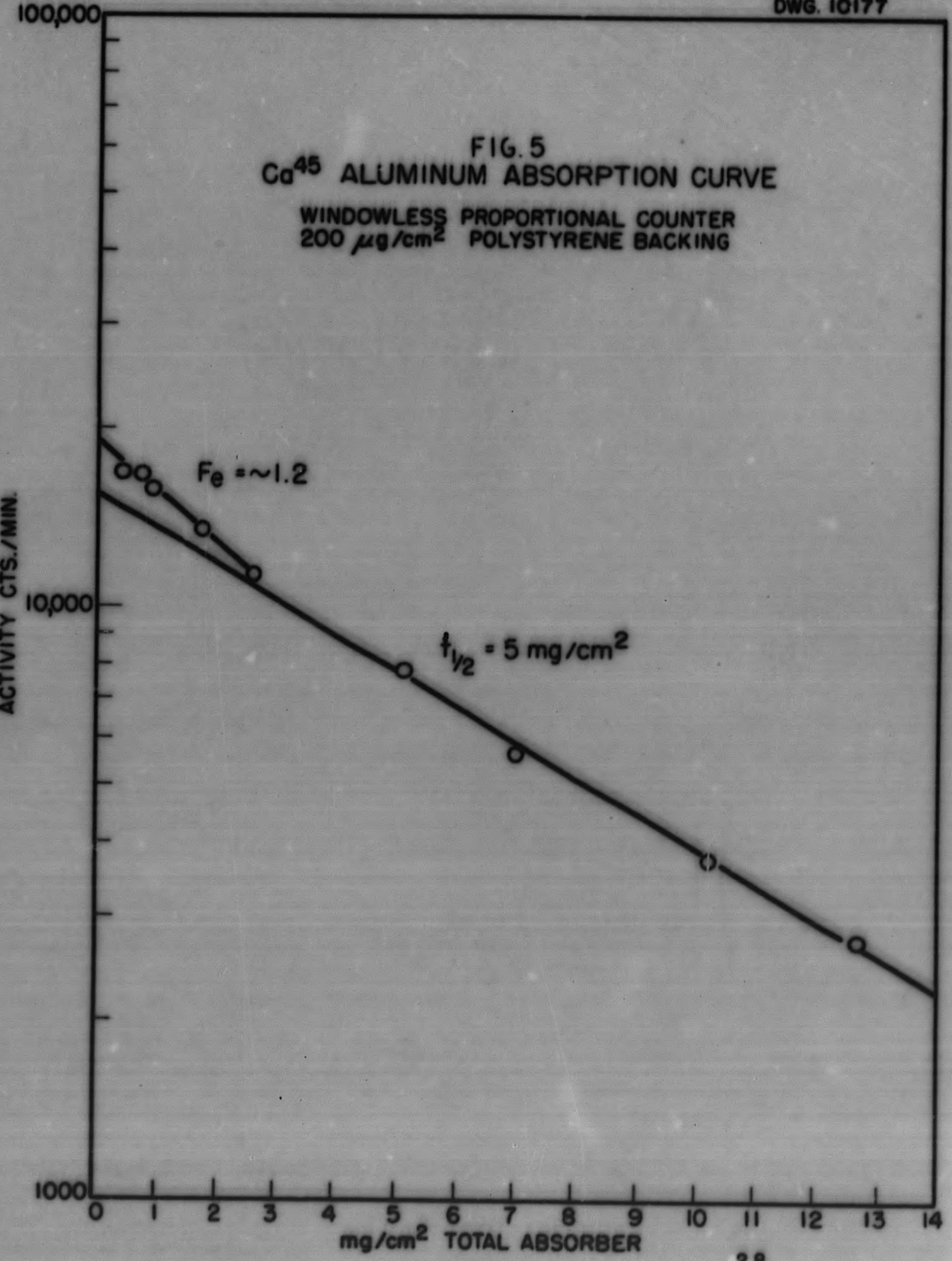

FIG. 5
Ca^{45} ALUMINUM ABSORPTION CURVE

WINDOWLESS PROPORTIONAL COUNTER
200 $\mu g/cm^2$ POLYSTYRENE BACKING

NOT CLASSIFIED
DWG. 10178

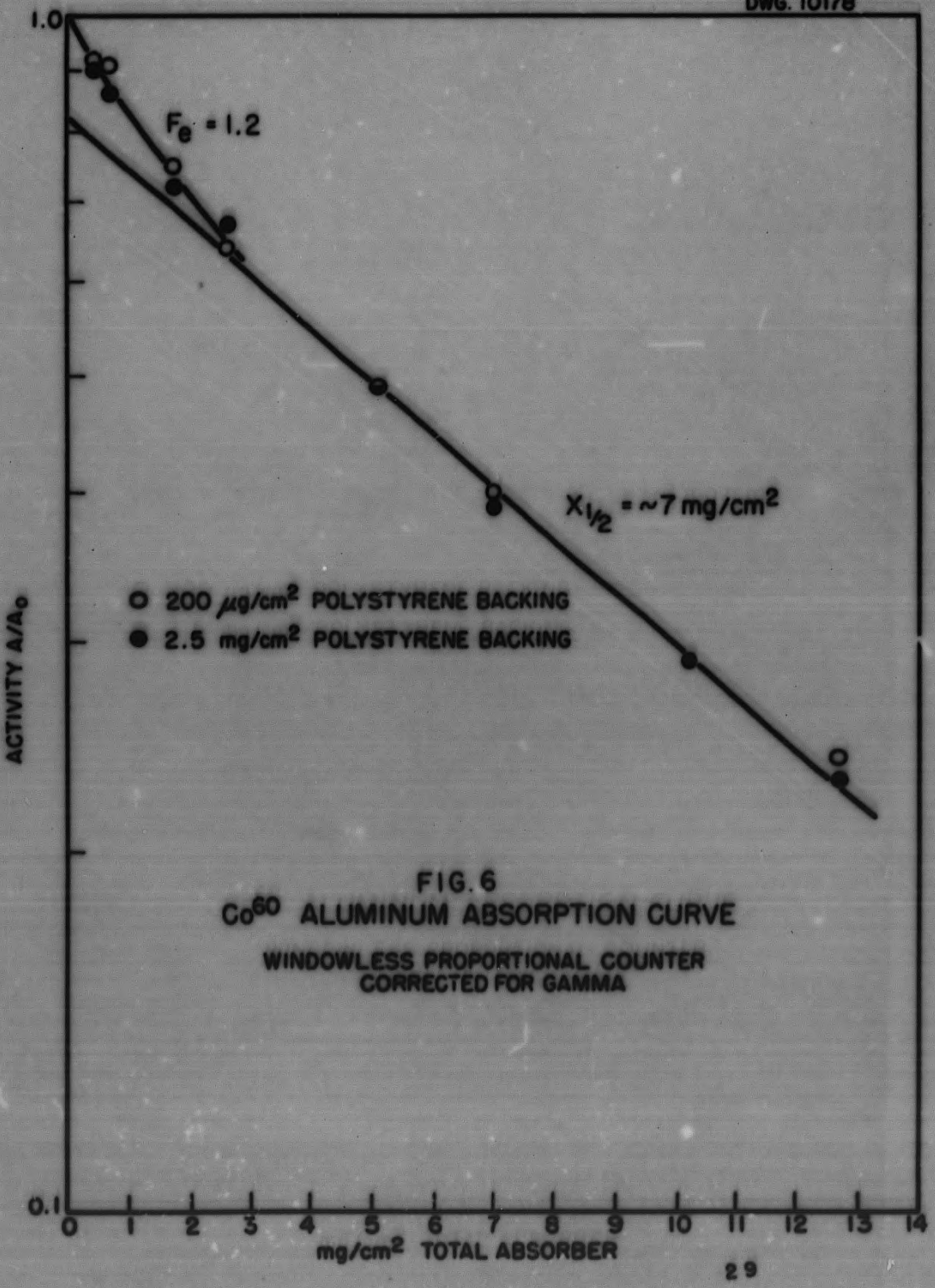

FIG. 6
Co^{60} ALUMINUM ABSORPTION CURVE
WINDOWLESS PROPORTIONAL COUNTER
CORRECTED FOR GAMMA

Since the method of calibration of end-window counters with known sources of various beta energies gives adequate results, little further work of this type is planned.

X-ray Counting (W. S. Lyon). The specially designed krypton-filled Be-window proportional counter for X-ray counting has been received. This counter appears to be approximately 40% more efficient for X rays than the mica end-window krypton-filled G-M counters now being used. However, the background of the Be-window counter is ten times greater than that of the end-window type, and this factor seriously limits its use. It is hoped that this difficulty can be overcome, perhaps by making the tube smaller.

4π Beta Proportional Counter (T. H. Handley). Further experimentation with this instrument has confirmed the belief that, in its present stage of development, it cannot be used for obtaining the absolute disintegration rate of nuclides that emit low-energy betas, such as Co^{60} (0.31-Mev beta).

ACTIVATION ANALYSES

Cd in Vinylite Resin (G. W. Leddicotte). Trace amounts of cadmium in vinylite resin have been determined. After bombardment, the resin was placed in a beaker. Twenty milligrams of Cd carrier and 5-mg quantities of the following carriers were added: Fe, Sr, Na, and PO_4. The mixture was treated repeatedly with concentrated H_2SO_4 and HNO_3 until the organic matter was destroyed. After adjusting the acidity of the solution, Cd was precipitated as the sulfide. The sulfide precipitate was dissolved in 6 *N* HCl and scavenged further after the addition of Fe, Pd, Sr, and Na carriers. Cd was finally precipitated as $CdNH_4PO_4 \cdot H_2O$. The results are summarized in Table 4.

TABLE 4

Cadmium Analyses in Vinylite Resin

SAMPLE	SPECTROGRAPHIC* ANALYSIS (ppm)	POLAROGRAPHIC** ANALYSIS (ppm)	ACTIVATION ANALYSIS (ppm)
A		228	220
B		Not found	30
C	980	452	449
D	225	***	214
E	45	15	38
F	175	142	128

* Spectrographic results as supplied by requester, C&CCD, South Charleston Plant.

** Polarographic results provided by H. H. Miller, ORNL Analytical Chemistry Division (Ionic Analyses - Research Group)

*** This sample was not reanalyzed polarographically.

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Rare Earths in Titanium (G. W. Leddicotte and S. A. Reynolds). A sample of "ultra pure" titanium metal submitted by H. Pomerance of the Physics Division was analyzed after bombardment for total rare earth activity by the procedure of Hume.(7) A samarium oxide standard was bombarded simultaneously, and by activity comparison, decay and absorption studies, and consideration of activation cross-sections the following upper limits were obtained: Sm, 1 ppm; Eu, Pr, Gd, Ho, Yb, Lu, 10 ppm.

On making the rare earth separation. it was observed that over half the activity which came down with this fraction was due to Sc^{48} which had been produced by the (*n,p*) reaction on Ti^{48}. A similar effect was also found in the determination of small amounts of Co in Ni [Co^{60} was formed by the (*n,p*) reaction on Ni^{60}]. These observations show the necessity of considering low yield products of bombardment of major constituents in activation analysis samples.

ANALYSIS OF RADIOISOTOPES

Radioisotope Routine Analysis Outline (S. A. Reynolds and E. I. Wyatt*). A manual summarizing the current radioisotope methods is being prepared. References on procedures, accuracies, etc., will be provided.

I^{131} (W. S. Lyon). The method previously described(8) for the assay of process and product I^{131} solutions, using the high-pressure ionization chamber, is now being used exclusively.

C^{14} (W. S. Lyon). C^{14} gas analysis equipment has been installed in Building 3038. The calibration of this apparatus and the evaluation of the method is being carried out by E. I. Wyatt's group.

Ba^{140} (W. S. Lyon). In cooperation with Radioisotope Analytical Group personnel, a factor converting from c/m of Ba^{140} plus carrier $BaCl_2$ as determined by radiochemical analysis to absolute c/m of Ba^{140} activity has been determined. This factor is for use with samples counted on the second shelf.

Te^{125m} (W. S. Lyon). Te^{125m} ($t_{1/2}$ = 60 days) has been reported to return to the ground state Te^{125} through emission of two highly converted gamma rays

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

(8) Lyon, W. S., "I^{131}," ORNL-867, *op. cit.*, p. 45, especially p. 49.

* Coordinator, Radioisotope Analytical Group.

of energy 110 and 34 Kev.(9) In order to assay this nuclide accurately the conversion coefficient and the amount of K conversion from each excited state must be known. Assay has been attempted by X-ray efficiency determined for Xe X-rays, e^- counting using a helium filled counter, and X-ray–X-ray coincidence counting. A coincidence to X-ray ratio of 1.3×10^{-2} was found, which is in agreement with the only previously determined value.(9) The value of 0.54% given for the K conversion coefficient of the 110-Kev gamma has not been checked. However, work is continuing in an effort to elucidate this decay scheme.

Cu^{64} (W. S. Lyon). A recent complaint concerning the amount of Cu^{64} activity in a pile unit shipped from ORNL has led to an examination of this activity. A standard unit of Cu (0.3 g of Cu irradiated for one week in the ORNL reactor) was dissolved in HNO_3, diluted to 25 ml, and submitted for assay. Using the decay scheme suggested in NBS-499(10) and the Seaborg compilation,(11) i.e., 54% K capture, 31% β^-, and 15% β^+, assay was made by the method of absolute beta counting and by reading the annihilation radiation of the positrons in a calibrated high-pressure ion chamber. Agreement between the two methods was within 5%. The activity of the site unit at pile dischargetime was approximately 130 mc total, which is in agreement with the catalogue value.

Ca^{45} (G. W. Leddicotte and S. A. Reynolds). Ca^{45} products are analyzed for Ca^{45} content (assay) and for purity. (Specifications require less than 0.1% impurity.)

The degree of purity from high-energy beta emitters may be established by the aluminum absorption curve technique. Samples counting at least 10,000 *c/m* are evaporated on 1-in. watch glasses, mounted, and counted as usual. The counting rate through an absorber of thickness 80 to 100 mg/cm² should be less than 0.1% of the initial rate.

The purity with respect to low-energy beta emitters is checked using the qualitative scheme given under "Identification of Radioelements" on p. 47.

The Ca^{45} assay may be done by the usual method of "absolute beta counting"(12) involving evaporation on a 1-mil polystyrene film and counting on a

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(9) Bowe, J. C., and Scharff-Goldhaber, G., "Decay Scheme of Te^{125m}," *Phys. Rev.* 76, 437 (1949).

(10) National Bureau of Standards, *Nuclear Data*, NBS Circular 499 (1950).

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

(12) Zumwalt, *op. cit.*

standard end-window counter, using the "Co^{60} geometry." However, if the material is of low specific activity (produced in the ORNL reactor), more accurate results are obtained by a radiochemical method.

If the product meets purity specifications, the direct-precipitation method is used, involving addition of a known amount of Ca carrier, neutralization with ammonia, and precipitation with saturated ammonium oxalate. The precipitate is filtered off by means of a small tared filter paper on a Hirsch funnel, dried with alcohol and ether, and weighed as $CaC_2O_4 \cdot H_2O$ to determine recovery. The sample is then covered with cellophane and counted.

If a sample contains significant amounts of activities other than Ca, the following procedure is used for assay: To the sample, standard Ca carrier is added as well as holdback carriers for Ag, Cu, Fe, Na, PO_4, and SO_4. H_2S and $(NH_4)_2S$ precipitations are made. The solution is acidified with HCl and boiled to remove H_2S, ammonia is added for neutralization, and Ca is precipitated by the addition of a saturated solution of ammonium oxalate. After being washed thoroughly with water, the precipitate is dissolved in dilute nitric acid. Ba and Sr holdback carriers are added and then precipitated with fuming nitric acid by the procedure of Coombe, Handley, *et al.*(13) The supernatant is evaporated to a small volume, diluted, and then neutralized with ammonia. Calcium is precipitated as the oxalate, weighed, mounted, and counted.

In order to determine the effect of self-absorption due to the calcium oxalate precipitate, a large enough aliquot of the sample was used to give a counting rate of several thousand counts per minute. Sufficient carrier was added, and the calcium was precipitated as the oxalate using ammonium oxalate. The slurry was then transferred to a 40-ml centrifuge tube and kept in motion with a magnetic stirrer while various aliquots (100 λ, 200 λ, etc.) were transferred to tared filter papers. The precipitates were washed and dried in the usual way, mounted, and counted. The counting rate corrected for yield was plotted against the weight of calcium oxalate in the sample. The resulting curve is given in Fig. 9.

Using this curve, a factor for the absorption effect of a given weight of oxalate can be established for correction of the sample counting rate. Correction must also be made for the effect of added absorption due to the window

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(13) Coombe, D. J., Handley, T. H., Leddicotte, G. W., Powell, R. H., and Reynolds, S. A., "Assay of Various Radioelements," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1949*, ORNL-607, p. 196, especially p. 199 (Mar. 7, 1950).

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DWG. 10314

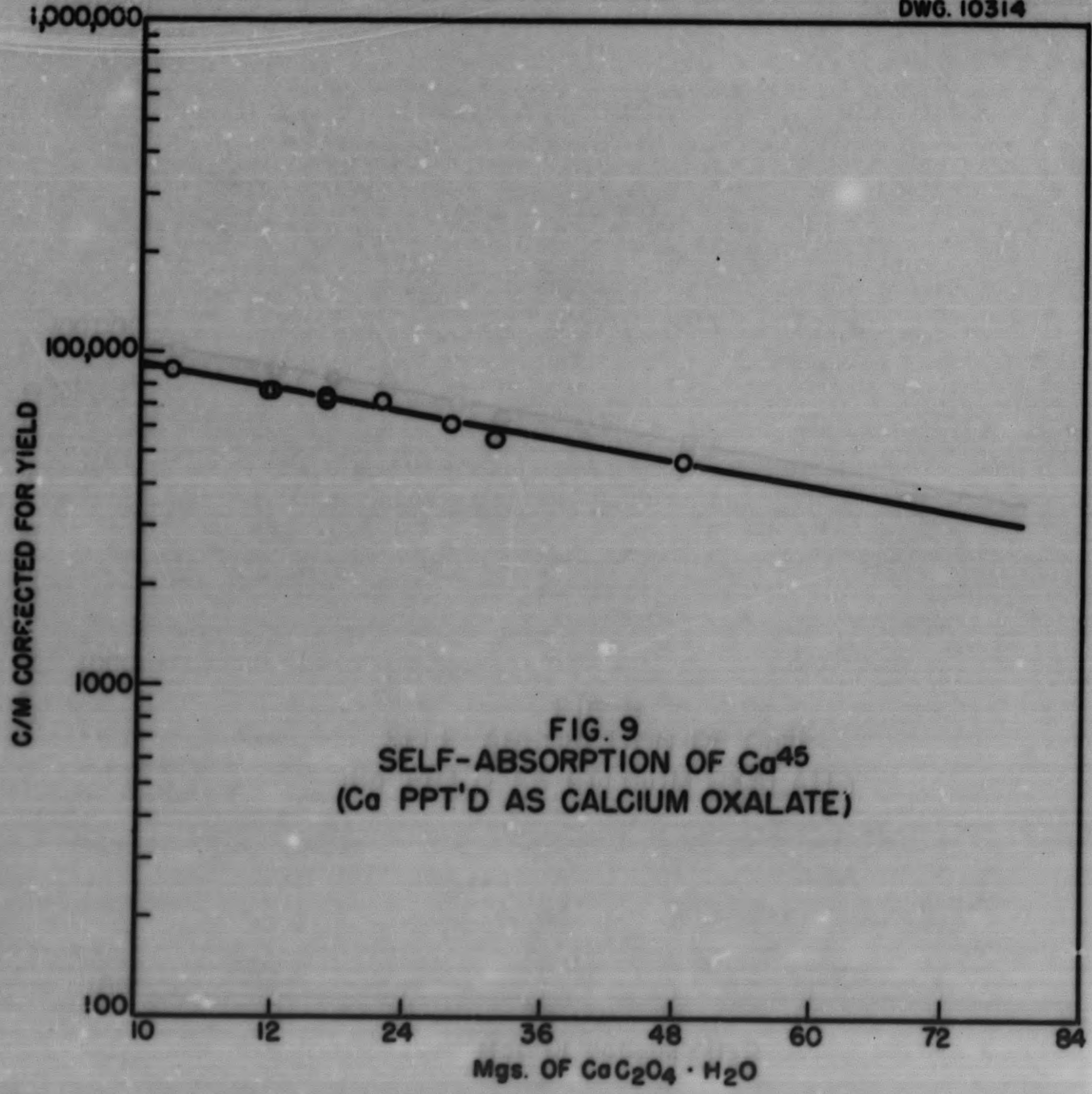

FIG. 9
SELF-ABSORPTION OF Ca^{45}
(Ca PPT'D AS CALCIUM OXALATE)

DECLASSIFIED

thickness of the counting tube used, the air gap between the sample and the counting tube, and the cellophane used to cover the sample.

