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ANALYTICAL CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING JUNE 30, 1950

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ANALYTICAL CHEMISTRY DIVISION

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

QUARTERLY PROGRESS REPORT

for Period Ending June 30, 1950

DATE ISSUED: OCT 4 1950

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ABSTRACT

ANALYTICAL CHEMISTRY DIVISION—X-10 SITE

Ionic Analyses—Research and Development. A method for the determination of alkyl phosphates in the presence of uranium is described. The determination of bromide and bromine in sodium bromate has been made. A procedure for the colorimetric determination of fluoride in impure solutions is being investigated.

A polarographic method for the determination of total Sb in Sb^{124} has been tested. Vinylite samples have been polarographically analyzed for Cd. A procedure for the polarographic determination of uranium in the presence of orthophosphate or iron is suggested.

Radiochemical Analyses—Research and Development. The results of a program which was instituted to determine the efficiency of Krypton-filled G-M tubes for electromagnetic radiations of low energy are reported here.

The mass assignment has been checked and the thermal neutron cross section has been determined for Hg^{203}. The half-life, β max, and thermal neutron cross section for the production of Hg^{205} have been determined.

A discussion of the problems of C^{14} assay is included. A procedure for the determination of Ni^{63} and Ni^{59} has been developed. The determination of I^{125}, I^{126}, and I^{131} in I^{125} samples is described. A method for the determination of Np^{237} is reported. An ion-exchange method for the determination of possible impurities in phosphorus-bakelite samples is proposed. A procedure for the electrodeposition of U^{233} tracer has been tested.

Spectrochemical Analyses—Research and Development. Completed sections for the review of photographic photometry for the Committee E-2 of the American Society for Testing Materials are listed. New working curves are included.

Experimental Homogeneous Reactor Chemical Control. Preliminary investigations of methods are given by which chemical control of the reactor solution would be possible. The results of tests conducted on the laboratory scale for the regeneration of chromic acid in the experimental homogeneous reactor solution are included.

[redacted]

Optical and Electron Microscopy. Results of a study of the relationship of inclusion to the corrosion attack on QRM Beryllium and Bureau of Mines Zirconium are given. An electron micrograph of colloidal Dowex resin is included.

Analytical Service. A total of 36,688 analyses have been performed this quarter.

ANALYTICAL CHEMISTRY DIVISION—Y-12 SITE

Service Analyses. A total of 4050 analyses have been completed this quarter. The following programs have submitted samples: Zirconium purification and preparation; Uranium recovery in phosphate rock; Lithium isotope separation studies; Fundamental chemistry of uranium-carbonate and uranium-carbonate-fluoride systems. Samples have also been submitted by NEPA and various divisions at the Y-12 plant site.

Methods Development. A procedure for the determination of oxygen in zirconium metal is reported. A spectrographic method for the determination of airborne thallium is suggested. A method for the determination of nitrogen in argon has been tested.

ANALYTICAL CHEMISTRY DIVISION

X-10 SITE

IONIC ANALYSES—RESEARCH AND DEVELOPMENT

DETERMINATION OF ALKYL PHOSPHATES IN THE PRESENCE OF URANIUM

P. F. Thomason

The determination of phosphorus in the presence of uranium and various solvents was requested by W. H. Baldwin, who is making a study of extraction properties of alkyl phosphates.

Before conventional methods of analysis could be used, the alkyl phosphates had to be converted to ionic orthophosphates. Simmons and Robertson[1] recently reported a satisfactory method of conversion of both aromatic and alphatic organic phosphates by a catalytic reaction using H_2SO, HNO_3, and $HClO_4$ in the presence of sodium molybdate.

As it was not known whether uranium or various solvents would interfere with this method, a number of synthetic samples were made and converted to orthophosphate. The final determination was made by the AOAC[2] alkimetric phosphorus method. Several known inorganic orthophosphates were analyzed by this procedure in order to become familiar with the technique and also to standardize the standard caustic solution in terms of phosphorus. The synthetic samples contained 1 ml of 20% triethylphosphate in CCl_4 plus 1 ml of 0.2 *M* $UO_2(NO_3)_2$. These samples when treated by the usual catalytic conversion method, were prone to bump badly upon evaporation. The conversion proceeded smoothly, however, when boiling stones of fritted glass were substituted for boiling beads. The inorganic phosphates were recovered within ± 1%.