Since Ca^{45} absorption curves are typical of a homogeneous beta radiation, it follows that over most of the absorption curve the usual logarithmic expressions can be employed in a manner quite analogous to the treatment of radioactive decay. Thus if A_0 represents the initial activity, the activity A after passage through a thickness t of absorber, is given by

$$A = A_0 e^{-\mu t}$$

where μ is the absorption coefficient. In a manner analogous to the expression

$$t_{½} = 0.693/\lambda$$

μ may be related to the value of the thickness, $d_{½}$, required to halve the initial strength by the relation

$$d_{½} = 0.693/\mu$$

From the observed half-thickness value of 5.90 mg/cm^2 in aluminum, the factors for absorption correction in Table 5 have been calculated from the expression given above.

The applicability of these factors was tested using a sample of high-specific-activity (HSA) Ca^{45} of low inactive Ca content (less than 0.01 mg/ml). The sample was diluted in 1 *N* HNO_3. Aliquots were placed on 1-mil polystyrene films and evaporated to dryness. The samples were then calculated on the basis of the results of an aluminum absorption curve and extrapolation through 5.5 mg/cm^2 of added absorption (air gap and window thickness). The results of four samples treated in this way indicated an absolute value of 1.90×10^8 c/m/ml.

Another series of analyses was run on the same solution, in which the addition of carrier was made and the calcium oxalate was mounted, counted, and then corrected for self-absorption effects of the oxalate and added absorption. The results on these samples indicate 1.90×10^8 c/m/ml.

TABLE 5

Ca^{45} Correction for Absorption

TOTAL ABSORBER* (mg/cm²)	FACTOR	TOTAL ABSORBER* (mg/cm²)	FACTOR
0.0	1.000	5.2	1.842
0.2	1.023	5.4	1.886
0.4	1.050	5.6	1.932
0.6	1.078	5.8	1.979
0.8	1.098	6.0	2.025
1.0	1.125	6.2	2.075
1.2	1.151	6.4	2.123
1.4	1.179	6.6	2.175
1.6	1.203	6.8	2.230
1.8	1.236	7.0	2.277
2.0	1.265	7.2	2.331
2.2	1.298	7.4	2.380
2.4	1.326	7.6	2.445
2.6	1.358	7.8	2.503
2.8	1.390	8.0	2.561
3.0	1.423	8.2	2.625
3.2	1.457	8.4	2.685
3.4	1.492	8.6	2.745
3.6	1.527	8.8	2.820
3.8	1.564	9.0	2.882
4.0	1.591	9.2	2.958
4.2	1.639	9.4	3.020
4.4	1.678	9.6	3.090
4.6	1.718	9.8	3.162
4.8	1.758	10.0	3.240
5.0	1.800		

* Includes window, air, and cellophane cover.

Tl^{204} (T. H. Handley). The assay of pure Tl samples is done by evaporating an aliquot of the sample to dryness on a thin polystyrene film and running an aluminum absorption curve. The resultant curve will have a slight upward trend in the region of thinner absorbers, no gammas, and a half-thickness of about 33 mg/cm². Extrapolation of this line to zero absorber and correcting for geometry and diluting will give the disintegration rate:

$$\text{mc/ml} = \frac{\text{extrapolated value x dilution factor x normalizing factor}}{\text{geometry x } 2.22 \text{ x } 10^9}$$

In testing the purity of Tl^{204} product, a method(14) which depends upon the extraction of Tl^{+} by dithizone from an ammoniacal cyanide solution is used. Pb, Bi, and stannous tin accompany thallium in this separation. If their presence is suspected, further separations will be necessary following the extraction. The extraction is made from HCl with ethyl ether after conversion of Tl^{+} to Tl^{3+}.

Special Reagents: (1) Extraction solution: Mix 15 ml of 10% KCN solution and 20 ml of 5% ammonium citrate solution with 53 ml of concentrated ammonium hydroxide and then add 450 ml of water. This solution is used to neutralize acid and provide the proper *pH* (9.5 to 10). (2) Dithizone solution: Dissolve 100 ± 1 mg of dithizone in 100 ml of chloroform.

Procedure: Place an aliquot of a neutral solution of the sample containing about 10^{6} dis/sec in a 60-ml separatory funnel, add several drops of hydroxylamine hydrochloride to convert thallium to the thallous state, 15 ml of the extraction solution, and 0.5 ml of concentrated nitric acid. Add dithizone solution, 3 ml at a time, shaking the separatory funnel after each addition until a slight purple tinge is noticed in the chloroform layer. (The purple tinge shows that enough dithizone has been added to combine with the Tl.) Separate the aqueous and chloroform layers.

If Bi, Pb, or Sn is suspected of being present, evaporate the chloroform layer to dryness and take up the residue in 15 ml of 6 *N* hydrochloric acid. Add several drops of 30% hydrogen peroxide and boil to convert Tl^{+} to Tl^{3+}. Cool and transfer to a 60-ml separatory funnel. Shake for 1 min with an equal volume of ethyl ether previously shaken with 6 *N* hydrochloric acid. Extract with two more portions of ether and combine the ether extracts. Examine the aqueous phase for impurities by evaporating to 1 ml and finally transferring to a watch glass and evaporating to dryness. The watch glass is mounted and counted for Pb, Bi, or Sn impurities.

If an appreciable amount of impurities has been found, the ether phase should be used for estimation of the Tl^{204} content, but if this is to be done care must be taken to make all transfers quantitative.

Place the aqueous layer in a 50-ml beaker and boil to dryness. Add 10 ml of concentrated nitric acid and again boil to dryness. Repeat this step

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(14) Sandell, E. B., *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1944.

several times to remove organic matter and thus reduce solids. (*Caution:* This should be done in a well-ventilated hood because of HCN fumes.) Finally transfer the residue to a watch glass, using small portions of concentrated nitric acid, evaporate to dryness, and mount for counting.

This mount will contain the impurities (if any are present) with the exception of Pb, Bi, and stannous tin. From the counting rate estimate the amount of impurities. If desired, an aluminum absorption curve may be run for a closer approximation by extrapolation to zero absorber. If impurities beyond specification are found, they should be identified to aid in further purification of the product.

43d Cd^{115m} (T. H. Handley). This nuclide was assayed by absolute beta counting. The purity was checked by examination of the residue after dithizone extraction of Cd.(15)

Mn^{52} and Mn^{54} (T. H. Handley). In analyzing samples containing only Mn activity, the following procedure is used:

An aliquot suitable for counting is evaporated to dryness on a polystyrene film 1 mil thick mounted on a standard counting card which has a 1-in. hole in the center. An aluminum absorption curve is run using an end-window tube filled with helium-alcohol, which will count the β^+ of Mn^{52} and not the X rays of Mn^{52} and Mn^{54}. The gamma component of the curve is subtracted and the weaker component extrapolated to zero absorber. This extrapolated value is used to calculate the Mn^{52} content in the following manner:

$$\text{mc/ml} = \frac{\text{extrapolated value x normalizing factor x dilution factor}}{\text{geometry x } 0.35 \text{ x } 60 \text{ x } 3.7 \text{ x } 10^7}$$

where the fraction 0.35 represents the 35% positron decay path.(16)

The gamma count of the sample is determined either on a pipetted aliquot or on the mounted sample by cutting out the circular polystyrene film. Either is placed in a 50-ml lusteroid tube and measured on the gamma ion chamber.(17)

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(15) Sandell, *op. cit.*

(16) Seaborg and Perlman, *op. cit.*

(17) Jones and Overman, *op. cit.*

Calculation of Mn^{54} Content.

(1) Correction for Mn^{52}:

$$\text{mv corr.} = \frac{\text{rutherfords of } Mn^{52} \text{ found per ml x relative efficiency of } Mn^{52}}{\text{rutherfords of } Co^{60} \text{ per mv}}$$

(2)

$$\text{rutherfords of } Mn^{54} = \frac{\text{rutherfords of } Co^{60} \text{ per mv x reading in mv x dilution factor} - \text{mv corr. for } Mn^{52}}{\text{relative efficiency of } Mn^{54}}$$

$$\text{mc/ml} = \frac{\text{rutherfords per ml}}{37}$$

If a manganese sample contains impurities, the following less exact procedure may be used: Manganese is oxidized to MnO_2 in acid solution by potassium chlorate.(18) The purified MnO_2 is first measured for Mn^{52} content by counting the β^+ emitted and for Mn^{54} by measurement in a high-pressure ion chamber. (A correction is made for Mn^{52} found.)

Procedure.

1. Take an aliquot estimated to be suitable for counting and place in a 50-ml glass centrifuge tube.

2. Add approximately 10 mg of standardized Mn carrier and about 2 mg of each of the following holdback carriers: Cr, V, Ti, Ca, Fe, Co, and Ni. Add a volume of concentrated HNO_3 equal to total volumes of all the carrier solutions plus the sample volume.

3. Boil and cautiously add several crystals of $KClO_3$. Wait after each addition for the evolution of gases. Continue until precipitation of MnO_3 is complete.

4. Centrifuge and discard supernatant. Wash MnO_2 twice with hot concentrated HNO_3 by centrifuging and decanting supernatant.

5. Dissolve the MnO_2 in about 2 ml of concentrated HNO_3 and add dropwise to the solution about 2 or 3 drops of 30% H_2O_2.

6. Again add holdback carriers as in step 2. Boil to decompose H_2O_2, and add concentrated HNO_3 to restore volume to approximately 15 ml.

7. Repeat steps 3 through 6 at least twice.

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(18) Furman, N. H., *Scott's Standard Methods of Chemical Analysis*, Van Nostrand, New York, 1939.

8. Repeat steps 3 and 4. After the MnO_2 is washed, make a slurry using about 1 ml of distilled water and transfer to a porcelain dish with a transfer pipet, taking care to transfer as much as possible.

9. Evaporate to dryness and ignite the MnO_2 to Mn_3O_4.

10. Transfer to a tared watch glass, weigh, and mount for counting.

11. Count the samples, using the procedure recommended for analyzing samples containing only Mn activity. The results are calculated in the same manner.

Cs^{137} (W. A. Brooksbank) A method involving ion exchange is being developed for the separation of Cs^{137}. (See "Ion Exchange and Chromatography in Radiochemical Analysis," p. 51.)

ANALYSIS FOR HEAVY ELEMENTS ($_{84}$Po to $_{96}$Cm)

Polonium (F. L. Moore) Previous workers(19) have observed that LaF_3 carried about 82% of the polonium from 2 *M* HNO_3 and less than 0.1% from 2 *M* HCl. Since the LaF_3 technique is well known at this laboratory, the conditions under which maximum carrying could be assured were investigated using Po^{210} tracer. It was found that

1. Using 1.25 to 3.00 mg of La(III) in a 2-ml volume of 1 *M* HNO_3, 90% or more of the polonium was carried by the LaF_3 precipitate.

2. The carrying of polonium by LaF_3 was decreased when the nitric acid concentration was increased above 1 *M*.

3. Very marked decreases in the carrying of polonium by LaF_3 were observed when the solution was made 0.5 *M* in HCl and 1 *M* in HNO_3.

4. Bismuth interfered (BiF_3 precipitated).

5. Polonium plated out somewhat on the platinum stirrers; plating occurred to a greater degree when glass stirrers were used.

In view of the above observations, it was thought desirable to consider a solvent extraction method. Previous workers(20) found that polonium could

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(19) Miller, D. R., and Halperin, J., *Detection of Polonium in Plutonium Solutions*, Chicago Report CN-1639 (July 17, 1944).

(20) Kraus, K. A., and Van Winkle, Q., *Isolation and Purification of Protactinium from Uranium Ore Residues*, Chicago Report CC-3365, p. 13 (Feb. 20, 1946).

be extracted from (1) a strong HCl medium with diisopropyl ketone, (2) a HNO_3-HCl solution with diisopropyl carbinol, and (3) a 6 *M* HCl solution with diisopropyl carbinol.

Using diisopropyl carbinol as the extractant, the effects of the following variables on the polonium recovery were studied: (1) HNO_3, HCl, and HCl-HNO_3 concentrations, (2) time of extraction, (3) volume of solvent used, and (4) interference from bismuth, aluminum, and copper. Details of this investigation will eventually be published separately. A recovery of about 99% was obtained when the procedure outlined below was used. (This method can be use remotely.)

Procedure.

1. Adjust a suitable aliquot of the sample solution to 6 *M* HCl. (The concentration of HNO_3 should be less than 1 *M* if possible.)

2. Add a volume equal to twice the sample volume of diisopropyl carbinol (previously shaken for 5 min with an equal volume of 6 *M* HCl) and extract 5 min. Allow the phases to separate. Drain the aqueous phase into another separatory funnel and extract again. Combine the two organic phases and centrifuge for 2 min.

3. Transfer an aliquot of the organic phase to a platinum or stainless steel plate, dry under an infrared lamp or a hot plate at "low heat," and count on an alpha proportional counter. The plate should not be flamed.

Since it was found that the solvent extraction method was satisfactory, the plating methods described in the literature were not investigated. These methods require preliminary separations, special equipment, heating during plating, and several hours for one analysis.

IDENTIFICATION OF RADIOELEMENTS

Qualitative Analysis Scheme (T. H. Handley). A general scheme has been developed for examining radioisotope products for impurities and for identifying unknowns. This scheme applies in a general way to all isotope products but in special cases it must be modified depending upon the chemical and physical properties of the product being examined. The distribution of the elements in the scheme is shown in Table 6, p. 50.

In special cases it may be advantageous to use a procedure in which the product may be separated in one or two steps from practically all other elements, for example, the extraction of Tl by dithizone followed by ether extraction, extraction of Zn by dithizone, or extraction of nickel dimethylglyoxime by chloroform.(21) For these special cases, Noyes and Bray,(22) Lundell and Hoffman,(23) and other texts on qualitative and quantitative methods may be consulted.

An aliquot of the sample of suitable size for counting is evaporated to dryness on a 1-in. watch glass and mounted in the conventional manner for counting in an end-window G-M counter. An aluminum absorption curve is run, plotted, and analyzed for its components. The apparent energies for these components obtained from the half-thickness may be compared with those reported in the literature for the product being examined. For nuclides with complex decay schemes, it is advantageous to build up a set of reference absorption curves obtained from sources known to be pure. The curve obtained from the sample of unknown impurity is compared with that of the curve obtained from a source of the same nuclide known to be pure. Thus it is possible to find impurities of the order of several per cent provided the half-thicknesses are sufficiently different. Also, the amounts of the various components are compared to the total counting rate at zero added absorber, and when these vary from the proportions in the pure source, it may correctly be assumed that a significant amount of impurity is present. However, this can be done only when counting conditions are identical for the unknown and the known. For further verification of conclusions drawn from the above discussion and the procedure following, a decay study of the gross mount used for absorption studies may be begun. Because of the time involved, it may not be possible to complete this study.

Procedure. An aliquot containing an adequate number of counts per minute is placed in a 50-ml glass centrifuge tube. The size of the aliquot should be such as to obtain 200 c/m of any single impurity separated if it is present in maximum allowable amount, thus enabling an absorption curve to be run in a reasonable length of time. Add about 5 mg of each of the following carriers: Ag, Cu, Fe, Co, Sr, and Na. In most instances, it is recommended that the

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(21) Sandell, *op. cit.*

(22) Noyes, A. A., and Bray, W. C., *A System of Qualitative Analysis for the Rare Elements*, Macmillan, New York, 1943.

(23) Lundell, G. E. F., and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, Wiley, New York, 1938.

carrier be added for that element which constitutes the product, eliminating one of the above carriers, depending on which group the product element falls in.

Group I. If chlorides are present, make the solution alkaline with NH_4OH to ensure mixing of Ag carrier and activity. Make acid with concentrated HCl and boil for several minutes.

Centrifuge and decant the supernatant, retaining it; wash the precipitate twice with 5 to 10 ml of distilled water. Finally add 1 ml of distilled water and make a slurry. Using a transfer pipet, transfer this to a 1-in. watch glass, evaporate to dryness, and mount for counting. Run aluminum absorption curves and start decay study if there is sufficient activity. This applies also to the subsequent groups.

Group II. To the supernatant from Group I of about 15 ml volume add 3 *N* NH_4OH slowly until a precipitate begins to form, then add 1 ml of concentrated HCl and heat to boiling. Pass H_2S through the solution for several minutes. Centrifuge and decant the supernatant, retaining it; wash the precipitate twice with 5 to 10 ml of distilled water, centrifuging and decanting each time. Add 1 ml of distilled water and make a slurry, transfer to a watch glass as for first group, evaporate to dryness, and mount for counting.

Group III. Transfer the supernatant to a 50-ml beaker and boil to remove H_2S, add 2 or 3 drops of 30% H_2O_2, and boil again. Add concentrated NH_4OH until precipitation begins, then 1 ml more. Centrifuge and decant the supernatant, saving it; wash precipitate with 5 to 10 ml of distilled water, and finally, using 1 ml of distilled water, transfer as for Groups I and II, evaporate to dryness, and mount for counting.

Group IV. Pass H_2S through the supernatant from Group III for several minutes, centrifuge, decant the supernatant, wash the precipitate, and transfer, evaporate, and mount as for other groups.

Group V. Acidify the supernatant from Group IV with HCl, boil to remove hydrogen sulfide, and finally make just slightly alkaline to phenolphthalein and add 2 to 3 ml of ammonium oxalate. Let stand for several minutes and centrifuge. Decant the supernatant and save. Wash the precipitate as for other groups, mount, and count.

TABLE 6

Distribution of Radioelements in the Scheme

Adapted from Lundell and Hoffman[24]

POSSIBLY LOST

C, Si, P, S, Cl, Ge, As, Se, Br, Ru, Sn, Sb, Te, I, Re, Os, Ir, Au, Hg

GROUP I

(*a*)* Si, Nb, Ag, Ta, W

(*b*)* P, S, Cl, Br, Zr, I, Ba, Hf, Tl, Pb, Ra, Th, Pa

GROUP II

(*a*)* Cu, Ge, As, Se, Mo, Ru, Rh, Pd, Cd, Sn, Sb, Te, Re, Os, Ir, Pt, Au, Hg, Pb, Bi, Po

(*b*)* V, Fe, Co, Ni, Zn, In, W, Tl

GROUP III

(*a*)* Be, Sc, Cr, Fe, Ga, Y, Zr, In, Re, Hf, Ac, Th, Pa, U

(*b*)* Si, P, V, Co, Zn, Nb, Hf, W, Ir

GROUP IV

(*a*)* Mn, Co, Ni, Zn, Tl

(*b*)* V, W

GROUP V

(*a*)* Ca, Sr, Ba, Ra

GROUP VI

(*a*)* Na, (Si),** (Cl),** K, (V),** Rb, Cs, (W)**

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* (*a*) precipitated more or less completely; (*b*) sometimes precipitated entirely or partially. This table may be revised occasionally because of new findings.

** Elements in parentheses are unlikely.

(24) Lundell and Hoffman, *op. cit.*

Group VI. Evaporate the supernatant to dryness and remove ammonium salts by flaming. Take up the residue in 1 ml of dilute HCl, transfer to a watch glass, evaporate, mount, and count.

The group in which the product nuclide falls is not counted, of course, because it will be too "hot." For further separation within this group, more carriers are added and separations are made using the general techniques already described, but it will not be necessary to do this in a preliminary examination. Details of separations within the groups are beyond the scope of this paper. If the activity in any other group is appreciable and analysis of the absorption curve shows that it is not the product nuclide, the decay is followed for at least one half-life, if time permits. From data thus accumulated the impurity activity present is postulated and the amount estimated.

This procedure is strictly limited in its scope and several broad assumptions have been made. Comparisons of the product nuclide and any impurities are made on a basis of counts per minute and not disintegrations. The following factors have not been considered: (1) the disintegration schemes, (2) the efficiency of counting the various radiations, (3) self-absorption, (4) back-scattering, and (5) possible losses during separation. It is strongly recommended that, in using this procedure, it be kept in mind that it is a *qualitative* and not a quantitative method.

Activity in Irradiated Water (G. W. Leddicotte). A sample of water from an experimental unit was submitted by the Naval Reactor Division of ANL. By means of qualitative tests, the following activities were detected: Sr^{89}, Mn^{56}, P^{32}, Na^{24}, and Si^{31}.

ION EXCHANGE AND CHROMATOGRAPHY IN RADIOCHEMICAL ANALYSIS

Ion Exchange

W. A. Brooksbank

New Ion-exchange Laboratory. An ion-exchange laboratory has been equipped in Building 3004. This laboratory, because of its proximity to the ORNL reactor, was also equipped for work with short-lived isotopes.

The equipment available for ion-exchange work includes:

(1) A steam-jacketed column for rare earth analysis.(25)

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

2. Two conventional "64" scaling circuits fitted with Streeter-Amet SCI-10 printing recorders and Microflex timing mechanisms.

3. Two logarithmic count-rate meters, continuously recording two points on a six-point Brown recorder.

The counting and recording equipment will handle four columns independently.

A 4π gamma chamber with a 300-cycle vibrating-reed electrometer feeding one of the points on the Brown recorder and a Q-762 "64" scaler feeding a five-pen Esterline-Angus recorder is for use with short-lived activities.

Separation of Alkali Activities. The procedure previously reported(26) has proved feasible only for the analysis of traces of alkali metals in the presence of bulk quantities of other alkali metals. When certain other metals (e.g., Mg or Al) were analyzed for traces of alkali metals, overloading of the resin occurred. Therefore a search was made for a resin which had enough capacity to retain the bulk metal and which would allow a rapid elution of the alkali metals.

Beukenkamp and Rieman(27) used colloidal Dowex-50 for the separation of Na and K from each other and from Mg. Several runs were made using this resin (bed size 6.44 cm^2 by 20.9 cm, flow rates of 0.4 to 1.0 ml/min/cm^2, and HCl concentrations of 0.4 and 0.75 *N* as eluents). Good separation of Na and K was obtained but the pairs K-Rb and Rb-Cs showed overlapping. Further experiments are contemplated.

Analysis of Waste Solutions for Cs^{137}. Waste samples containing bulk amounts of Na and K may be analyzed for Cs^{137} using the standard radiochemical method.(28) This method is, however, potentially hazardous because the submitted samples contain organic matter and an addition of perchloric acid is required.

An ion-exchange method could be used for the separation of Na and K from Cs if the conditions under which Na and K would be eluted from the column before the Cs had moved very far down the resin bed could be determined. The Cs could then be backwashed with a minimum volume of eluent and the eluent analyzed for Cs^{137} using the chlorostannate method.(28)

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(26) Brooksbank, W. A., "Application of Ion Exchange to Radiochemical Analysis," ORNL-867, *op. cit.*, p. 52.

(27) Beukenkamp, J., and Rieman, W., III., "Determination of Sodium and Potassium, Employing Ion-exchange Separation," *Anal. Chem.* 22, 582 (1950).

(28) Reynolds, S. A., *Special Radioisotope Methods*, unpublished manual, 1948.

Several small columns (1 cm^2 by 14 cm) were prepared, each containing 10 g (dry weight) of IR-100 (80 to 100 mesh). Runs were made simultaneously using Na^{22} and Cs^{137} tracers. The results are listed in Table 7.

TABLE 7

Performance of Cs Separation Columns

ELUENT	COLUMN 1, 0.1 *N* HCl	COLUMN 2, 0.2 *N* HCl	COLUMN 3, 0.4 *N* HCl
Flow rate (ml/min/cm^2)	1.4	1.5	1.4
Time for Na^{22} elution (hr)	2.25	2.08	0.67
Approximate travel of Cs^{137} during this time (cm)	1	2	4

These results indicate that 0.2 *N* HCl would elute Na and K from the column in a short time without the Cs moving so far as to require excessive volume of 6 *N* HCl backwash.

To make the procedure as simple as possible, the ion-exchange columns for the routine analyses will be prepared by this group. Cs carrier will be added to the submitted samples before the analysis is begun in order to measure recovery. The reservoir for the eluent will be graduated, and the instructions will call for a certain volume of eluent to be run through the column. From a second reservoir, entering at the bottom of the column, a known volume of 6 *N* HCl will be used as backwash, and the sample will be collected from a side arm just above the resin level. The volume of the eluent will be measured, and the Cs will be determined radiochemically.

Experiments are in progress to determine (1) sample size, (2) sample pretreatment, (3) optimum volume of acid to use, and (4) the behavior of other isotopes present (Sr^{90}-Y^{90}, Zr^{95}-Nb^{95}, Ru^{106}, and U) and the recovery of each of these elements in the backwash.

Rare Earth Separations. The steam column has been assembled and the resin bed is being degassed. Samples of Dy, Lu, Tm, and Tb are to be analyzed.

Chromatography

W. S. Lyon

A literature survey on the subject of paper chromatography has indicated that this process might be used as an analytical radiochemical method. In general, mixtures of partially miscible organic-water solutions are used. The separation depends upon the difference in partition between the mobile phase and the water-saturated cellulose. The data are recorded in the form of *Rf* values where *Rf* is defined by the relation

$$Rf = \frac{\text{distance traveled by ion}}{\text{distance traveled by liquid front}}$$

To ascertain the value of this method, the following procedure was used in preliminary studies: To a strip of filter paper approximately 25 cm long and 3.5 cm wide, 5 to 20 λ of the radioactive solution was added approximately 3 cm from the end of the strip. The paper was suspended in a glass cylinder containing a few centimeters of specific solvent such that the last centimeter of the paper was immersed in the solvent. The cylinder was stoppered and the solvent was allowed to diffuse up the paper. After the liquid front had advanced about 20 cm, the paper was removed and the distance of travel of the liquid was marked. After drying, the paper was counted using a slit-window counter. Fairly sharp separation seems possible.

Using Co^{60} and Zn^{65} and a solvent mixture containing 50% butanol, 10% acetic acid, 5% acetoacetic ester, and 35% water, studies have been begun on the effect of carrier material on the *Rf* values. Preliminary data indicate that there is an increasing change in *Rf* as the carrier contained in the active solution is varied from less than 1 to 100 λ.

It is planned to continue gathering *Rf* values for active ions, using varied solvent mixtures. In addition, it is planned to attempt quantitative separations using filter pulp columns.

SOLVENT EXTRACTION METHODS

Extraction of Anion Complexes (F. L. Moore). Smith and Page,(29) utilizing the principal that aqueous-insoluble amines form the corresponding

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(29) Smith, E. L., and Page, J. E., "The Acid-binding Properties of Long-chain Aliphatic Amines," *J. Soc. Chem. Ind.* 67, 48 (1948).

amine salts which are, in general, insoluble in water and preferentially extractable into organic solutions, developed the following method to effect anionic separations: A known quantity of acid was shaken with a slight excess of a 5% chloroform solution of an amine. The organic phase was then "stripped" with excess NaOH and both aqueous phases were analyzed for ions of the acid.

An investigation of this method was begun with the immediate goal of developing a separation for phosphoric acid and extending the work, as time allowed, to other anionic separations and to anionic radioactivity separations. This work has been in progress for two quarters.

Nine amine reagents were tested for the extraction efficiency of HCl, HNO_3, H_2SO_4, and H_3PO_4. One-milliliter samples of 1 *N* acid were used. The best extraction efficiencies were obtained when tribenzylamine and methyldioctylamine were used. The results are given in Table 8. Blank extractions with $CHCl_3$ (no amine) indicated that negligible quantities of the acids were extracted.

TABLE 8

Acid Extraction

AMINE	ACID EXTRACTED* (%)			
	HCl	HNO_3	H_2SO_4	H_3PO_4
Tribenzyl	50	68.4	0	1.5
Methyldioctyl	96.8	98.3	97.6	76.5

* Average of at least two determinations.

No attempt was made to extract the acid remaining in the aqueous phase. In most cases, this represents the slight solubility of the amine salt in the aqueous phase, and it is assumed that the remaining acid could be removed by an additional extraction with $CHCl_3$.

While of no value for extraction of H_3PO_4, it is interesting to note that tribenzylamine may have application in extracting certain anions from sulfuric acid solutions.

It was observed that the extraction of H_3PO_4 with methyldioctylamine (MDOA) seemed to vary with the aqueous volume used. This was checked experimentally (Table 9) by performing a series of extractions in which the aqueous volumes were varied while the H_3PO_4 concentration and the volume of $CHCl_3$ containing a slight excess of MDOA were kept constant. The organic phase was 7.65 ml of $CHCl_3$ containing 5 ml of MDOA. Five-minute extraction periods were selected arbitrarily.

TABLE 9

Phosphate Extraction with MDOA

AQUEOUS VOLUME (ml)	H_3PO_4 EXTRACTED (%)	OBSERVATIONS
2	87.1	Aqueous phace cloudy; cleared up on dilution
2	86.5	
5	76.6	Same as above
5	76.4	
10	54.0	Much foam; slow phase separation
10	53.9	
20	34.3	Stable foam persisted
20	32.1	

A series of extractions of H_3PO_4 was made to which various solvents were added to eliminate the foam emulsion which formed. In general, it was found that (1) the foam was readily broken by making the aqueous phase 1 *M* in HNO_3, HCl, or H_2SO_4, (2) "Aerosol O.T." made the foam worse, (3) HF (2 to 3 *M*) prevented foam trouble and gave good phase separation, (4) NaCl and NaF prevented foam trouble but the presence of the Na^+ reduced the recovery of H_3PO_4, and (5) "DC Antifoam A" (commercial antifoam agent) prevented foam formation when large quantities were used.

A search was made for a nonextractable acid which would render the aqueous phase acidic enough to prevent hydrolysis of the cations which might be present. It was also thought that increasing the H^+ concentration would render the H_3PO_4 more extractable by repressing its ionization. The extraction of HF and various organic acids with MDOA was, therefore, studied. The results are given in Table 10. (Values for MDOA extraction of HCl, HNO_3, H_2SO_4, and H_3PO_4 are listed in Table 8.)

TABLE 10

Extraction of Weak Acids with MDOA

ACID	AMOUNT EXTRACTED* (%)	BLANK (%)
HF	87.1	0.1
HCOOH	89.9	0.5
CH_3COOH	75.8	7.2
CCl_3COOH	98.7	10.2
Aspartic	0	0
Glutamic	0.3	<0.5
Glutaric	86.9	<0.5
Picric	>96.0	54.0
Fumaric	95.9	0
Maleic	97.5	<1.0
Malic	90.8	0

* Average of at least two determinations.

It appeared possible to use this method to effect anionic radioactivity separations. Tracer solutions of plutonium and polonium were prepared and preliminary extraction experiments were run using 5% tribenzylamine in $CHCl_3$. Test results indicate that polonium in 6 *M* HCl seems to be 99.0% present as a negatively charged chloride complex and PuO_2^{++}, when made 6 *M* or 9 *M* in HCl, appears to be anionic approximately 51 and 74%, respectively.

It is thought that several practical separations may be made by exploiting the anionic species of various elements.

Extraction with Tributyl Phosphate (D. J. Coombe and E. V. Jones*). For about one and one-half years, part-time work, the extraction of various radioactive elements with *n*-tributyl phosphate (TBP) has been studied. Work was

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* University of Alabama, formerly (1949-1950) a research participant at ORNL.

begun as assistance to the Spectrochemical Group in determining distribution coefficients for various elements under conditions where uranium is largely extracted. This leads to a useful method for determining impurities in uranium.(30)

The system investigated consists of 20% TBP in *n*-hexane and 5 *N* nitric acid. Uranium concentrations and concentration of the carrier for the element being studied are varied. Occasionally other compounds, such as sulfuric acid, are added. The effect of temperature is being studied for extraction of certain elements.

For iron, Fe^{59} tracer has been used. The distribution coefficient is about 3×10^{-3} regardless of the uranium concentration.

Studies of extraction of Zr, Hf, and Sc are in progress. Other elements will be investigated.

MISCELLANEOUS ACTIVITIES

Zr-Hf Ratios (R. B. Hahn). The determination of zirconium-hafnium ratios with *p*-bromomandelic acid is being investigated. The precipitate of combined zirconium and hafnium *p*-bromomandelate is dried, weighed, and then ignited to the oxide which is also weighed. From these data the ratio of Zr to Hf can be computed easily.

Experiments with various mixtures of pure zirconium and hafnium oxychlorides give results with less than 1% error. The effect of various foreign ions is now being investigated. A detailed report will be issued later.

Measurement of Uranium Beta and Gamma Radiations (S. A. Reynolds). To check agreement between X-10 and K-25 groups in determination of beta and gamma radiations from samples of recovered uranium, A. C. Jealous submitted ten solutions for analysis. Nine of these solutions contained aged pure natural uranium; the tenth was a solution of recovered uranium which also contained small amounts of fission products. These samples were analyzed for uranium, gross beta activity, and gross gamma activity by members of L. T. Corbin's and E. J. Frederick's groups at X-10, and by J. S. Fox at K-25.(31)

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(30) Feldman, C., Murray, M., Estepp, A., and Gillespie, J., "Spectrochemical Analyses — Research and Development. Analysis of U Compounds for Impurities," ORNL-607, *op. cit.*, p. 204.

(31) Fox, J. S., *Comparison of Radioactivity Analysis of Uranium Solutions by K-25 and X-10 Groups*, ELI-689 (Sept. 13, 1950).

Uranium was determined colorimetrically with ammonium thiocyanate, beta activity by counting on the standard end-window counter, and gamma activity by means of the high-pressure ionization chamber described by Jones and Overman.(32)

Table 11 summarizes the results on uranium analyses and beta and gamma activities. X-10 and K-25 results are in good agreement except where low intensities of radiation made accurate measurement difficult.

TABLE 11

Uranium, Beta, and Gamma Analyses

SAMPLE*	URANIUM (mg/ml)	GROSS β (c/m/ml)	β (% of normal**)		GROSS γ (mv/ml)	γ (% of normal**)	
		X-10	X-10	K-25	X-10***	X-10	K-25
1A	82	7.2×10^3	107	100	0.28	96	101
1B	85	7.1	101	102	0.30	99	107
1C	82	6.9	102	100	0.28	96	101
2A	55	4.5	100	97	0.18	92	104
2B	55	4.5	99	106	0.20	102	129
2C	55	4.4	98	98	0.18	92	103
3A	19	1.9		101	0.08	118	125
3B	19	1.5	96	99	0.06	89	166
3C	19	1.5	98	100	0.08	118	152
BP-32	42	4.5	129	128	0.28	187	210

* 1A-3C are aged, purified uranium (UX in equilibrium); BP-32 is recovered uranium.
** Refers to aged, purified uranium.
*** Gamma chamber in Room 10, Building 3550.

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(32) Jones and Overman, *op. cit.*

It was suspected that self-absorption of the weak gamma rays of uranium daughters might cause the ion chamber reading per unit weight to vary with the uranium concentration. Natural uranium contains in equilibrium Th^{234} (UX$_1$), decaying about 20% by a 0.09-Mev gamma, and Pa^{234} (UX$_2$), decaying about 2% by a 0.8-Mev gamma, with a small amount of Th^{231} (UY) with a 35-Kev gamma and Pa X rays.(33,34) Thus it is apparent that a rather large amount of weak gamma radiation will be emitted by natural uranium. Since most of the activity is contributed by UX (Th + Pa), a sample of this material was obtained for study from W. C. Waggener of the Chemistry Division. An absorption curve was taken by means of cup-shaped absorbers in the ion chamber, using a 100-λ sample. This indicates that about half the radiation measured by the ion chamber is weak (Fig. 10).

Solutions of uranium concentrations of 25 to 400 mg/ml were made up, and gamma radiation from 100-ml samples was measured in the gamma chamber (Fig. 11). The results are summarized in Table 12. The factor A/A_0 should be used to correct gamma readings when aged natural uranium is used as a reference standard for "clean-up" of recovered uranium. Obviously, if the design of the gamma chamber is different from that described by Jones and Overman, the factors will not apply.

TABLE 12

Self-absorption of Gamma Radiation in Uranium

CONCENTRATION OF U (mg/ml)	GAMMA ACTIVITY		A/A_0** (avg.)
	RATE OF DRIFT (div/min/mg)	DIRECT READING (mv/mg)*	
25	0.0236	~0.0030	0.95
50	0.0222	0.00286	0.90
100	0.0212	0.00267	0.85
200	0.0208	0.00260	0.83
300	0.0200	0.00250	0.80
400	0.0192	0.00234	0.76

* 10^{11} resistance scale.