The results of the synthetic samples are shown in Table I.

These data show that uranium in concentration of 0.2 *M* does not interfere with this method.

---

(1) Simmons, W. R., and Robertson, J. H., "Determination of Total Phosphorus in Organic Phosphates," *Anal. Chem.* 22, 294 (1950).

(2) *Association of Official Agricultural Chemists, U. S. Dept. of Agriculture for Library of Congress*, p. 22 (1945).

TABLE I

Phosphorus Analysis of Mixtures of TEP, Uranium, and Carbon Tetrachloride

SAMPLE	COMPOSITION	P FOUND (mg)	P PRESENT (mg)
A	KH_2PO_4	19.8	20.0
B	KH_2PO_4	19.9	20.0
C	1 ml TEP (20% in CCl_4)	38.05	--
D	1 ml TEP + 1 ml 0.2 *M* $UO_2(NO_3)_2$	38.08	--
E	1 ml TEP + 1 ml 0.2 *M* $UO_2(NO_3)_2$	38.05	--

DETERMINATION OF BROMIDE AND BROMINE IN SODIUM BROMATE

P. F. Thomason

J. Cobble of the Chemistry Division is making a study of the decomposition effect of radiation on sodium bromate. It became necessary, therefore, to determine small amounts of bromides and bromine in sodium bromate. An automatic titration method with $AgNO_3$ for the determination of microgram amounts of halides has been previously reported.[3] This offered a convenient, fast method for the determination of bromide, but before the total bromide and bromine could be determined, any free bromine present would have to be reduced to the bromide without affecting the $NaBrO_3$.

High results were obtained when sodium sulfite was used to reduce the free bromine present. This was probably due to the partial reduction of the $NaBrO_3$ to bromide. A neutral 2.0% solution of sodium arsenite was made by dissolving pure $NaAsO_2$ in distilled water and adjusting the *p*H to 6.5 with

(3) Miller, F. J., "Determination of Chloride with the Automatic Titrator," *Chemistry Division Quarterly Report for Period Ending December 31, 1949*, ORNL 607, 187 (Dec. 21, 1949).

dilute HNO_3. Small aliquots of this solution were added to a bromine water solution, which had been previously standardized iodiometrically, and titrated for bromide. The results are shown in Table II.

TABLE II

Titration of Br Water (Containing 190 γ Free Bromine/ml)

SAMPLE	VOLUME	MICROGRAMS OF BROMIDE FOUND
1	0.1 ml	15
2	0.1 ml + .02 ml $NaAsO_2$	18
3	1.0 ml	159
4	1.0 ml + .02 ml $NaAsO_2$	184

These data show that approximately 85% of the bromine is titrated by the $AgNO_3$. When the $NaAsO_2$ is added to the bromine water, 97% of the bromine is titrated.

Several 10 ml aliquots of a neutral solution containing 1 g of pure $NaBrO_3$ in distilled water were titrated. This $NaBrO_3$ was found to contain 8 ppm of bromide. Sodium arsenite solution (20 λ) was added to several aliquots of the $NaBrO_3$ and titrated. No increase in bromide resulted. Several aliquots of the $NaBrO_3$ were spiked with a known amount of KBr and the sodium arsenite added. The results are shown in Table III.

TABLE III

Titration of 1 Gram $NaBrO_3$ + 80 Micrograms of Bromide

SAMPLE	BROMIDE FOUND
1	83
2	84
3	86

These data show that the $NaAsO_2$ does not interfere with the bromide titration. Therefore, several aliquots of the $NaBrO_3$ were spiked with known amounts of bromine water and KBr, treated with $NaAsO_2$ and titrated. The results are presented in Table IV.

TABLE IV

Titration of $NaBrO_3$ Containing Known Amounts of KBr and Br Water

SAMPLE	COMPOSITION	TOTAL Br^- AND BROMINE FOUND	PRESENT
1	1 g $NaBrO_3$ + 80 γ Br^- + 48 γ bromine	138	136
2	1 g $NaBrO_3$ + 50 γ Br^- + 48 γ bromine	108	106
3	1 g $NaBrO_3$ + 30 γ Br^- + 48 γ bromine	84	86

These data show that it is possible to determine the total bromide and bromine in bromate by using $NaAsO_2$ to reduce the free bromine. A number of irradiated samples have been analyzed by this procedure for Cobble and the results have been satisfactory.