** Activity per milligram divided by extrapolated activity per milligram at zero concentration.

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(33) National Bureau of Standards, Circular 499, *op. cit.*

(34) Seaborg and Perlman, *op. cit.*

SECRET
DWG. 10179

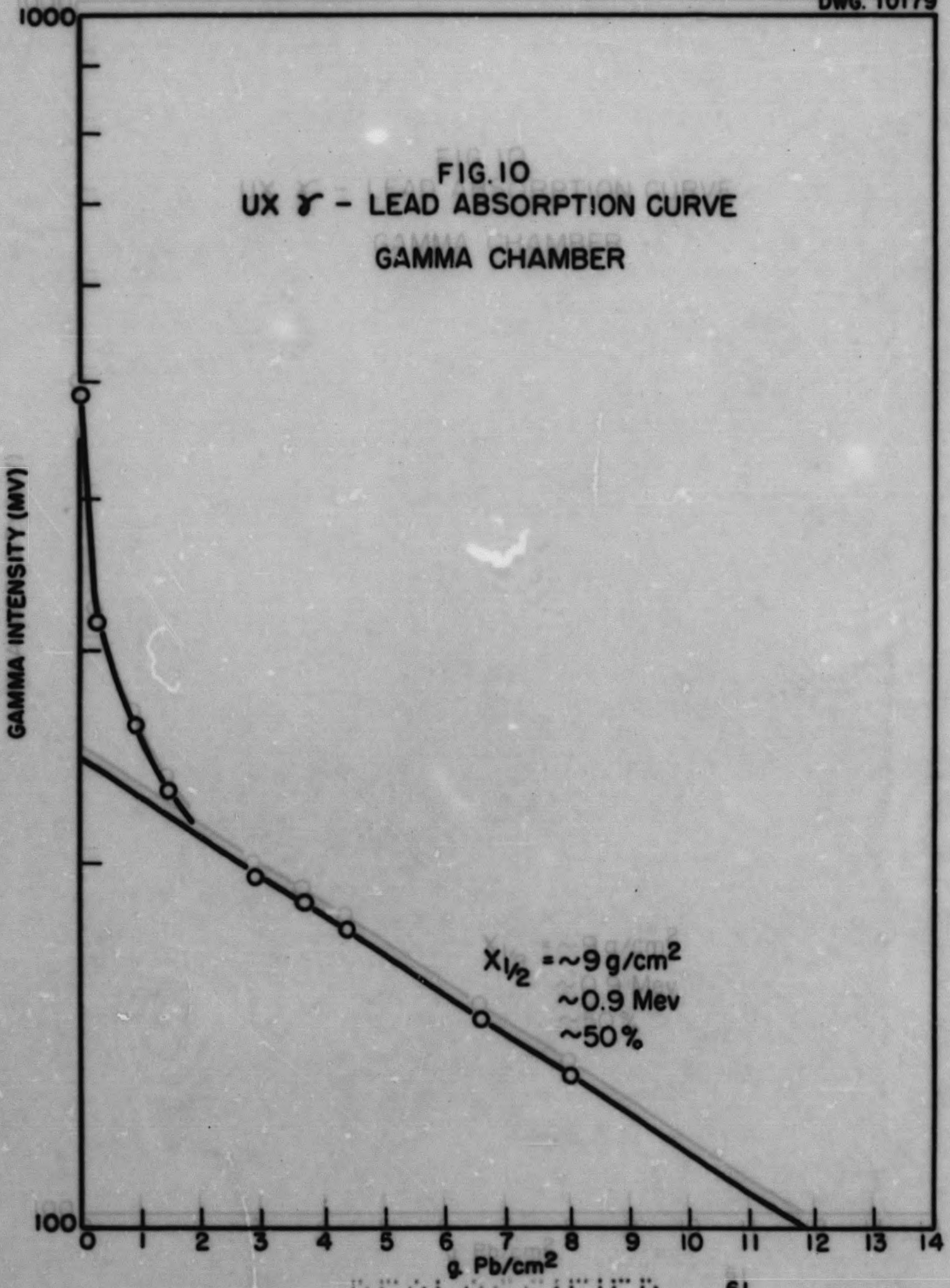

FIG. 10
UX γ - LEAD ABSORPTION CURVE
GAMMA CHAMBER

SECRET
DWG. 10180

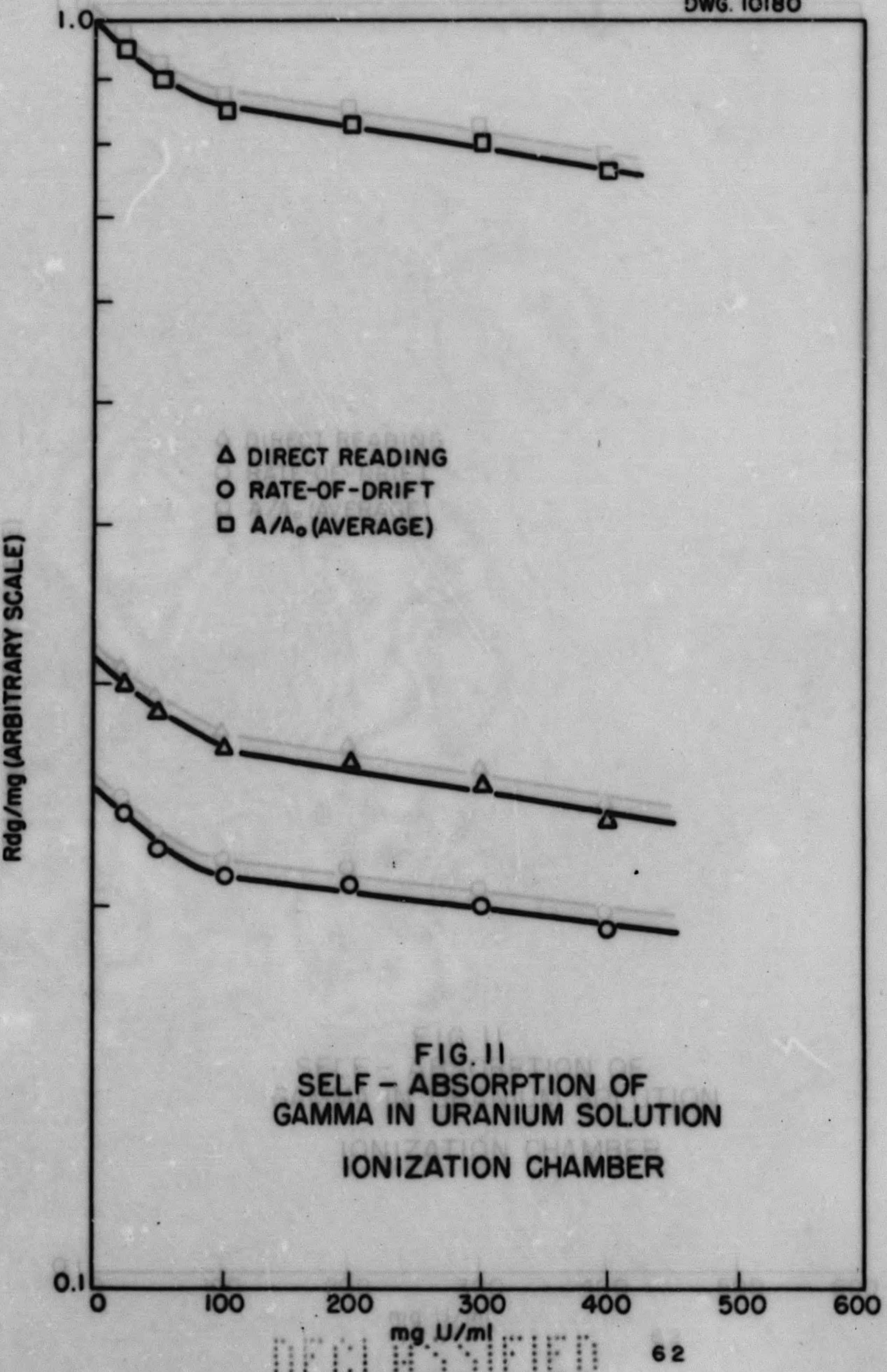

FIG. 11
SELF – ABSORPTION OF
GAMMA IN URANIUM SOLUTION
IONIZATION CHAMBER

It is apparent that self-absorption of the weak gamma component in concentrated uranium solutions is important. If gamma radiation from solid compounds was measured, the correction would be even larger.

Radiochemistry Demonstration for ORSORT (S. A. Reynolds). Laboratory sessions have been conducted for the Oak Ridge School of Reactor Technology in which the pile flux (neutrons/cm^2/sec) is measured by manganese activation and Ba^{140} yield in U_3O_8 samples. Typical results are given in Table 13.

TABLE 13

Flux Determinations, Reactor School

EXPERIMENT	FLUX (x 10^{-11}) (neutrons/cm^2/sec)		
	Ba	Mn	Power
II-1	7.3	7.4	6.2
II-2	7.3	7.2	6.1
II-3	6.4	6.7	6.4
II-4	8.4	7.3	6.4

3. SPECTROCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT

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

Spectrochemical methods were developed for performing the following analyses by the porous cup technique:

0.4 - 12.5% Ta in Nb
0.04 - 1.00% Nb in Ta
0.25 - 2.00% As in Cu
0.31 - 10.0% Ge in Cu
0.13 - 1.00% Zn in Cu
140 - 630 ppm Mn in Be
25 - 200 ppm Zn in 10% H_2SO_4
25 - 200 ppm Sn in 10% H_2SO_4
6.1 - 50 ppm Y in 0.025% Ca solution

A suggested method for Photographic Photometry was completed for Committee E-2 of the A.S.T.M.

In the "Review of Photographic Photometry" being written for the same organization, the following parts were completed:

1. A graphical presentation of reciprocity failure and its effects on photometric procedures.
2. Variation in emulsion sensitivity and its effect on photometric procedures.

4. SERVICE ANALYSES

RADIOCHEMICAL ANALYSES — DEVELOPMENT GROUP

S. A. Reynolds

Samples were analyzed for fission product molybdenum for the Chemical Technology Division. Analyses for the Operations Division included assay and purity tests on various radioisotopes. Activation analyses were performed for the companies Dow Chemical, Carbide, and Bell Telephone. Radiobarium and pile flux determinations were made for the Reactor School. Radioelement identifications were made for the Argonne National Laboratory Group working at this site.

IONIC ANALYSES — DEVELOPMENT GROUP

P. F. Thomason

The increase in the number of service analyses performed this quarter was due principally to the HRE samples submitted by the Chemistry Division. The HRE solutions were analyzed for total uranium, uranium(IV), chromium, iron, chloride, sulfur other than sulfate, and *p*H. The following methods were used:

1. Total uranium: Automatic microvolumetric⁽¹⁾
2. Uranium(IV): LaF_3⁽²⁾
3. Chromium: Spectrophotometric, using diphenylcarbazide
4. Iron: Spectrophotometric, using orthophenanthroline
5. Chloride: Automatic semimicrovolumetric (see pp. 12-15)
6. Sulfur other than sulfates: Indirect polarographic⁽³⁾ (S, H_2S, or thiosulfate)
7. *p*H: Determined with Model G Beckman *p*H meter using one-drop electrodes

There was also an increase in requests for capacity determinations of various cation-exchange resins. Service work for the Radioisotope Production

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(1) Miller, F. J., "Automatic Micro Titrations," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part II. Analytical Chemistry*, ORNL-686, p. 9 (May 18, 1950).

(2) Horton, A. D., Miller, F. J., and Thomason, P. F., "Separation of U(IV) from U(VI) by the Lanthanum Fluoride — Carrier Method," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*, ORNL-867, p. 16 (Dec. 28, 1950).

(3) Horton, A. D., Kelley, M. T., and Thomason, P. F., "Indirect Polarographic Determination of Sulfites and Thiosulfates," ORNL-867, *ibid.*, p. 18.

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Department included ionic analyses for P, Mn, Zn, Co, Ru, Te, Ca, and Ag. Other service work involved miscellaneous analytical requests such as water determination by the Karl Fischer method, hydrazine determination by iodometric titration, and yttrium by the gravimetric oxalate method.

GENERAL RADIOCHEMICAL ANALYSES

C. L. Burros

The RCA laboratory is operating at 90% maximum efficiency owing to the reconstruction of the building.

The major portion of the analyses performed this quarter were requested by the Chemical Technology Division. Active-constituent assays were made on samples contributed by (1) the decontamination studies program of the Purex process including laboratory column studies for ruthenium and zirconium removal, complexing of ruthenium and zirconium in the "A" column, and using carbon tetrachloride as a diluent for varsol, (2) the decontamination studies program of homogeneous pile fuel, and (3) the fluorination studies program.

Samples contained in an organic medium were frequently submitted for ruthenium analysis. The standard procedure(4) was adapted to these samples with the following modification: Before the addition of perchloric acid was made, the distillation apparatus was assembled and heat was applied. The organic mixture distilled and formed a layer on top of the caustic solution contained in the receiver. Perchloric acid was then added to the distillation flask, the apparatus was reassembled, and heat was again applied. By carefully controlling the rate of distillation, it was possible to avoid contact of the perchloric acid with the organic layer on the caustic solution in the receiver.

Although this method was successfully tested, it was apparent that if the rate of distillation accidentally became too rapid, contact between the perchloric acid and the organic mixture could not be avoided and, consequently, an explosion could occur.

It was decided, therefore, to pretreat the sample before assembling the distillation apparatus. The sample was placed in the distillation flask and 1 to 2 ml of alcohol was added. The mixture was swirled. Two milliliters of

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(4) Hume, D. N., Ballou, N. E., and Glendenin, L. E., *A Manual of the Radiochemical Determination of Fission Product Activities*, Chicago Report CN-2815 (Sept. 25, 1945).

ruthenium carrier was then added. The sample and the carrier were allowed to be in contact about 5 min before the flask was placed on a hot plate (low heat) to volatilize the organic mixture. The sample was evaporated almost to dryness. The flask was removed from the hot plate and cooled and then the standard procedure was used.

In order to evaluate the modified procedure, an aqueous solution of ruthenium tracer was prepared and three series of determinations were run. Aliquots of the aqueous solution were analyzed by the standard method. Aliquots to which 1 ml of hexone had been added (contact time, 15 min) were analyzed using the modified procedure. Since the results of all three runs agreed closely, it is recommended that all samples be pretreated using the described method.

In cooperation with C. D. Watson of the Chemical Technology Division, a considerable amount of work was done on the decontamination of concrete blocks. The results of this study will be reported by Mr. Watson. (ORNL CF-51-3-34).

In assaying alpha emitters, the sample, after chemical processing, is evaporated on a flat stainless steel plate and counted in the alpha proportional counter. For the past 11 months plates have been used in this laboratory which measure approximately 1.94 in. in diameter and 0.0285 in. in thickness and weigh about 11.2 g.

In anticipation of a possible steel shortage, a study was made to determine the effect of substituting for the plates now being used plates weighing about 0.66 g and having a diameter of about 1.13 in. and a thickness of about 0.005 in.

Series of gross alpha and plutonium alpha determinations were run independently by two analysts. (The same stock solution was used by both analysts.) The samples were evaporated on plates of each size and counted in the same counter at 52% geometry.

The results compared favorably; the smaller plates can therefore be successfully substituted for the plates now being used.

WATER ANALYSIS LABORATORY

J. H. Edgerton

Samples containing mercury, uranium, and versene were submitted for mercury assay by the Chemical Technology Division. After the samples were treated with nitric acid to break the versene complex, the mercury was reacted with a 0.001% dithizone solution (diphenylthiocarbazone), extracted with carbon tetrachloride, and measured spectrophotometrically.

Corrosion-test solutions submitted by the Reactor Technology Division were analyzed for hydrogen peroxide, zirconium, nitrogen, carbon, zinc, aluminum, thorium, and uranium. Before the ammonium thiocyanate colorimetric method for the determination of uranium was used, chromium, present as sodium dichromate, was volatilized with perchloric acid and sodium chloride.

Nitrogen and total nitrate determinations were made for the Metallurgy, Chemistry, and Chemical Technology Divisions. The Kjeldahl method was used for macro concentrations; micro quantities were determined colorimetrically, using phenoldisulfonic acid as the chromogenic agent.

Thorium, phosphorus, and fluoride analyses were performed for the Thorium Breeder Salts Program of the Chemistry Division.

The chromium, nickel, and molybdenum contents of a stainless steel tube, which had been filled with lead and heated for 40 hr at 1000°C, were determined for the Metallurgy Division. Titanium-thorium alloys were also analyzed. Thorium was separated by precipitation with ammonium oxalate. The titanium in the filtrate was precipitated with tannic acid. Silicon concentrations in silicon-aluminum alloys were determined. The columbium content of thorium-columbium alloys was estimated by the following procedure: The samples were calcined, treated with hydrogen peroxide, and completely oxidized by ignition. The percent of columbium was then calculated using simultaneous equations.

A new carbon combustion furnace has been installed, and samples have been run for the Reactor Technology, Physics, Chemistry, and Metallurgy Divisions.

Beryllium in the presence of thorium and titanium was determined gravimetrically after extracting the thorium with 2% TTA in carbon tetrachloride at a *p*H of 2.5.

Miscellaneous analyses were also performed for the Health Physics and Physics Divisions, Operations, Argonne National Laboratory, and the ORNL Power House.

LABORATORY AND SEMI-WORKS CONTROL UNIT

L. T. Corbin

This quarter the Chemical Technology Division submitted 96.17% of the total number of samples analyzed by this laboratory. Of this percentage, approximately 67.5% of the samples were contributed by the group doing development work on the Purex process. Uranium, plutonium, thorium, aluminum, and acid assays and gross beta and gamma activity determinations were run. A high-pressure ionization chamber was used to determine gamma activity.

Miscellaneous analytical requests were made by the Chemistry Division. The potentiometric method, using ferric sulfate as the titrant, was used for the uranium analyses performed for the Metallurgy Division.

PILOT PLANT LABORATORY

E. J. Frederick

The control laboratory began operations on a 24-hr day, 7-day week schedule with the start-up of the pilot plant Purex process on December 1. The analytical procedures which are being used are essentially the same as those previously used for assaying samples submitted by the Redox program with the exception that the potassium oxalate potentiometric method for the determination of nitric acid has been replaced by the alcohol-ferrocyanide potentiometric procedure. This method utilizes the fact that the uranium ferrocyanide precipitates from a solution saturated with KNO_3. (Methyl alcohol is added to keep the solution saturated.) The free nitric acid is titrated potentiometrically with standard sodium hydroxide.

It has been found that better than the required 3% accuracy can be obtained with the indirect colorimetric method for the determination of sodium if the sodium zinc uranyl precipitate is dissolved in water and diluted to a volume of 10 ml in calibrated centrifuge cones.

A study of the TBP extraction method(5) versus straight dilution on aqueous-waste and product-stream samples indicated that uranium in the concentration range of 10 to 50 γ/ml could be determined within the ±20% accuracy possible with the fluorimetric method. Neither stream showed evidence of

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(5) Kelley, M. T., Thomason, P. F., Corbin, L. T., Reynolds, S. A., Burros, C. L., and Frederick, E. J., *The Manual of Analytical Procedures for the U^{235} Recovery Process*, ORNL-983 (to be issued).

"quenching" interferences. The TBP method will be used exclusively for the analysis of stream samples.

Organic samples containing more than 10 γ/ml of uranium are diluted with low-blank Amsco solvent in preference to any other diluent to avoid the introduction of any foreign impurities before the samples are analyzed fluorimetrically.

RADIOISOTOPE ANALYTICAL GROUP

E. I. Wyatt

The high-pressure ionization chamber located in the Building 3038 laboratory is now being used for the routine determination of I^{131} concentrations in iodine product solutions. The method has been previously described.(6) More consistent values are obtained with this method than with the gross beta counting technique used heretofore.

A method for assaying $BaC^{14}O_3$ samples, in which the ionization current produced by the gaseous $C^{14}O_2$ evolved from a known weight of $BaC^{14}O_3$ is measured and corrected to the radiochemical value, was investigated. Initial test results obtained using $BaC^{14}O_3$ standard material indicate that this method is not so dependable as the one now being used.(7) It is felt, however, that if a microbalance is used for weighing $BaC^{14}O_3$, much better results might be obtained.

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(6) Lyon, W. S., "I^{131}," ORNL-867, *op. cit.*, p. 45, especially p. 49.

(7) Lyon, W. S., "Problems of C^{14} Assay," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-788, p. 28 (Oct. 4, 1950).

TABLE 14

Summary of Service Analytical Work for Period
October 1 Through December 25, 1950

GROUP MAKING ANALYSES	NO. OF PERSONNEL		NO. OF ANALYSES MADE FOR									
	TECH.	NONTECH.	BIOLOGY	PHYSICS	CHEMISTRY	CHEMICAL TECHNOLOGY	METALLURGY	REACTOR TECHNOLOGY	OPERATIONS	HEALTH PHYSICS	MISC.	TOTAL
Radiochemical Development	8	2				12			110		140	262
Ionic Development	4	1			338	20	3				15	376
Spectrochemical	4	0		34	72	251	98			10		465
General Radiochemical	4	6			8	4,751				73		4,832
Water Analysis	2	7		54	71	302	61	4,986	3	26	70	5,573
Laboratory and Semi-Works Control	2	10			302	13,715	123					14,140
Pilot Plant	5	17			13	1,785						1,798
Production Control	7	17			386	1,925			6,606		354	9,271
Total	36	60		88	1,190	22,761	285	4,986	6,719	109	579	36,717

5. INORGANIC PREPARATIONS

PREPARATIONS FOR THE THORIUM BREEDER SALTS PROGRAM

D. E. LaValle

Preparation of Thorium Fluosilicate and Related Compounds. Five preparations were made using various combinations of $Th(NO_3)_4$ and H_2SiF_6 with and without HF. To prevent the formation of the hydroxy compound some of the reactions were carried out in concentrated HNO_3, but on analysis all these preparations contained about 20% F, indicating that $Th(OH)_2SiF_6 \cdot xH_2O$ was being formed. In an attempt to replace the -OH groups with F, these compounds were treated with anhydrous HF at various temperatures up to 400°C. The results have been inconclusive.