POLAROGRAPHIC DETERMINATION OF ANTIMONY

P. F. Thomason

A radioisotope product, Sb^{124} in a HCl solution, had to be analyzed for total Sb content in order to determine the specific activity. A polarographic determination was desirable because of the high activity of the sample.

Kolthoff and Lingane[4] have reported a well defined wave with the dropping mercury electrode for the antimonite ion in 1 *N* NaOH at -1.17 volts vs. the SCE. This was verified by running polarograms of standard solutions made by dissolving pure antimony metal in a small amount of hot concentrated H_2SO_4 and diluting to a known volume with 1 *N* NaOH.

(4) Kolthoff, I. M. and Lingane, J. J., *Polarography*, New York Interscience Publishers, Inc., 262 (1941).

When polarograms were run of the Sb^{124} samples diluted in 1 *N* NaOH, waves were not obtained at -1.17 volts. It seemed reasonable to assume that the antimony had become oxidized to the quinquivalent state in the production process. The antimonate ion is probably similar to the arsenate ion[5] and, therefore, would not be reduced with the dropping mercury electrode.

Hillebrand and Lundell have reported[6] that quinquivalent antimony can be reduced to the trivalent state by an acidified solution of KI. A few crystals of KI were added to an aliquot of the Sb^{124} sample, followed by a few crystals of Na_2SO_3 to dispel the liberated iodine. The solution thus treated gave a normal antimonite wave at -1.17 volts vs. the SCE.

Duplicate samples of the Sb^{124} were run by this procedure using the standard addition method

POLAROGRAPHIC DETERMINATION OF SULFATES

A. D. Horton P. F. Thomason

The work on this project has been completed, and the report is now being written.[7]

COLORIMETRIC DETERMINATION OF FLUORIDES

A. D. Horton F. J. Miller
P. F. Thomason

Pure sodium fluoride solutions containing 5 - 500 γ F^- were successfully analyzed colorimetrically and the standard curve has been published.[8]

---

(5) Kolthoff, I. M. and Lingane, J. J., *op. cit.* p 262.

(6) Hillebrand, W. E. and Lundell, G.E.F., *Applied Inorganic Analysis*, New York, John Wiley and Sons, Inc., 232 (1929).

(7) Horton, A. D. and Thomason, P. F., *Polarographic Determination of Sulfates*, ORNL 755.

(8) Thomason, P. F. and Miller, F. J., "Tentative Colorimetric Method for the Determination of Fluorides," *Chemistry Division Quarterly Report for Period Ending March 31, 1950, Part II. Analytical Chemistry*, ORNL 686, 13 (May 18, 1950).

Separation of fluorides in the above range from impure solutions is proposed by using an adaptation of the Willard-Winter method.[9] These authors have reported that fluoride samples may be distilled with either perchloric or sulfuric acids and collected free of impurities provided the temperature during distillation does not exceed 135°C. This process was developed for analysis of samples containing 0.1 - 40 mg of fluoride. The distillate was analyzed by a photofluorimetric titration method using quercetin as a fluorescent indicator and titrating with thorium nitrate.

In the proposed modification of the Willard-Winter still, the sulfide micro still[10] has been altered to allow steam distillation, and a thermostatically controlled heater is used to heat the distillation flask.

The sample, made basic with NaOH, is boiled down to 2 ml in the distillation flask. A few quartz chips and 2 ml of 70% $HClO_4$ are added to the flask and sufficient NaOH is added to the receiver to maintain the *p*H of the distillate above the neutral point. The temperature is allowed to rise to 110-120°C. Steam is admitted to the flask and the thermostatic control is then set at 135°C and the temperature is allowed to rise rapidly to that point. (The most efficient distillation temperature is near the maximum of 135°C.) Eight ml of distillate are collected. To the distillate are added two crystals of KBr to reduce the chlorine oxides and sufficient 1% phenol solution to remove excess bromine.