In an attempt to prepare thorium fluosilicates from an anhydrous medium, the solubilities of the following compounds were tested: sodium fluosilicate, ammonium fluosilicate, vanadyl fluosilicate, triethanolamine fluosilicate, uranyl fluosilicate, and calcium fluosilicate. The results of this study are given in Table 15.

TABLE 15

Solubility Study of Fluosilicate Compounds

COMPOUND	SOLVENTS TESTED	OBSERVATIONS
Sodium fluosilicate	Alcohol, ether, acetone, glacial acetic acid, dioxane, liquid ammonia	Insoluble in all solvents tested
Ammonium fluosilicate	Same	Same
Vanadyl fluosilicate*	Same	Same
Triethanolamine fluosilicate*	Alcohol, ether, acetone	Slightly soluble in alcohol; soluble in water
Uranyl fluosilicate*	Alcohol, ether, acetone, glacial acetic acid, dioxane, liquid ammonia	Soluble to some extent in alcohol
Calcium fluosilicate*	75% alcohol, 100% alcohol	Soluble in 75% alcohol (after some initial decomposition seemed to be stable in this solvent)

* Prepared in this laboratory.

Uranyl fluosilicate was chosen for further study. Alcoholic solutions of this compound were mixed with $ThCl_4$ in varying concentrations, but all attempts to bring down a precipitate failed.

Preparation of Thorium Fluophosphates. Thorium fluophosphate, $Th(PF_6)_4$, was prepared by the following method:

$$Ag_2CO_3 + 2HF \longrightarrow 2AgF + H_2CO_3$$

$$2AgF + Ca(PF_6)_2 \longrightarrow CaF_2\downarrow + 2AgPF_6$$

$$4AgPF_6 + ThCl_4 \cdot 8H_2O \longrightarrow 4AgCl\downarrow + Th(PF_6)_4 + 8H_2O$$

The $Ca(PF_6)_2$ used was obtained commercially as a solution and the exact strength was not known. It was found that AgF could not be added to $Ca(PF_6)_2$ because it was not completely soluble in this solution. The reverse procedure, however, produced the white CaF_2 precipitate directly. A small excess of AgF was used to ensure complete precipitation because it could be readily removed later.

When $ThCl_4 \cdot 8H_2O$ was added, colloidal AgCl formed which could not be centrifuged out. This difficulty was overcome by using more dilute solutions.

The final solution of $Th(PF_6)_4$ was found to be slightly acidic. An excess of freshly precipitated $Th(OH)_4$ was added and then removed by centrifuging.

An attempt was made to prepare $Th(PO_3F)_2$ by dissolving $Th_3(PO_4)_4 \cdot 4H_2O$ in concentrated H_3PO_4 and then adding HF. Also, the preparation of $Th_3(PO_3F_2)_4$ was attempted by reacting $Th_3(PO_4)_4 \cdot 4H_2O$ directly with HF. In each case the resulting mixture was hydrolyzed and submitted for analysis.

PREPARATION OF METALLIC NICKEL

D. E. LaVali

The reduction of the oxides of three isotopes of nickel was carried out with hydrogen at 700°C. Absorbed hydrogen was removed by maintaining these specimens at this temperature under vacuum for another hour.

PREPARATION OF Mn_2Sb

D. E. LaValle

Plates of electrolytic Mn were cleaned in dilute HCl and then shattered to a fine powder (200 mesh) in an inert atmosphere (CO_2). Antimony metal in lump form was similarly crushed. The two metals were mixed in stoichiometric proportions in an inert atmosphere, put into a clay boat, and placed in the cool end of a tube furnace through which hydrogen was passing. When the temperature of the furnace reached 1100°C, the boat was pushed into the hot zone and the temperature was slowly reduced through the solidification point of the metals (948°C). The resulting compound was magnetic, and X-ray analysis showed the presence of foreign material.

Two attempts were then made to produce the compound in a vacuum. In the first run the quartz tube, in which the reaction mixture had been placed directly, cracked on withdrawal from the hot zone. In the next run, the reaction mixture was placed in a clay boat which was in turn inserted into a quartz tube and the tube was then sealed under vacuum. (It was believed that this procedure would allow for either expansion or bubbling of the material when heat was initially applied.) This tube did not crack. The surface of the product was coated with a film, and the tube surface above the boat was coated with a thin film of green MnO. Products of both runs have been submitted for X-ray examination.

PREPARATION OF FERROUS OXIDE

D. E. LaValle

Several attempts were made to produce pure FeO according to the method of Foex.(1) Fe and Fe_2O_3 were mixed in stoichiometric proportions and placed in a quartz tube which was evacuated, sealed, and inserted in a furnace which had been heated to 1200°C. After 1 hr the tube was quickly withdrawn and quenched in water. The tube, which shattered, was found to have been attacked by the mixture. Another run was made in which the reaction mixture was heated at 1100°C for 20 min. The tube did not shatter and did not appear to have been attacked by the mixture. The product was analyzed and found to be about 95% pure.

(1) Foex, M., "A Type of Transformation Common in the Lower Oxides of Manganese, Iron, Cobalt, and Nickel." *Compt. rend.* 227, 193 (1948).

It was decided to pretreat the starting materials. Iron powder was reduced in hydrogen at 700°C and then ground to 200 mesh in an inert atmosphere, and Fe_2O_3 was dried and then screened to obtain only 200-mesh particles. Both materials were analyzed for Fe gravimetrically. The determined percentages of Fe were used in mixing the reaction materials.

Three runs were made using purified material, and, in each case, the quartz tube shattered, twice on quenching and once in the furnace.

A literature search is being made for another method of preparation of this compound.

PREPARATION OF COBALTOUS FLUOSILICATE

D. E. LaValle

A request was received for the preparation of $CoSiF_6 \cdot 6H_2O$, which is to be used in experiments at near-absolute-zero temperatures. Initially $2CoCO_3 \cdot 3Co(OH)_2$ was treated with H_2SiF_6 in various proportions. One of two things happened: either SiO_2 was thrown out of solution or the entire solution turned into a gel.

Further experiments indicated that the compound $CoSiF_6$ is similar to $CaSiF_6$ in its stability. It was finally prepared by dissolving Co metal power in an excess of H_2SiF_6, centrifuging the solution, removing the insoluble material, and separating the $CoSiF_6 \cdot 6H_2O$ by crystallization.

In trying to prepare a large crystal of this compound, a carefully saturated solution was placed in a desiccator, without evacuation and over NaOH, to ensure slow enough evaporation to prevent formation of a film on the surface. A seed crystal was placed in the solution to prevent simultaneous multitudinous formation of small crystals. A fairly large but irregular crystal has been formed.

PREPARATION OF CALCIUM FLUOSILICATE

D. E. LaValle

Considerable difficulty was encountered in preparing $CaSiF_6 \cdot 2H_2O$. $CaCO_3$ was treated with H_2SiF_6, but, as the solution became neutral, colloidal silica separated out. It was finally made by adding $CaCO_3$ to H_2SiF_6, stopping the addition while the solution was still fairly acid. Since preliminary experiments had shown that silica precipitated when the solution was heated, it was allowed to concentrate by evaporation at room temperature. After a certain amount of solid deposited, the supernatant was discarded. The solid was transferred to a platinum dish and then dried by vacuum desiccation over NaOH. The product was brittle, white, and crystalline.

PREPARATION OF LITHIUM COMPOUNDS

R. H. Sampley

Using the procedure previously described(2) the following series of compounds were prepared for the Physics Division: lithium titanates, lithium zirconates, lithium calcium zirconates, and lithium titanozirconates.

PREPARATION OF PURE LITHIUM CARBONATE

R. H. Sampley

About 500 g of purified lithium carbonate was prepared by precipitating the sulfide, hydroxide, ammonium, and oxalate groups from stock lithium chloride (it was felt that these groups comprised the impurities listed as being present in the stock lithium chloride) and then precipitating the lithium as the carbonate.

All acids and water used in the purification were double distilled.

PREPARATION OF LITHIUM COMPOUNDS USING PURIFIED LITHIUM CARBONATE

R. H. Sampley

The following compounds and mixtures were prepared using purified lithium carbonate: $Li_2Si_2O_5$, $Li_2Si_2O_5$ + 1% Cu, Li_2SiO_3, and Li_2SiO_3+ 1% Cu.

The following solutions were also prepared: 1.725 *M* Li_2SiO_3 + 0.010% Cu, and 0.1 *M* Li_2SiO_3 + 0.032% Cu.

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(2) Sampley, R. H., "Preparation of Lithium Compounds," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*, ORNL-867, p. 69 (Dec. 28, 1950).

6. ANALYTICAL CHEMICAL CONTROL OF THE HOMOGENEOUS REACTOR SOLUTION

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

A detailed report of the progress on the analytical chemical control of the reactor solution appears in ORNL-925, the HRE Quarterly Progress Report for the period ending Nov. 30, 1950. The development of apparatus for an electromagnetic densitometer and for a *Q* coil is described.

A float, magnetic coil, and pressure bomb have been completed for laboratory testing of the densitometer. Electrical equipment has been assembled for measurement of the field strength of the coil and for the measurement of temperature to an accuracy of ± 0.1°C using a thermocouple.

If a microformer could be utilized as a float position-detecting device, it should be more sensitive than the previously reported magnetic switch and radiation methods of detection.(1) Therefore several custom-built microformers have been ordered. These units will consist of lava forms and Ceroc wire in the hope that these materials will withstand reactor conditions. Although the magnetic switch may not be used as a float-detection device, the investigation of the effect of radiation on alnico magnets will be completed.

Progress in the fabrication of a *Q* coil in a suitable insulator is also reported in ORNL-925. A platinum coil has been embedded in powdered, compressed Lava, Grade A, and successfully fired and machined by E. S. Cantrell and R. J. Fox of the Research Shops. Heretofore no workers, including those of the American Lava Company, have reported any success in embedding a coil in Grade A Lava. This ceramic, however, is porous and Dr. Hans Thurnauer of the American Lava Company is attempting to develop a suitable glaze. There is a possibility that platinum can be embedded in one of the other Lava ceramics for which glazes have already been developed. All materials used for the fabrication of the *Q* coil will ultimately have to be pile-tested.

Cadmium borofluosilicate, a neutron-absorbing glass supplied by Dr. Alexander Silverman of the University of Pittsburgh, has been exposed in the

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(1) Davenport, W. H., Jr., and Powell, R. H., "Analytical Chemical Control of Homogeneous Reactor Solution," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*. ORNL-867, p. 71 (Dec. 28, 1950).

ORNL pile. The test results are promising enough to warrant a more critical examination of this glass, and experiments are being designed also to test other specimens having similar neutron radiation properties.

7. OPTICAL AND ELECTRON MICROSCOPY

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

AN INVESTIGATION OF THE MICRO CHARACTERISTICS OF MULTILAYER FILMS FOUND ON PRETREATED STAINLESS STEEL BEFORE AND AFTER IMMERSION IN 0.17 *M* URANYL SULFATE SOLUTION CONTAINING 0.1 *M* NITRIC ACID AT 250°C

This study, instigated in connection with the HRE Project, will be more thoroughly treated in a forthcoming HRE report. However, because of its possible widespread interest, a brief discussion is given here.

The samples used for microscopic study were prepared by the Corrosion Section of the Reactor Technology Division. Sample classifications were as follows:

1. Stainless steel type 347 pretreated in 1% HNO_3 at 250°C.
2. Stainless steel type 347 pretreated in 2% chromic acid at 250°C.
3. Stainless steel type 347 pretreated in 1% HNO_3 and then immersed in 0.17 *M* UO_2SO_4 containing 0.1 *M* HNO_3 at 250°C for 3200 hr.

Macro examination of samples in the three groups disclosed distinct differences in the surface characteristics of the formed films. Figures 12*A*, *B*, and *C* show the surface of a typical sample in groups 1, 2, and 3, respectively (magnification 200×).

It can be observed that the film material covering the sample in class 1 above is fairly compact at this magnification and follows the contours of the machining striations. The surface material on the sample pretreated in chromic acid appears, by comparison, to be coarse and uneven. Higher power microscopy disclosed that the rough appearance is caused by the building up of mounds or projections of agglomerated microcrystallites. Samples in group 3 had what appeared to be a compact surface layer much the same as that in group 1, with the exception that it was much less regular and contained open areas where the outer crust had formed imperfectly or had chipped off. Subsequent observations made during replica preparations showed this outer layer to be poorly bonded to the material below.

SECRET
PHOTO ME-683,
ME-682,
ME-644

A. Pre-treated in 1% nitric acid at 250°C.
B. Pre-treated in 2% chromic acid at 250°C.
C. Pre-treated in 1% nitric acid and then immersed in 0.17 M uranyl sulfate solution containing 0.1 M nitric acid at 250°C for 3200 hours.
200X

FIG. 12
PHOTOMICROGRAPHS OF SURFACE OF STAINLESS STEEL 347

Thickness measurements of the surface coverings of the samples in the three groups gave the following:

Group 1: mean thickness, approximately 5 μ

Group 2: mean thickness, approximately 7 μ

Group 3: mean thickness, approximately 7 to 10 μ

Inasmuch as the thickness of the protective film on passivated stainless steel has been reported by various observers to be from 100 to 400 A,(1-3) it was suggested that the examined samples must be covered by built-up layers of the same composition as the original protective film or by film layers different in nature from the protective film.

To determine more exactly the physical nature of the films, an attempt was made to remove large segments of the material by cross-hatching the surface and immersing the sample in a solution containing 10% bromine in methanol until the material floated free. This material was then washed with methanol. Microscopic examination of this material at high magnification showed that the surface films in groups 1 and 2 appeared to be made up of two layers, somewhat different in nature, and surface films on samples of group 3 consisted of three layers. Figure 13 shows a segment of film removed from a sample in group 3.

X-ray examination of the outermost layer of surface film of group 3 samples gave one strong line of U_3O_8, the material which had, by earlier examination, been shown to be present on the walls of the stainless steel bombs used in static corrosion tests. The composition of the material present below this layer was determined to be either Fe_2O_3 or Cr_2O_3.

Electron micrographs of replicas of the material composing the surface of the samples of the three groups showed them to be quite different in nature (see Figs. 14*A*, *B*, and *C*) and led to the conclusion that any material formed on the surface during pretreatment or corrosion tests above the substrate was nonprotective in nature because of its permeability and might possibly, in the case of stainless steel pretreated in chromic acid, be deleterious with respect to removing uranium compounds from the solution more readily than in the case of material pretreated in HNO_3. The latter effect has to do strictly with the nature of the surface exposed to UO_2SO_4.

(1) Gulbransen, E. A., Phelps, R. T., and Hickman, J. W., "Oxide Films Formed on Alloys at Moderate Temperatures," *Ind. Eng. Chem. Anal. Ed.* 18, 640 (1946).

(2) Mahla, E. M., and Nielsen, N. A., "A Study of Films Isolated from Passive Stainless Steel," *J. Electrochem. Soc.* 93, 1 (1948).

(3) Vernon, W. H. J., Wormwell, F., and Nurse, T. J., "The Thickness of Air-formed Oxide Films on Iron," *J. Chem. Soc. London* 1939, 621.

SECRET
PHOTO M-580

A. Semi-transparent, pale brown film by transmitted light. Probably the protective film found next to the metal surface.

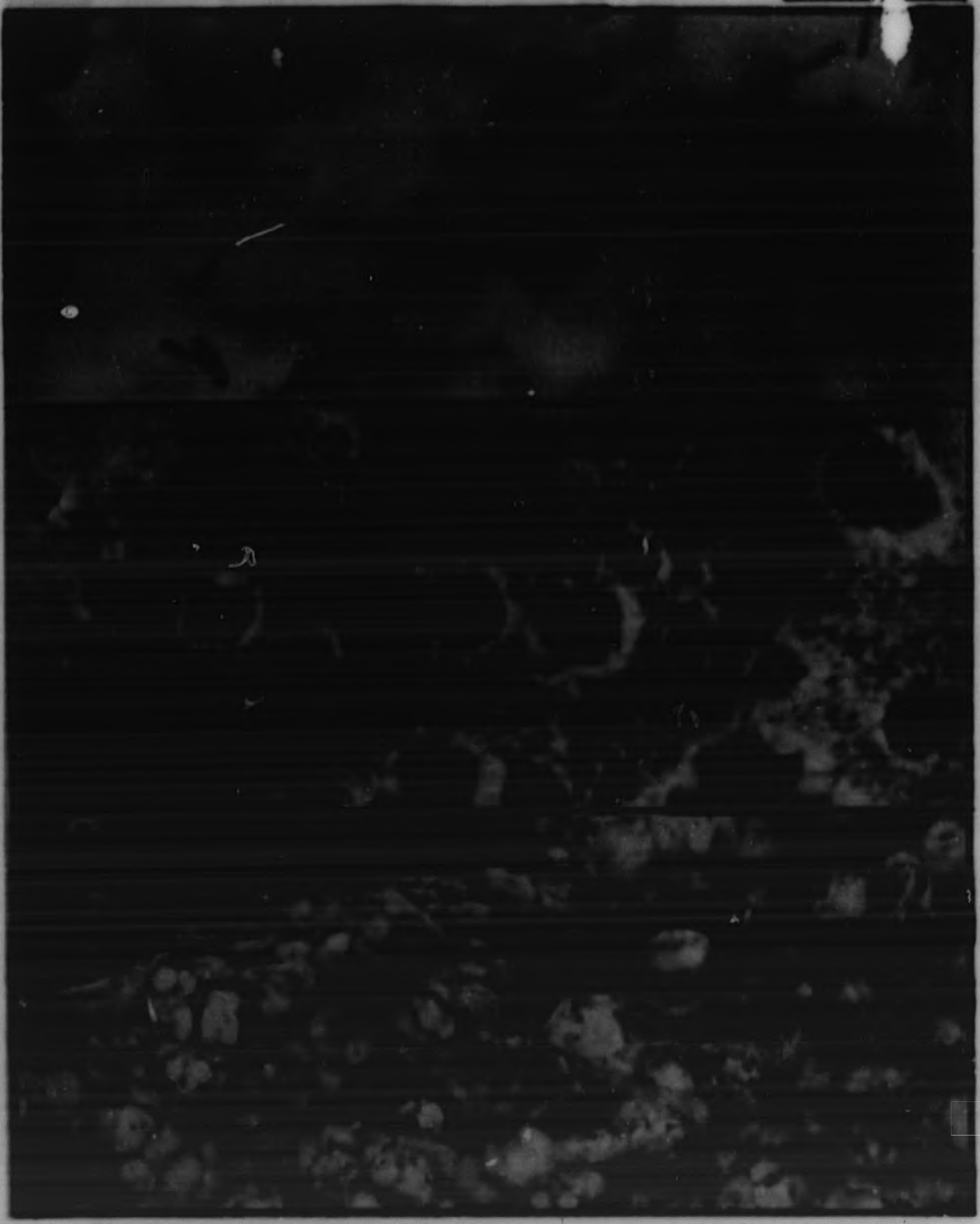
B. A much thicker, nearly opaque layer, reddish-brown to amber by transmitted light.