One ml thorium nitrate (80 γ Th^{+4}/ml), five drops 13 *M* HCl and 250 λ 0.2% thoron reagent are added, and the volume is made up to 10 ml. Samples are compared in the Beckman Spectrophotometer at 545 mμ, with a blank which contains only HCl and thoron reagent.

Samples containing 40 γ and 50 γ F^- have been distilled under the above conditions, with fairly precise but low results. Since the results are consistently low, it is evident that a volume of 8 ml is insufficient to recover all the fluoride in the higher range. It is expected that a distillate volume of ~12 ml will be sufficient to recover all the fluoride within the specified range. The standard fluoride curve, therefore, will be based on a total volume of 15 ml.

---

(9) Willard, H. H. and Winter, O. B., "Volumetric Method for the Determination of Fluorine," *Ind. and Eng. Chem., Anal. Ed.* 5, 7-10 (1933).

(10) Boaz, H. E., Numerof, P. Portratz, H. A., and Throckmorton, W. H., *Chemical and Spectrochemical Analysis of Uranium and Plutonium Materials*, LA-416, 139 (Jan. 24, 1946).

POLAROGRAPHIC DETERMINATION OF CADMIUM IN VINYLITE

H. H. Miller

George Leddicotte has determined the amount of cadmium in vinylite by activation analysis. Since the manufacturer had submitted only approximate values for the concentration of cadmium present, it was essential that a series of results obtained by an independent method also be available.

It has been previously shown that low concentrations of cadmium can be polarographically analyzed.[11] If a suitable method could be found for destroying the vinylite without the loss of cadmium, the samples could successfully be analyzed polarographically.

A one gram sample of vinylite was treated with 25 ml of concentrated sulfuric acid and heated for about one hour. An addition of 10 ml of concentrated nitric acid was then made and the mixture was again heated until no solid material remained. Ten ml of 70% perchloric acid were added. The solution was heated until the oxidation of all organic matter was indicated by the clearing of the solution. This solution was transferred to a vitrosil dish and evaporated to dryness. The residue was taken up in 10 ml of 0.1 *M* $HClO_4$ and polarographically analyzed.

The results will be reported in the next report for comparison with the activation analysis results.

POLAROGRAPHY OF DILUTE SOLUTIONS USING THE CURVE-FOLLOWER

H. H. Miller

A report is in progress on the polarography of lead in concentrations ranging from 10^{-6} to 10^{-7} *M*.

POLAROGRAPHIC SERVICE ANALYSES

H. H. Miller

A number of service analyses have been completed with the polarograph this quarter.

---

(11) Miller, H. H., "Polarographic Determination of Cadmium in Cadmium Contaminated Aluminum," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950, Part II. Analytical Chemistry*, ORNL 686, 21 (May 18, 1950).

DETERMINATION OF SMALL AMOUNTS OF U(IV) IN THE PRESENCE OF LARGE AMOUNTS OF U(VI)

F. J. Miller

A suitable method was sought for the determination of U(IV) concentrations of less than 1% in the uranyl sulfate solutions which are to be used in the homogeneous reactor.

The following methods were investigated:

Method	Remarks
1. Direct titration of U(IV) with ferric sulfate	The inapplicability of this method is probably due to the small difference in the total U:U(IV) ratio
2. TTA extraction of U(IV) and subsequent colorimetric estimation	A recovery of about 60% was obtained.
3. Lanthanum fluoride carrier precipitation of U(IV)	The recovery was in the order of 80%.
4. Oxalate precipitation using thorium as a carrier	Approximately 60% of the U(IV) was recovered.

This is a summary of the preliminary work done. The lanthanum fluoride method shows the most promise and this will be more thoroughly investigated.

POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF ORTHOPHOSPHATE

F. L. Conover G. R. Wilson

The preliminary investigation of the effect of orthophosphate on the polarographic determination of uranium showed that the polarographic wave height of uranium in a solution containing orthophosphoric acid below a concentration of 0.2 *M* varied widely with the concentration of the orthophosphoric acid. If, however, the concentration of the orthophosphoric acid as a supporting electrolyte is held within the optimum limits of 0.2 *M* to 0.5 *M*, the

polarographic wave height is proportional to the concentration of uranium regardless of the concentration of phosphate within these limits.