C. A thick layer, dark brown to black by transmitted light.

1000X

FIG. 13.
PHOTOMICROGRAPHS OF FILM LAYERS APPEARING ON SURFACE OF STAINLESS STEEL (347) AFTER 3200 HRS IN URANYL SULFATE SOLUTION AT 250°C

SECRET
PHOTO E-873-4,
E-872-3,
E-840-1



A. Pre-treated in 1% nitric acid at 250°C
B. Pre-treated in 2% [illegible]c acid at 250°C
C. Pre-treated in 1% nitric acid and then immersed in 0.17 M uranyl sulfate solution containing 0.1 M nitric acid at 250°C. for 3200 hours.

9000 X

FIG. 14
ELECTRON MICROGRAPHS OF SURFACE REPLICAS OF STAINLESS STEEL 347

DECLASSIFIED

Examination of samples which had undergone in-pile corrosion tests seem to indicate the necessity of having as smooth a surface as possible on the stainless steel to avoid the building up of products formed in the solution.

STUDIES OF THE MICROSTRUCTURE OF THERMOCOUPLE AND BOMB ASSEMBLIES PREPARED BY INDUCTION BRAZING

Microscopic examination of the cross-sections of a number of samples of stainless steel assemblies prepared by induction brazing methods suggests that to avoid excessive grain growth in the affected zone of the assembly, and possible diffusion of the silver solder into the stainless steel matrix, it is necessary that the induction temperature not exceed 1850°F. Assemblies prepared at this temperature and below appeared to be acceptable with respect to mechanical qualities and possible future resistance to corrosion fatigue.

Figure 15 shows the microstructure of an assembly of the unheated parent metal in comparison with the microstructure of an assembly heated to a temperature exceeding 1850°F. Note the excessive grain growth and the diffusion of silver solder through the stainless steel matrix.

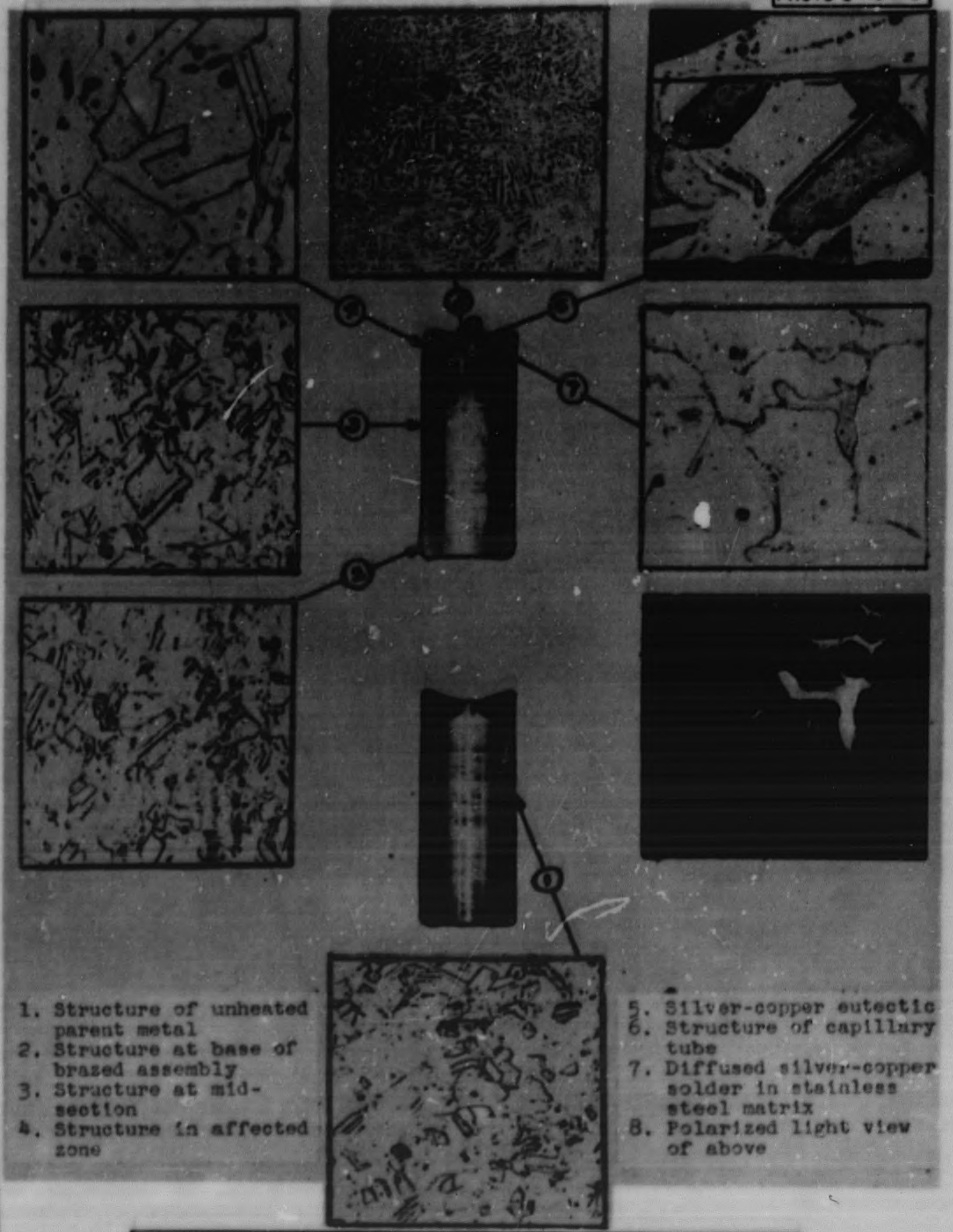
SUMMARY OF WORK DONE BY THE OPTICAL AND ELECTRON MICROSCOPY SECTION

During the period from Sept. 20, 1950 to Dec. 11, 1950 the following samples were received, microscopic work was done, photographs were taken, and prints were made:

Samples received		74
Electron micrographs (82 of 5 frames each)	410	
Electron diffraction patterns	6	
Metallographs	60	
Photomicrographs	40	
Lantern slides	15	
Copy plates	5	
Total pictures	536	
Prints made	1000 (approx.)	

The bulk of the work done in this section during the period has been in connection with various phases of the HRE project where microscopic investigation appeared to offer the most fruitful source of information.

NOT CLASSIFIED
PHOTO C-154-5



1. Structure of unheated parent metal
2. Structure at base of brazed assembly
3. Structure at mid-section
4. Structure in affected zone
5. Silver-copper eutectic
6. Structure of capillary tube
7. Diffused silver-copper solder in stainless steel matrix
8. Polarized light view of above

FIG.15
STRUCTURE OF STAINLESS STEEL (347) THERMOCOUPLE ASSEMBLIES BEFORE AND AFTER INDUCTION BRAZING

Although the above work was stressed, service work was continued in resinography, crystallography, metallography, and related fields. Particle size determinations on the electron microscope were made for K-25.

A large amount of time was also spent on spot observations for which no work requests were necessary, or on setting up equipment for the use of other members of the laboratory.

The electron microscope was disassembled and cleaned, electronic circuits were checked, the fluorescent screen was removed and rephosphored, and the stage was recentered and adjusted. The RCA field engineer, assisted by members of the laboratory staff, did this work.

ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

8 IONIC ANALYSES – RESEARCH AND DEVELOPMENT

COLORIMETRIC DETERMINATION OF IRON

H. P. House

A colorimetric method for the determination of iron in low concentrations in the presence of high concentrations of uranium, in which dimethylglyoxime was used as the chromogenic agent, was developed some years ago. This work was declassified recently, thus making it available for publication. A revision of the procedure in form suitable for publication is in preparation.

It is obvious that the list of components studied with respect to their interference, while adequate for the specific application for which the method was tested, is rather limited. A substantial extension of the interference tests requiring additional experimental work, would, no doubt, materially enhance the value of this study and is, therefore, being considered.

Also, some time has been given to a literature search covering work published since the completion of this study in order to determine whether a similar application has been reported. This literature survey is not yet complete.

DETERMINATION OF OXYGEN IN SODIUM

C. M. Boyd W. J. Ross
J. C. White

Although the method of Pepkowitz and Judd(1) has been adapted for the routine analysis of oxygen in sodium, it has not proved entirely satisfactory. The precision of the method has not been particularly good, and it does not permit a spectrographic analysis to be performed on the same sample. From the standpoint of uniformity and economy in sampling, it is important to find a method which will permit all desired determinations to be made on the same sample.

A search is being made for a reagent other than mercury which will take sodium into solution but will not react with or dissolve sodium monoxide. A

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

number of organic solvents were tested with regard to their reactivity with sodium and sodium monoxide. All these reagents were dried and distilled in accordance with standard procedures. Results, in decreasing order of reactivity with sodium, are presented in Table 16.

TABLE 16

Reactivity of Certain Reagents with Sodium and Sodium Monoxide

REAGENT	REACTION WITH SODIUM	REACTION WITH SODIUM MONOXIDE
Piperidine	Very rapid	Slow
Ethyl acetoacetic ester	Very rapid	None
Ethylene chlorohydrin	Very rapid	Slow
Monoethanolamine	Rapid	None
1,3-Diaminopropanol	Rapid	None
β-Diethylamine ethyl alcohol	Rapid	None
Ethyleneglycol monomethyl ether (methyl cellosolve)	Rapid	None
Ethyleneglycol monoethyl ether (ethyl cellosolve)	Rapid	Possible reaction
n-Hexanol	Fairly rapid	None
Ethyleneglycol monobutyl ether (butyl cellosolve)	Fairly rapid	None
Pyridine	Fairly slow	Fairly rapid
2-Methyl-2,4-pentanediol	Slow	None
Hydroxyethyl ethylenediamine	Slow	None
Acetonylacetone	Slow	None
tert-Butyl alcohol	Slow	None
Dimethyl dioxane	Slow	None
Isopropylamine	Very slow	None
Triethanolamine	Very slow	None
Ethyleneglycol dibutyl ether (dibutyl cellosolve)	Very slow	None
Ethyleneglycol	Very slow	Fairly rapid
Glyceral trichlorohydrin	Very slow	None
Aniline	Extremely slow	None
Trichloroethylene	None	None
Ethylene dichloride	None	None
Amylene dichloride	None	None

As may be seen from the table, nearly all the reagents investigated reacted with sodium, but the rate of the reaction differed widely. The monohydroxy-group compounds reacted with sodium to produce an insoluble residue which was quite basic and generally soluble in water. Compounds which contained an ethyleneglycol-ether linkage reacted vigorously with the evolution of heat and produced a dark-red solution. This solution, upon standing, was characterized by the formation of a residue which was readily soluble in water and which produced a basic reaction. The smoothest reaction occurred with monoethanolamine; ethyl acetoacetic ester and acetonylacetone were also satisfactory. These compounds were selected for further study. The other reagents are less promising because of their high viscosity and the jelly-like consistency of the compound formed by the reaction with sodium. Only a very few of the reagents dissolved or reacted with sodium monoxide.

Monoethanolamine was substituted for mercury in the Pepkowitz and Judd apparatus. Two bulbs of sodium from a batch which gave 0.02% oxygen when analyzed by the Pepkowitz and Judd method, gave 0.05% and 0.5% oxygen when monoethanolamine was used as the solvent for sodium. The second result is high because all the excess reagent was not removed before titration of the sodium monoxide solution. The reaction of monoethanolamine with sodium was accompanied by an evolution of considerable heat which caused the reagent to volatilize and condense on the walls of the reactor. The excess reagent, because of its high boiling point, cannot be removed easily. It is essential that all the excess reagent be removed since it is a weak base and will be titrated along with the sodium hydroxide formed when the sodium monoxide is washed out.

The sodium salt of monoethanolamine was evaporated to dryness with difficulty because of water-soluble residue deposited during evaporation. Attempts to add excess sulfuric acid and by evaporation to obtain the sodium as sodium sulfate were unsuccessful; the solution polymerized into a black tarry mass. These disadvantages indicate that monoethanolamine is not suitable for this purpose.

Further study of ethyl acetoacetic ester and acetonylacetone, along with other reagents, is contemplated.

The use of liquid ammonia for separating sodium from sodium monoxide has also been considered. Liquid ammonia has several advantages, particularly the ease with which it dissolves sodium metal, its probable nonreactivity with sodium monoxide, and its low boiling point, -33.5°C, which would permit rapid evaporation of the solvent from the sodium solution. This low boiling point is also its main disadvantage. Special vacuum-jacketed equipment and adequate protection for the operator would be required for handling the liquid ammonia. The possibility of using liquid ammonia will be investigated further if a suitable organic solvent is not found.

Methylamine or ethylamine, while they are likely to have a reactivity toward sodium and sodium monoxide similar to that of liquid ammonia, have a higher boiling point and do not require so much special equipment and handling. The closest homolog of ammonia available for experimental work was isopropylamine, which has a boiling point of 37°C. As noted in Table 16, however, it is quite unreactive toward sodium. Attempts are being made to obtain methyl- and ethylamines so that their specific reactivities with sodium can be determined.

Difficulty was encountered in preparing suitable samples to check the accuracy obtained by the Pepkowitz and Judd method. Samples were prepared by drawing molten sodium into an evacuated glass vial containing a weighed amount of mercuric oxide. However, the reaction between sodium and mercuric oxide to produce sodium monoxide was so vigorous that the glass vial was shattered.

Sodium was then added in the form of an amalgam to mercuric oxide. Determinations of the amount of oxygen so added were low, averaging about 50% of the actual amount added.

Samples were next prepared by adding sodium and mercuric oxide in separate glass vials to the reactor of the apparatus. A layer of mercury was placed in the reactor to fill the capillary of the stopcock. The vials were broken and the reaction was allowed to proceed inside the reactor. Test results for samples formed in this manner indicate that the reduction of mercuric oxide was complete. Representative results were as follows:

OXYGEN ADDED (%)	OXYGEN FOUND (%)
0.13	0.14
0.057	0.065
0.17	0.14

Work is also continuing on the improvement of the accuracy and precision of the Pepkowitz and Judd method.

A detailed study was made of the Pepkowitz and Judd method with regard to the actual time spent in the various operations when the method was performed on a routine basis. It was possible, on the basis of the study, to make several changes designed to speed up the operation. It was concluded that one man could be expected to do eight determinations per day and two men sixteen per day with apparatus consisting of two purification trains and four reactors. An interdepartmental report was written in which the results of the time study along with a detailed procedure are given.

An additional assembly of the Pepkowitz and Judd type for the determination of oxygen in sodium has been set up and tested. The equipment consists of a purification train and two reactors.

MICROANALYSIS OF SILICON CARBIDE

W. J. Ross and J. C. White

Some fourteen samples of irradiated silicon carbide were submitted for determination of free silicon and silicon dioxide. Since the average weight of the samples before subdivision for analysis was around 50 mg, a microanalytical method had to be used. When received, the total carbon, free carbon, and nitrogen contents of the samples had been determined. Results of spectrographic tests indicated that the samples contained about 0.5% Fe and 0.6% Ni along with traces of a number of other metals, including beryllium.

The Bureau of Standards method(2) for the analysis of silicon carbide does not distinguish between free silicon, silicon dioxide, and silicon carbide. All silicon is reported under the heading of "total silicon." The statement is made that existing methods for the separate determinations are of insufficient precision to warrant reporting as such.

A literature search was made for methods of separation and determination of silicon in the presence of the dioxide in silicon carbide. Conflicting statements pertaining to the reactivity of free silicon with sulfuric and hydrofluoric acids were noted. Reich(3) based a separation of free silicon from silicon dioxide on the assumption that silicon is unattacked by HF and

(2) National Bureau of Standards Certificates of Analysis of Standard Sample 112 (method for analysis of silicon carbide included therein).

(3) Naish, W. A., and Clennell, J. E., *Select Methods of Metallurgical Analysis*, p. 253, Wiley, New York, 1930.

H_2SO_4 while silicon dioxide reacts to liberate SiF_4. This treatment was repeated until a constant weight was obtained, after which HNO_3 was added along with HF to oxidize silicon to silicon dioxide and subsequently liberate SiF_4. However, Miklashevskii(4) reported that free silicon was extracted by treatment with HF and H_2SO_4. Kall(5) supported Reich's contention that silicon dioxide was removed by this procedure but also indicated that silicon was slowly attacked.

An investigation was made of the feasibility of Reich's method. Samples containing 5 to 10 mg of standard silicon carbide were treated with HF and H_2SO_4. The loss in weight was found to average 3%, but attempts to reach a constant weight by additional treatments, as suggested by Reich, resulted in further losses in weight.

A further search of the literature revealed that silicon metal exists in two allotropic forms, amorphous and crystalline, of which only the amorphous form reacts readily with HF. Some authors report that crystalline silicon is slowly attacked by HF and conclude that ordinary, free silicon is probably a mixture of the two forms. This conclusion was supported by the experimental results obtained in this laboratory when spectrographically pure silicon was treated with HF and H_2SO_4 and weighed. A small loss in weight occurred after each addition. When HNO_3 was added with HF, a vigorous reaction took place with complete volatilization of the element. It was concluded that Reich's method was of no value in this particular determination, since it cannot be assumed that all metallic silicon present in the samples is in the crystalline or nonreactive (to HF) form.

Britzke(6) proposed a method in which silicon carbide is volatilized in a stream of dry chlorine gas at high temperatures. He reported that silicon dioxide is not attacked. Mellor(7) stated that silicon is volatilized at 350°C as $SiCl_4$ but that the carbide does not react with chlorine below a temperature of 900°C.

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(4) Miklashevskii, A. I., "Rapid Determination of Silicon Carbide in Carborundum," *Zavodskaya Lab.* 7, 1433 (1938).

(5) Kall, G. A., "The Chemical Analysis of Refractory Hard Materials," *Oberflächentech.* 15, 159 (1938).

(6) Britzke, E., "The Separation of Silica from Silicon and Carbon," *Chem. Ztg.* 33, 1098 (1910).

(7) Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol. VI, p. 960, Longmans, Green and Co., London, 1925.

On the basis of this information, Bureau of Standards samples of silicon carbide weighing 5 to 10 mg were heated to constant weight in a stream of dry chlorine at 350°C. The losses in weight for three samples thus treated (1.71, 1.74, 1.74%) were remarkably constant. It is evident that chlorination of the carbide will yield reproducible results for loss in weight, but there is doubt as to whether the loss is due entirely to removal of the silicon. The Bureau of Standards reports 0.45% Fe present in their silicon carbide, some of which may be volatilized as $FeCl_3$. Only traces of iron, however, were found in the trap washings in the off-gas line. Aluminum (0.23%) may volatilize as $AlCl_3$ but only if it exists as the free metal, which is highly unlikely. The presence of silicon in the trap washings was confirmed by a qualitative test based on the blue color produced by the interaction of silicomolybdic acid and benzidine.

Synthetic samples prepared by mixing Bureau of Standards silicon carbide (freed of silicon and silicon dioxide by treatment with nitric, sulfuric, and hydrofluoric acids to constant weight) and silicon metal were also subjected to the chlorine treatment. The silicon, amounting to less than 5% of the 10-mg synthetic sample, was quantitatively removed. These samples, however, do not duplicate the conditions found in the actual sample.

The proposed procedure for determining silicon and silicon dioxide in the carbide is as follows: React the material with chlorine and determine the loss in weight. Also determine the amount of iron which is volatilized (by analysis of trap washings) and deduct this from the loss in weight. The loss in weight, corrected for iron, represents free silicon. Next, determine silicon and silicon dioxide together, the determination being based on loss in weight when a sample is treated with nitric, hydrofluoric, and sulfuric acids. This loss in weight minus free silicon yields the silicon dioxide content.

DETERMINATION OF TURPENTINE

J. C. White

The Health Physics Department has requested that a method be developed for the determination of small quantities of turpentine in samples of contaminated air. The samples will be taken in the vicinity of a machine tool, and it is anticipated that they may be rather heavily contaminated with graphite and oil.

A colorimetric method, based on the intensity of a blue color developed by the reaction between turpentine and vanillin in a hydrochloric acid solution, was investigated. This reaction is conducted in an alcoholic medium since the presence of water hinders the development of color. The common method of separating turpentine from its contaminants, namely, by steam distillation, was undesirable because it introduces water.

This investigation was divided into two phases: (1) the separation of turpentine from the graphite and oil in the sample by some method that avoids the introduction of water into the sample, and (2) the development of a chromatographic method for turpentine.

In pursuance of the first objective, a synthetic sample of 15 parts of turpentine to 1 part of graphite plus oil was diluted tenfold with alcohol and passed through a 20-mm column containing a 2 in. length of 60-mesh silica gel. The graphite and oil were retained at the top of the column, but most of the turpentine passed through. When the gel was washed with alcohol to remove the fraction of the turpentine which was adsorbed, a part of the oil was also carried through. In another test the sample was diluted tenfold with petroleum ether. In this case the oil was not carried through, but a greater portion of the turpentine was adsorbed.

A 20-mm column filled with 2 in. of fuller's earth was used to filter the sample. When alcohol was used as a diluent very little turpentine was adsorbed, and the small fraction which was adsorbed was removed by subsequent washing. No traces of oil were washed through the column as was the case when silica gel was the adsorbent. Adsorption-grade aluminum oxide also proved to be a satisfactory filtering agent. It has been concluded that the sample can readily be purified by this method for colorimetric analysis.

In an attempt to develop a chromatographic method for turpentine, experiments were performed with 8-mm columns containing about 12 in. of 60-mesh silica gel, through which alcohol-turpentine and petroleum ether—turpentine solutions, each containing 100 γ of turpentine, were passed. About 5 to 10 psi of nitrogen pressure was maintained at the top of the column to aid in increasing the flow rate. Petroleum ether solutions were far more satisfactory than alcoholic solutions with regard to flow rate. A 1% solution of vanillin in HCl was passed through the column for the purpose of forming a blue color with the turpentine, and alcohol was used to develop the band. A visible band was obtained from as little as 1 γ of turpentine. None of the bands formed, however, were well enough defined so that their lengths could be measured with any degree of accuracy.

It is believed that further work might lead to the establishment of conditions under which sharply defined bands would be developed. The width of the bands might then be related to the quantity of turpentine in the sample. At this point, however, the investigation was discontinued because of the pressure of other work. It appears probable that the desired analyses can be performed satisfactorily by the colorimetric method.

DETERMINATION OF CARBON IN ZIRCONIUM PHTHALATE

J. C. White

Certain test results for carbon in production samples of zirconium phthalate were at variance with the anticipated values, and a question was raised as to the reliability of the carbon determination on this type of material. To test this point, two Bureau of Standards samples of potassium acid phthalate were analyzed for carbon. The results were satisfactory, varying less than 0.2% from the calculated value. On the basis of these findings, together with the fact that the precision of previous carbon determinations on zirconium phthalate had been satisfactory, there seems to be little question as to the reliability of this carbon determination.

Tests were next made to determine whether the method of drying the sample (overnight at 150°C), which is received in the form of a wet cake, was satisfactory. A sample as received was divided into four portions. Each portion was dried by a different method, the dried material was analyzed for carbon and zirconium, and the C/Zr ratio was computed. The results were as follows:

METHOD OF DRYING	ATOMIC RATIO, C/Zr
Overnight at 150°C	8.21
3 hr at 150°C	8.15
Air-dried	8.34
Vacuum-dried	8.35

Since there is no significant difference in the C/Zr ratio, it may be concluded that the method regularly used for drying the wet cake is adequate and that no serious error is introduced by water left in the sample when thus dried.

DETERMINATION OF AMMONIUM PHTHALATE IN RECYCLE LIQUOR

W. K. Miller

In the zirconium refining process, which is now in the pilot plant stage of development, zirconium is precipitated from solution by the addition of ammonium phthalate solution. In a later step of the process, the ammonium phthalate is regenerated. Since it is necessary to adjust the concentration of the solution before the ammonium phthalate can be recycled to the precipitation step, a simple and rapid method of determining phthalate concentration was required.

The possibility of using conductivity measurements as the basis of this determination was first considered. It was found that a maximum conductivity was reached for a solution of ammonium phthalate when the solution was more alkaline than a *p*H of about 7.5 and that the value of the maximum conductivity depended on the concentration of phthalate. A working curve was constructed by plotting phthalate concentration versus maximum conductivity. By means of this curve the concentration of any pure ammonium phthalate solution could be determined by adjusting the *p*H of the solution with ammonium hydroxide and measuring the conductivity. However, high results would be obtained if appreciable concentrations of ionizable impurities were present.

One difficulty was caused by the high concentration and resulting high conductivity of the phthalate liquor, which exceeded 0.012 mho/cm, the maximum specific conductance which could be measured by means of the Leeds and Northrup conductivity bridge that was available. This bridge was altered by the insertion of an additional ratio resistor, thus permitting the measurement of conductivity in the desired range. A conductivity versus phthalate concentration curve is shown in Fig. 16.

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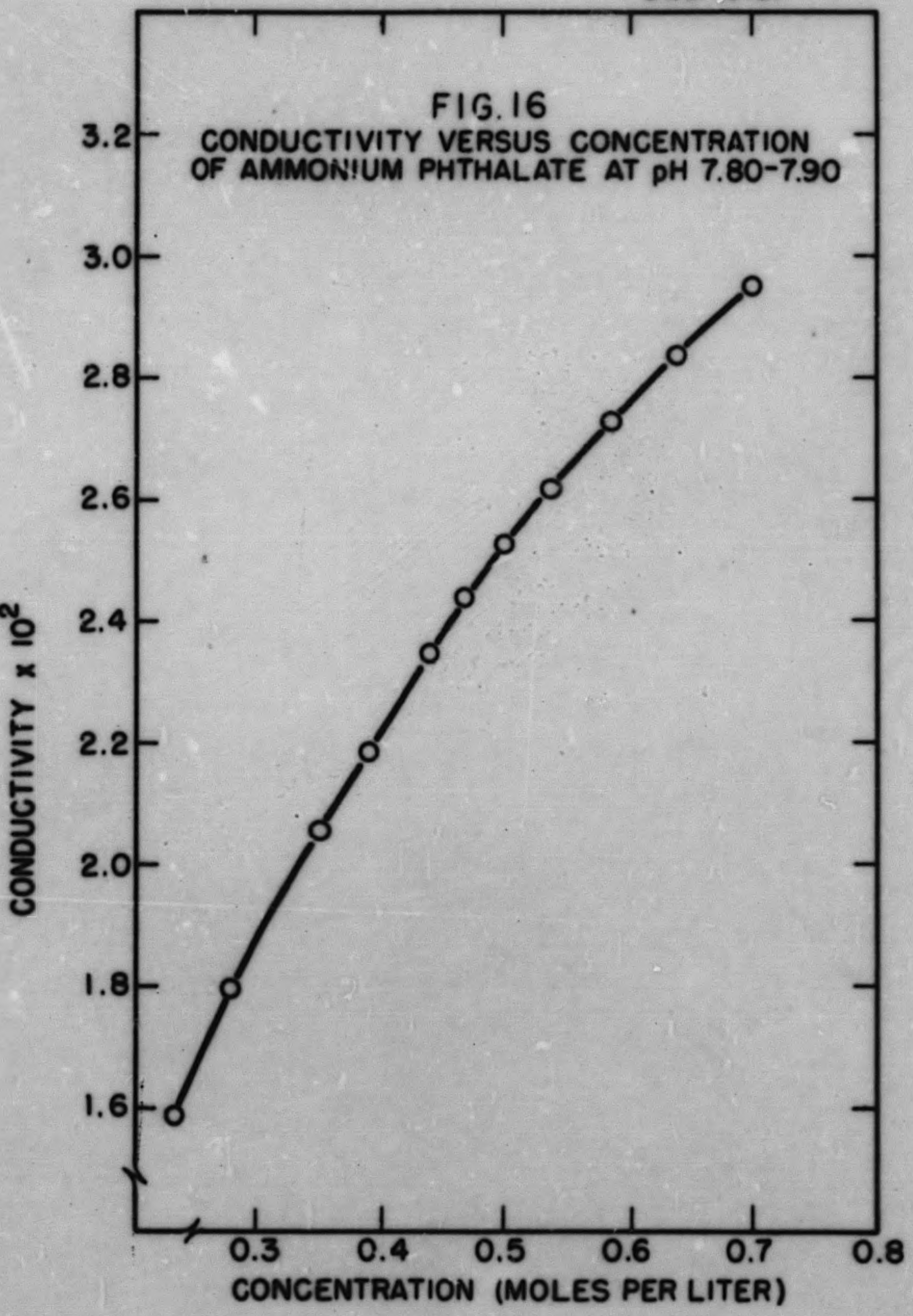

FIG. 16
CONDUCTIVITY VERSUS CONCENTRATION
OF AMMONIUM PHTHALATE AT pH 7.80-7.90

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Although satisfactory results were obtained when synthetic solutions of ammonium phthalate prepared by adding ammonium hydroxide to phthalic anhydride were analyzed, a number of samples of recycle liquors gave unusually high conductance readings. Further study indicated that the abnormal conductance values were due to a high concentration of ammonium chloride in the liquor, caused by incomplete washing of the zirconium phthalate precipitate after filtration.

Since conductivity measurements on actual recycle liquors were shown to be of no value, a method was sought for the determination of phthalate in the presence of high concentrations of ammonium chloride. A method based on ultraviolet absorption was next considered. This method, is, of course, subject to certain disadvantages which it was hoped to avoid by the use of conductivity measurements. Whereas an ideal method would be (1) rapid, (2) continuous-reading, and (3) capable of application without filtration or dilution of the solution, the absorption method requires filtration or centrifugation in addition to dilution and would be very difficult (although not impossible) to apply on a continuous basis.

For the absorption measurements it was necessary to choose a wavelength at which the thiocyanate ion, which may also be present, does not interfere. Measurements were made of the ultraviolet absorption spectra of the thiocyanate and phthalate ions in aqueous solutions of potassium thiocyanate and potassium hydrogen phthalate. The spectra are plotted in Fig. 17 (I and II). From these curves it appears that at any wavelength longer than 260 mμ the thiocyanate ion would not interfere.

The effect of *p*H on absorption of the phthalate ion was also determined by measuring the absorption of ammonium phthalate in excess ammonium hydroxide (*p*H 10.8) and comparing the resulting spectrum (Fig. 17, III) with that of potassium hydrogen phthalate (Fig. 17, II) in slightly acid solution. A definite shift of the absorption curve was noted, which indicated that the *p*H must be adjusted before the absorption method can be used. No further shift of absorption was observed in solutions which were more basic than *p*H 10. Thirty drops of 1:1 ammonium hydroxide per 100 ml of dilute ammonium phthalate solution was found to adjust the *p*H to approximately 10.8. The alkalinity of all subsequent test solutions was so adjusted.

From curve III of Fig. 17 it is evident that a wavelength of 271 mμ would be suitable for quantitative absorption measurements, since the spectrum is

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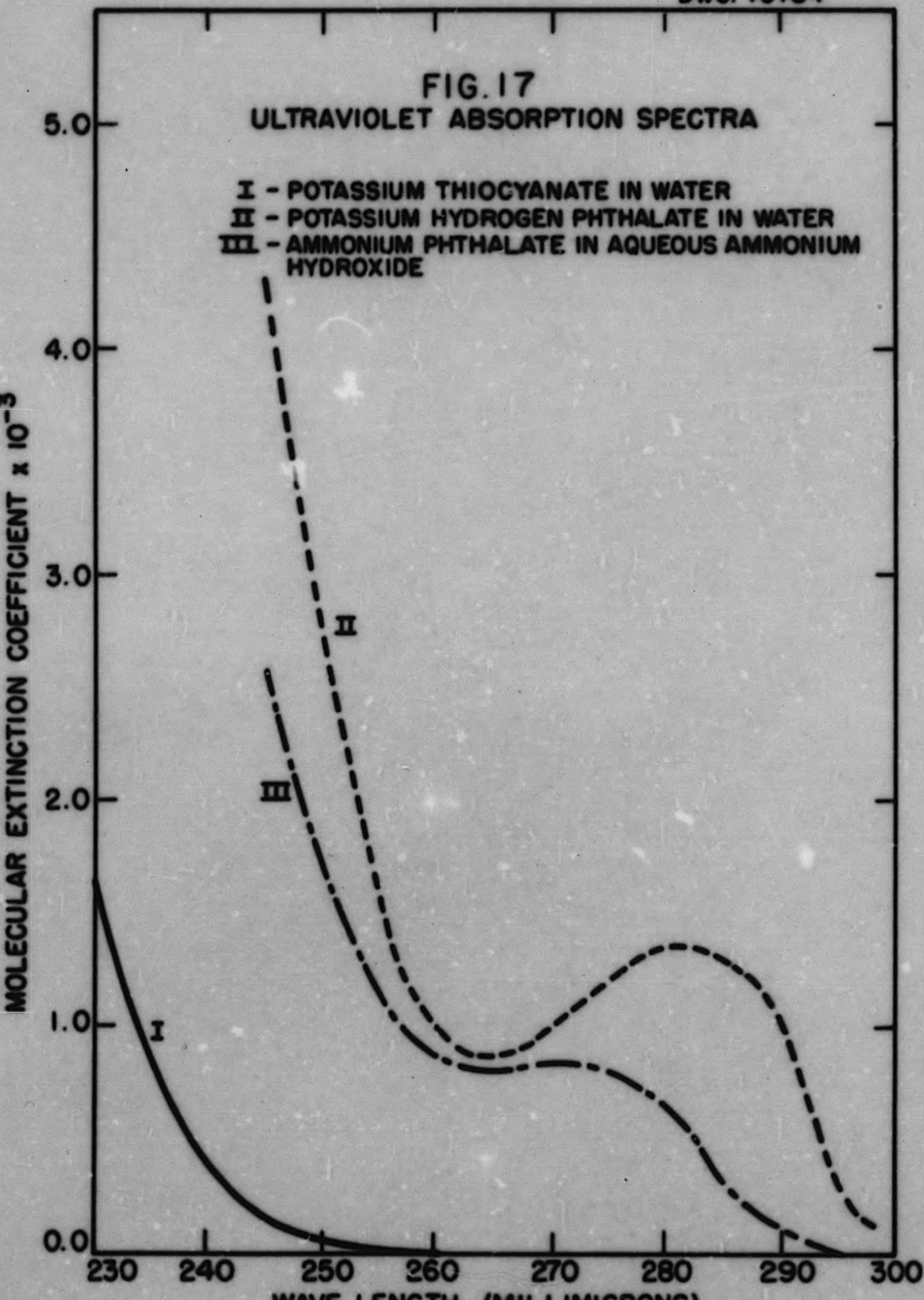

reasonably flat in this region and thiocyanate does not absorb. The probable range of phthalate concentration in the recycle liquor, furthermore, is such that dilutions of 1 to 1000 should be used for density measurements at 271 mμ.

A working curve representing the change of optical density with change in concentration of phthalate at *p*H 10.8 and 271 mμ was constructed (Fig. 18). The curve was tested by adding excess ammonium hydroxide to weighed quantities of phthalic anhydride, diluting to a definite volume, and measuring the optical densities of the solutions both with and without the addition of NH_4Cl and NH_4SCN. In every case, the measured densities were in close agreement with those for the corresponding concentrations as read from the standard curve. As an additional check, measurements were made on two samples of recycle liquor in which phthalate had been determined by the lead acetate method.(8) The results are shown in Table 17.

TABLE 17

Determined Concentration of phthalate

SAMPLE NO.	LEAD ACETATE METHOD* (moles per liter)	SPECTROGRAPHIC METHOD (moles per liter)
X_1	0.333	0.330
X_2	0.321	0.357

*The values determined by the lead acetate method were reported in terms of percent phthalate. In the conversion to molarity, a density value of 1.05 for the ammonium phthalate was used.

The accuracy which can generally be expected of an ultraviolet absorption method is of the order of 1 to 2%. It will be observed that in the case of sample X_1 the two methods check each other within this range. In the other case, the check is not satisfactory, and, in an effort to find the cause of the discrepancy, the determination of phthalate by the lead acetate method in sample X_2 is being repeated.

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

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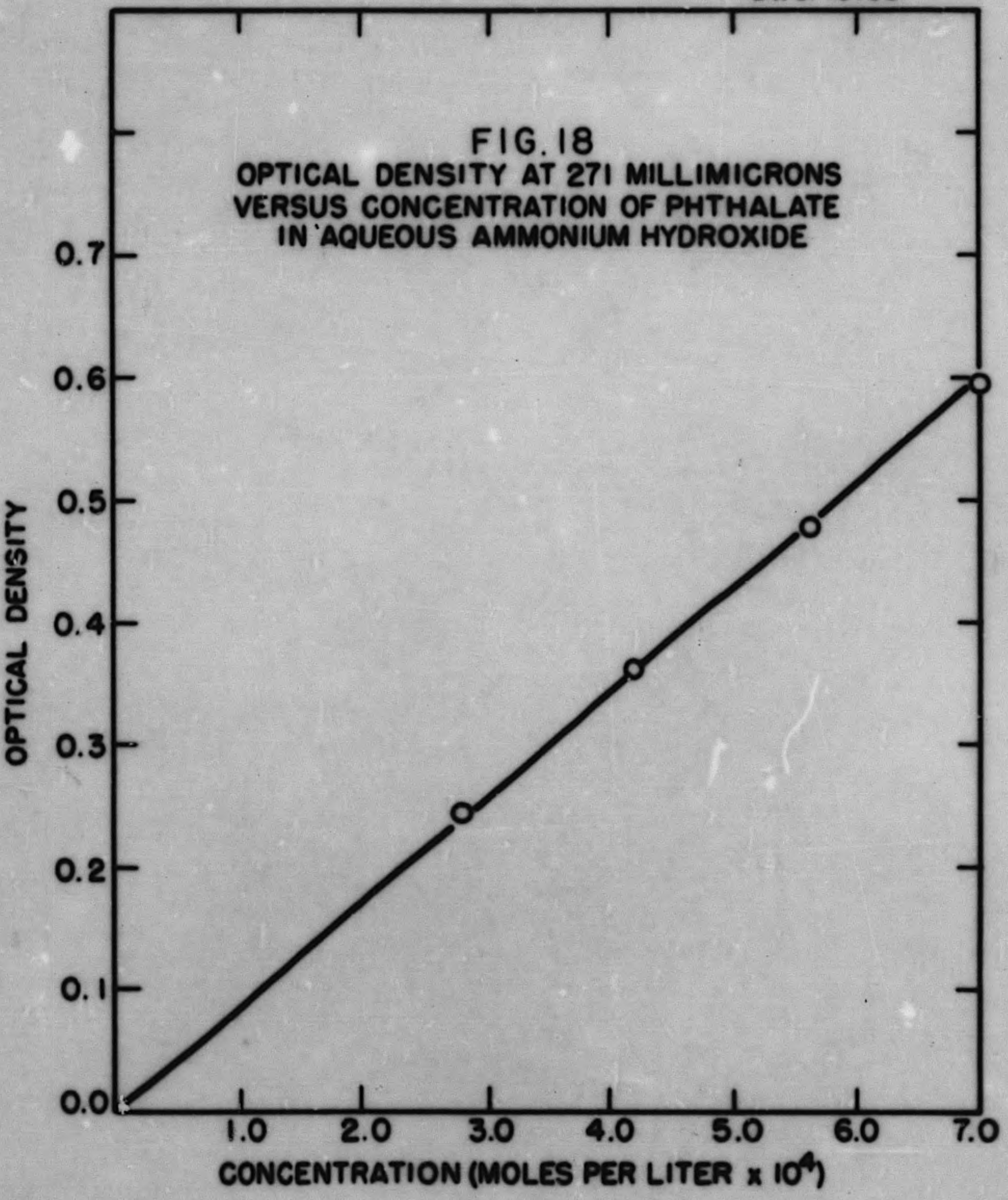

FIG. 18
OPTICAL DENSITY AT 271 MILLIMICRONS VERSUS CONCENTRATION OF PHTHALATE IN AQUEOUS AMMONIUM HYDROXIDE

While the results are encouraging, it cannot be said that the absorption method has been proved in actual practice. Further check measurements will be made on samples of recycle liquor for which phthalate concentrations are known as soon as these solutions become available.