A procedure has been suggested for the polarographic determination of uranium in solutions containing varying unknown concentrations of orthophosphoric acid by the standard addition method.

A summary of the investigations is tabulated below:

Series	Composition of Solution Analyzed	Results
I	0.02 *M* H_3PO_4 0.1 *N* HNO_3 Uranium conc. varied from 20 γ to 200 γ/ml	The wave heights were proportional to conc. of U. A straight line was obtained when the wave height versus the U(VI) concentration was plotted.
II	0.02 *M* H_3PO_4 0.1 *N* HNO_3 Sample 1. 240 γ U/ml Sample 2. 320 γ U/ml	Anomalous waves which could not be measured were repeatedly obtained. The anomalous effects of the presence of orthophosphoric acid on the polarographic detn. of U have been observed at various times.(12) Under these conditions, the maximum concentration of U that can be polarographically determined is 200 γ/ml.
III	U conc. constant at 0.0002 *M* (approx. 50 γ/ml) 0.1 *N* HNO_3 H_3PO_4 conc. was varied from 0.0002 *M*–2.2 *M*	The polarographic wave heights were plotted against the molarities of H_3PO_4 (Fig. 1). Although the wave heights increased rapidly with increasing phosphate concentrations in the lower ranges, they attained a constant value throughout the concentration range of 0.2 - 0.5 *M*. At higher phosphate concentrations, the polarographic waves exhibit very short base lines and are difficult to measure. Under these conditions, the wave height is independent of the phosphate concentration within the indicated range of 0.2 - 0.5 *M*. Figure 1 shows that in solutions of H_3PO_4 concentration substantially

(12) Marshall, E. D., Voss, F. S., and Baer, E. M., *Polarographic Determination of U(VI) in Solutions Containing Orthophosphate*, K-585 (Mar. 31, 1950).

Series	Composition of Solution Analyzed	Results
		lower than 0.2 *M*, the uranium wave heights will be lower than in solutions whose H_3PO_4 concentrations lie between 0.2 - 0.5 *M*. The plot of uranium wave heights in the solutions where the H_3PO_4 concentration was uniformly 0.02 *M* lies in a lower range than when the H_3PO_4 concentration is 0.5 *M*.
IV	0.5 *M* H_3PO_4 0.1 *N* HNO_3 Uranium concentration was varied from 20 γ - 320 γ/ml	Measurable uranium waves whose heights were proportional to the concentration of uranium were obtained.
V	0.84 *M* H_3PO_4 0.1 *N* HNO_3 Uranium concentration 320 γ/ml	This sample, with relatively very high concentrations of both uranium and phosphoric acid, gave a polarographic wave which was normal, readily measured, and whose height fitted the straight line plot of wave heights obtained in Series IV.

The following procedure is suggested for the polarographic determination of uranium in solutions containing varying unknown concentrations of orthophosphate: To a measured volume of the original solution, standard H_3PO_4 is added to make the H_3PO_4 concentration ~ 0.4 *M* (in addition to any phosphate that might have been originally present). HNO_3 need not be added. The polarogram is made, and the determination completed by the standard addition method.

The optimum concentration of uranium for this procedure lies in the range of 20 γ/ml to 100 γ/ml. If the wave first obtained indicates an exceptionally high or low uranium concentration, it is preferable to adjust the dilution of the sample so that the uranium concentration lies within, or near these limits. The concentration of added H_3PO_4 is maintained ~ 0.4 *M*. (This phosphate concentration corresponds to the "plateau region" indicated in Fig. 1 and also assures that it will remain in that region after enhancement by the standard addition.)