The recommended procedure is as follows: A 5-ml sample of the recycle liquor, which is usually 0.3 to 0.6 *M* in phthalate, is diluted to 250 ml. A 5-ml aliquot of the resulting solution is pipetted into a 100-ml volumetric flask, 30 drops of 1:1 ammonium hydroxide is added, and the solution is diluted to the mark with distilled water. The optical density is then measured at 271 mμ by means of a Beckman spectrophotometer (Model DU) with a hydrogen-lamp ultraviolet light source. The phthalate concentration of the solution is determined by reference to the working curve (Fig. 18), and the concentration of the original recycle liquor can be calculated by multiplying the measured concentration by 10^3, the dilution factor. The method is not applicable in the presence of other ions which absorb appreciably at 271 mμ.

DETERMINATION OF AMMONIUM HYDROXIDE IN AMMONIUM PHTHALATE SOLUTIONS

W. K. Miller

In the zirconium refining process, the zirconium is precipitated as the hydrous oxide by the addition of an excess of ammonium hydroxide. For control purposes it is necessary to be able to determine the amount of excess ammonium hydroxide contained in the filtrate which also contains a high concentration of ammonium phthalate.

A simple, easily applied method was devised for determining the excess ammonium hydroxide in an ammonium phthalate solution. It was experimentally established that the *p*H of such a solution is a function of the concentration of ammonium hydroxide and, further, that the *p*H is little affected by dilution.

A standard curve was constructed by plotting the *p*H of a 0.7 *M* ammonium phthalate solution to which an excess of ammonium hydroxide ranging from 0 to 10% was added. By referring the *p*H of an ammonium phthalate—ammonium hydroxide solution to this working curve (Fig. 19), the percentage of excess ammonium hydroxide can be readily determined. The actual concentration of the phthalate, over a wide range of concentrations, is not a critical factor.

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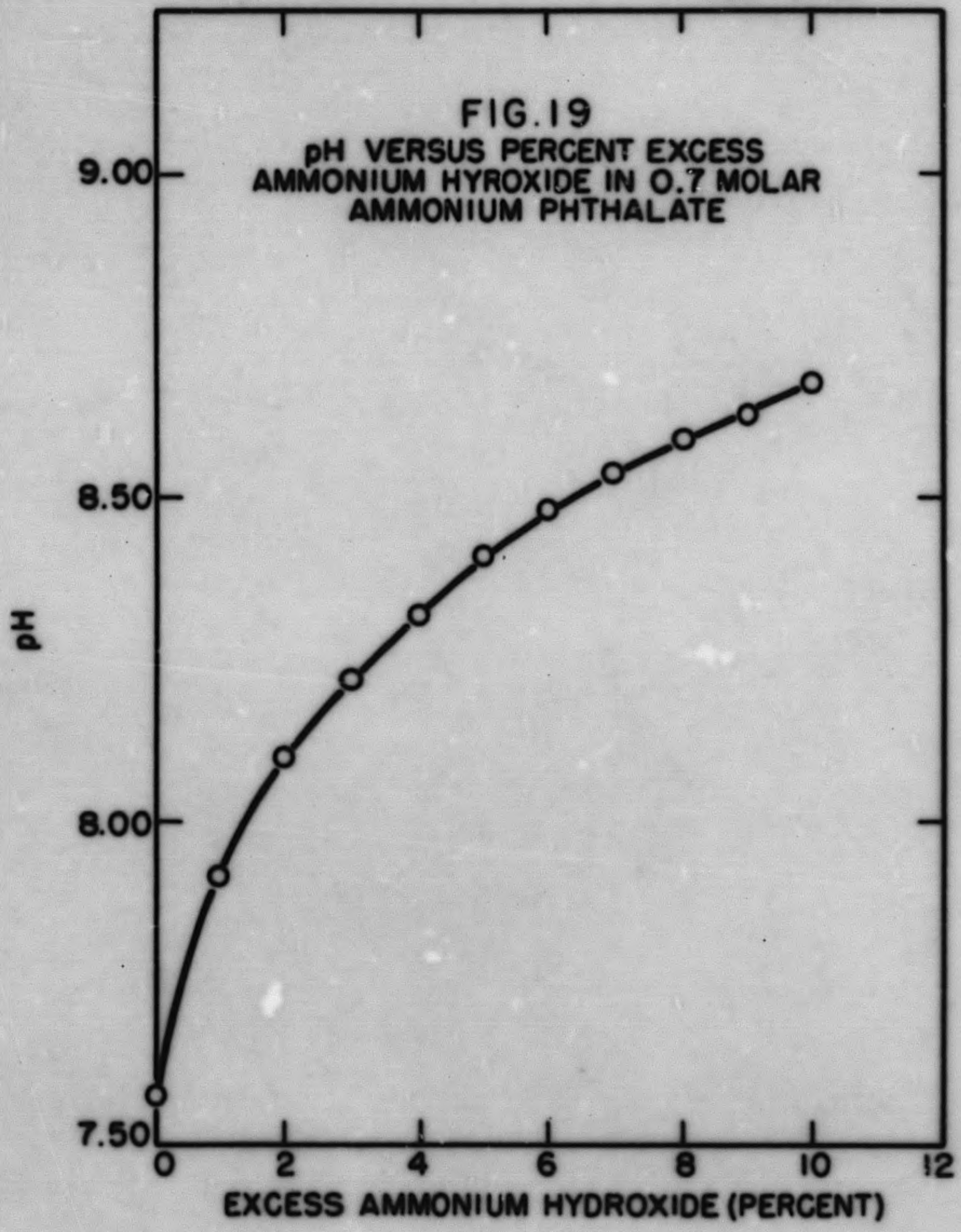

FIG. 19
pH VERSUS PERCENT EXCESS AMMONIUM HYROXIDE IN 0.7 MOLAR AMMONIUM PHTHALATE

DETERMINATION OF BORON

J. R. Lund and W. K. Miller

Efforts have been made to overcome difficulties encountered in the analysis of boron carbide, boron nitride, and other boron-containing materials for boron. This work has been closely correlated with the routine analysis of samples, and for this reason it is discussed in the section "Analytical Service Work for NEPA" on p. 110.

STABILITY TESTS OF A SILICONE OIL IN CONTACT WITH SODIUM

W. J. Ross and J. C. White

At the request of the ANP Experimental Engineering Group an investigation was made of the stability of Dow Corning Silicone Oil (DC 550) in the presence of sodium at elevated temperatures. This material is a clear, slightly yellowish liquid of exceptional heat stability, and it has a high resistance to oxidation, a low volatility, and a high flash point (600°F, minimum). Because of these properties it is being considered as a pressure-transmitting agent in equipment in which the oil would be in contact with sodium metal at temperatures of 300 to 350°F. In the event of certain types of failure of the apparatus, however, the oil would be in contact with sodium at considerably higher temperatures. This investigation was made because of the possible existence of an explosion hazard or of reactions which, though less violent, might produce deleterious effects.

In order to simulate conditions approaching those which might be encountered in the case of an apparatus breakdown, samples of oil and sodium were heated together at temperatures up to 1050°F. Four tests were made:

Experiment 1: Oil alone, short period, high temperature.
Experiments 2 and 3: Oil plus sodium, short period, high temperature.
Experiment 4: Oil plus sodium, long period, low temperature.

In each experimental run the sample was placed in a test tube under an atmosphere of helium, immersed in a lead bath behind a brick barricade, and viewed indirectly by means of a mirror. Temperatures were measured by a thermocouple which was inserted into the oil. The experimental observations are given in Table 18.

TABLE 18

Stability of Silicone Oil (DC 550) in Contact with Sodium

TEMPERATURE (°F)	EXPT. 1, 5 ml OIL, NO SODIUM	EXPT. 2 AND 3, 5 ml OIL, 0.1 g SODIUM	EXPT. 4, 5 ml OIL, 0.1 g SODIUM
75	Oil slightly yellow; n_{28}^{D}, 1.494	Sodium floated on oil	Sodium floated on oil
400 - 450	No change	Sodium melted, floated on surface of oil; no indications of reaction noted	Sodium melted, floated on surface of oil; temperature maintained for 6 hr and then tube removed from bath; no visible change noted
625		First indication of fumes	
700	Fumes observed	Oil began to fume steadily	
730	Steady boiling observed		
750		Oil began to darken slightly	
850	Profuse evolution of fumes		
900	75% of oil had volatilized; residue was viscous	About 60% of oil had volatilized; sodium still visible, oil definitely brown	
1000	Oil held at this temperature for 15 min and then removed from bath	Fuming ceased; residue boiled	
1050		After 30 min at this temperature oil was removed from bath; lumps of sodium observed but amount appeared to be slightly less than before heating	
75*	Residual oil very viscous; n_{28}^{D}, 1.513	Oil had polymerized into hard, oily, crystal-like solid; sodium still present as metal.	Oil appeared unchanged; sodium segregated in one mass

*After cooling test samples to room temperatrre.

It is evident that the presence of sodium in the oil at 1050°F caused the oil to solidify on cooling. The solid formed in experiments 2 and 3 was oily in nature, and individual particles were resistant to crushing between the fingers, insoluble in water and alcohol, and only slightly soluble in acetone. A qualitative test showed the presence of sodium.

A qualitative test for hydrogen made on the fumes liberated in experiment 3 gave negative results.

The lump of sodium was removed from the oil in experiment 4, and the oil was then shaken with water to extract any sodium that might be reacted. This water extract was basic whereas the water extract from the oil from experiment 1 was neutral. This fact indicates a possible reaction of sodium with the oil, even at the comparatively low temperature (450°F) reached in this test.

The results of these experiments indicate that Silicone Oil DC 550 is stable in the presence of sodium at 400 to 700°F for short periods and, therefore, can safely be employed as a pressure-transmitting agent.

9. SERVICE ANALYSES

IONIC ANALYSES — SERVICE GROUP

J. W. Robinson

The greater part of the increased work load evidenced during this quarter is attributable to the accelerated activity of the Materials Chemistry Division. Samples from X-10 sources were also analyzed.

The laboratory is now in possession of a precision Dow Recordomatic Titrator. It is anticipated that the potentiometric titrations that are required for a large number of uranium analyses as well as other titrations will be made much faster and with greater accuracy when this instrument is employed.

Some difficulty was experienced in the analysis for arsenic in synthetic leach solutions containing uranium, vanadium, arsenic, iron, and phosphate. The most expedient method of analysis appeared to be that in which the arsenic was separated as the sulfide and weighed. Attempts to separate the arsenic either as As_2S_3 or As_2S_5, however, failed to yield complete precipitation of the sulfides unless the initial precipitate was filtered off, the filtrate heated, and a second precipitation made. This second precipitation was undesirable because it was time-consuming and also because an appreciable amount of sulfur precipitated with the arsenic sulfide when the filtrate was heated, thus complicating the washing and purification of the precipitate. In addition, before the filtrate from the first precipitation was heated the presence of an excess of oxidizing or reducing reagent — depending on whether As_2S_5 or As_2S_3 was sought — had to be assured to avoid the precipitation of a mixture of the sulfides. Until a satisfactory alternate procedure is developed, arsenic will be separated by distillation.

Boron in concentrations of the order of 0.5 ppm was determined in samples of graphite. With slight modification, the methods described by Naftel(1) and by Staple *et al.*(2) were found to be adequate for making these determinations. These methods are based on the intensity of the color complex,

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(1) Naftel, J. A., "Colorimetric Microdetermination of Boron," *Ind. Eng. Chem. Anal. Ed.* 11, 7 (1939).

(2) Staple, E., Marshall, E. D., Nelson, F., and Simon, W., *A Method for the Determination of Boron in* TF_6, Report A-3629 (Mar. 18, 1946).

curcumin-boron, which is produced. The adequacy of these methods was proved by the "standard addition" technique.

The ascorbic acid method developed by Rothenberger and Grimes,(3) which is commonly used for the colorimetric determination of moderately low concentrations of uranium, was found to be applicable to solutions containing small quantities of vanadium provided that tartaric acid was added to the aqueous phase (70% saturated with calcium nitrate) to prevent extraction of vanadium into the diethyl ether phase along with the uranium. When, however, a fair amount of vanadium was present (10 mg or more), this procedure failed to prevent extraction of significant amounts of the vanadium by the ether unless the aqueous phase was completely saturated with calcium nitrate. Accordingly, the procedure of Rothenberger and Grimes was modified by bringing the calcium nitrate concentration in the aqueous phase to saturation prior to the addition of tartaric acid and the ether extraction. Under such conditions the extraction of vanadium was inhibited so that no interference was encountered in the determination of uranium.

The cadmium concentration of silver-cadmium alloys has been determined polarographically.

Colorimetric methods have been adapted to the determination of very low concentrations of components commonly found in corrosion-test solutions. Using these methods, the following elements can be readily determined when present in amounts as low as 2 γ/25 ml: Fe, Al, Ni, Mn, Mo, W, Cu, and Pb.

10 QUALITY CONTROL

R. L. McCutchen

CHEMICAL ANALYSES

Sodium Determinations. One or more sodium control samples was included with each group of regular samples analyzed for sodium by means of the Beckman flame photometer. In all, 35 such samples were analyzed during this quarter.

At one time during the period it became evident, through test results for control samples, that this determination was out of control. The difficulty was eventually traced to the need for replacing the amplifying tubes of the spectrophotometer; when the replacement was made no further difficulty was encountered.

Carbonate Determinations. For some time it has been apparent that there is a barely perceptible positive bias in the test results on control samples for the carbonate determination in the lowest range of concentration (approximately 0.6 mg/ml). In the highest range for which control samples were submitted (approximately 3.0 mg/ml), a bias of equal magnitude but of opposite sign has been observed. Attempts are being made to correct the difficulty, even though the discrepancies are so small as to be of slight practical importance.

Uranium Determinations. Uranium control samples were prepared by dissolving Bureau of Standards U_3O_8 in nitric acid. Suitable dilutions were used for checking the accuracy and precision of uranium determinations by three methods: (1) potentiometric titration,(1) (2) colorimetric by means of *l*-ascorbic acid,(2) and (3) fluorimetric.(3)

The test results indicate that the colorimetric and potentiometric methods are satisfactory with regard to accuracy. On the basis of the limited data available, however, it appears that there is a positive bias in the case of the fluorimetric method. The average values of the test results are presented in Table 21, along with other significant data.

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(1) Casto, C., Ealey, N., Smellie, R. H., Jr., and Price, T. D., *TEC-CEW Manual of Standard Analytical Methods*, Carbide and Carbon, Y-12 Report CD-3801 (December, 1945).

(2) Rothenberger, C. D., and Grimes, W. R., *Use of l-Ascorbic Acid as a Colorimetric Reagent for Uranium*, Carbide and Carbon, Y-12 Report M-4.360.13 (June 9, 1947).

(3) Grimes, W. R., *Analysis of Special Salvage Sample*, to C. D. Susano, Carbide and Carbon, Y-12 Memorandum Y-B32-15 (Dec. 5, 1947).

TABLE 21

Determination of Uranium

METHOD OF ANALYSIS	NUMBER OF DETERMINATIONS (N)	ACCEPTED VALUE (Y)	AVERAGE VALUE ($\bar{X} \pm ts/\sqrt{N}$)	STANDARD DEVIATION (s)
		Uranium, total milligrams		
Potentiometric titration	6	17.04	17.1 ± 0.1	0.08
	5	25.6	25.4 ± 0.5	0.17
	5	42.6	42.4 ± 0.2	0.12
		Uranium, milligrams/milliliter		
Colorimetric (*l*-ascorbic acid)	8	0.34	0.33 ± 0.024	0.02
	8	0.68	0.66 ± 0.030	0.02
	4	1.02	1.01 ± 0.03	0.01
		Uranium, milligrams/liter		
Fluorimetric	6	2.04	2.48 ± 0.23	0.14
	11	6.8	7.8 ± 0.45	0.40

t = probability factor at 99% confidence level based on $N - 1$ degrees of freedom.

s = standard deviation, $\sqrt{\Sigma(X - \bar{X})^2/(N - 1)}$.

$ts/\sqrt{N}$ = standard error of the average at 99% confidence level.

It will be observed that for the fluorimetric method, the differences between average test values ($\bar{X}$) and true values (Y) are well outside the limits imposed by the standard error of the average. The standard error states the reliability of the average on a 99% confidence level. It is clear, therefore, that a bias exists in this determination.

Too few control samples for uranium have been analyzed by the three methods to provide a basis for definite conclusions as to the precision attained. It is anticipated, however, that sufficient control data for this evaluation should be available for publication in the next quarterly progress report.

Uranyl Fluoride Analyses. A considerable number of uranyl fluoride solutions containing sodium, along with excess fluoride, are now being analyzed for uranium, fluoride, and sodium. A control program to check on the accuracy of these determinations has been started.

SPECTROGRAPHIC ANALYSES

A number of regular spectrographic control samples and special control solutions were analyzed spectrographically, using the porous cup method. It was found that more satisfactory results could be attained by this method if the solutions were prepared in glassware that had been cleaned by treatment with hot concentrated sulfuric acid followed by alcohol and water washes than if a cold nitric acid wash was used to clean the glassware. The sulfuric acid-alcohol cleaning procedure is now being used on all glassware intended for processing spectrographic test solutions.

A test was conducted to determine whether, in the usual procedure for the preparation of solutions for spectrographic analysis, the addition of 0.1 ml of platinum solution as an internal standard is accurate and reproducible. The conclusion reached was that no significant difference could be attributed to variations in the concentration of platinum when added in the usual manner.

A study of recent spectrographic test results on control solutions for sodium metal analysis indicates that there has been an improvement in both precision and accuracy. The improvement is believed to be due to the experimental work done by the spectrographic laboratory which has been aimed at satisfactory control of the variables found in the porous cup method of analysis.

11. INORGANIC PREPARATIONS

PURE ZIRCONIUM OXIDE

H. P. House

A report describing the preparation of zirconium oxide of purity suitable for use as spectrographic standard material is being written. Particular emphasis is being given to the method which proved successful, namely, the recrystallization of zirconium as the oxychloride from strong hydrochloric acid solutions. Other methods, which were tested but found to be less successful, are also treated but in less detail. The rather voluminous analytical data collected have been reviewed, and tables of selected data have been arranged to emphasize pertinent facts while avoiding loss of focus through the presentation of data in too much detail.

PREPARATION OF URANIUM NITRIDE

H. P. House

A quantity of uranium nitride (189 g) prepared by the Chemical Division at the Y-12 Plant has been added to the collection of uranium compounds which is maintained by the Analytical Chemistry Division.

PREPARATION OF PURE URANYL NITRATE SOLUTION

O. Menis

At the request of the Isotopes Analysis and Methods Laboratory of the Stable Isotope Division, a solution of uranyl nitrate was prepared, for use as a primary standard, by the following procedure. A weighed quantity of uranous fluoride was fumed with perchloric acid to remove fluoride. The solution was diluted and filtered. Ammonium hydroxide was added to the filtrate to precipitate ammonium uranate. The precipitate was ignited to the oxide at 800°C and then dissolved in an equivalent quantity of nitric acid.