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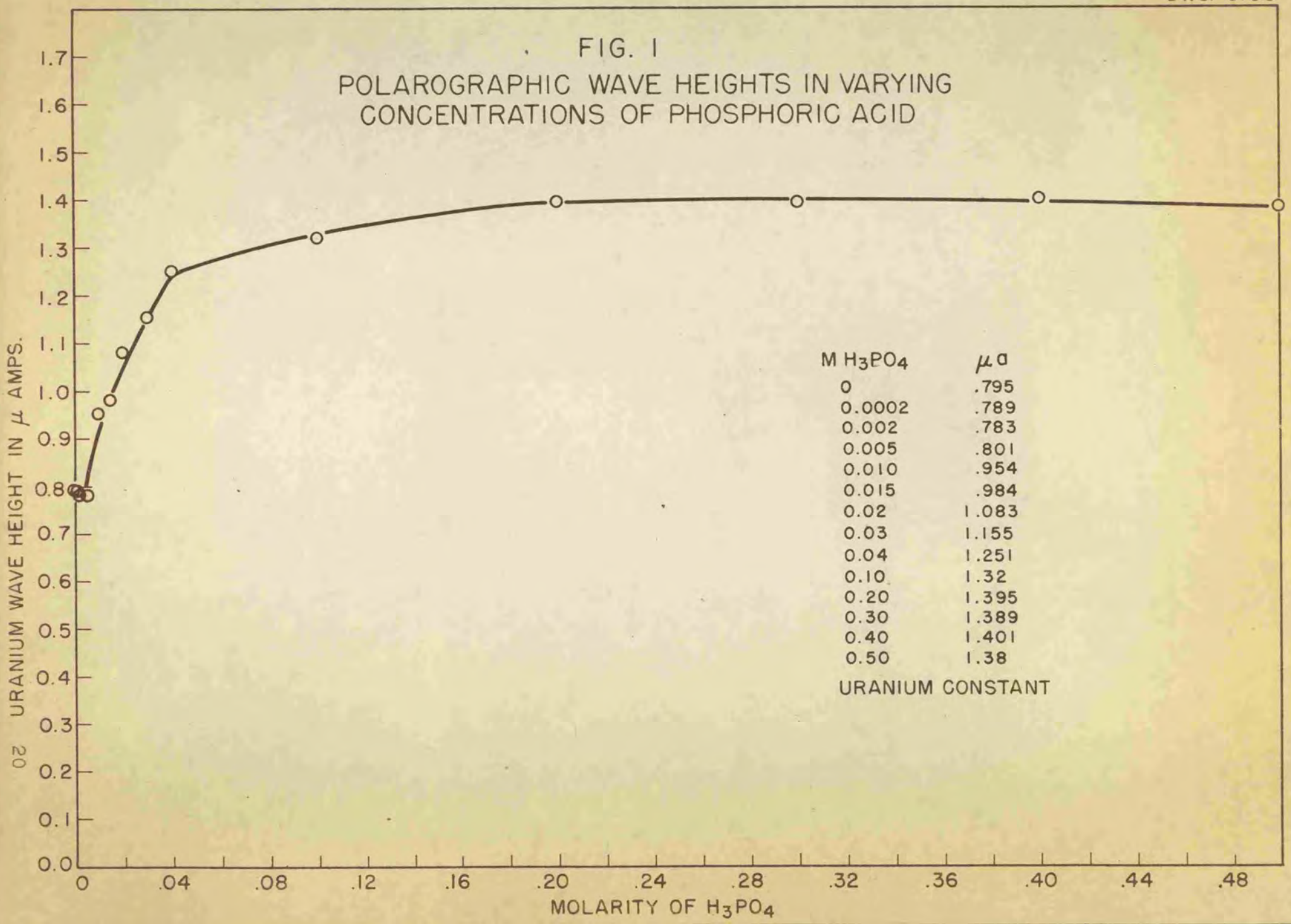
FIG. 1

POLAROGRAPHIC WAVE HEIGHTS IN VARYING CONCENTRATIONS OF PHOSPHORIC ACID



M H_3PO_4	μa
0	.795
0.0002	.789
0.002	.783
0.005	.801
0.010	.954
0.015	.984
0.02	1.083
0.03	1.155
0.04	1.251
0.10	1.32
0.20	1.395
0.30	1.389
0.40	1.401
0.50	1.38

URANIUM CONSTANT

To test this procedure, six samples containing varying uranium and phosphoric acid concentrations were prepared by Paul F. Thomason. These samples were analyzed polarographically by the suggested method and the results are tabulated below:

TABLE V

Analytical Results Obtained by Suggested Polarographic Method for Determination of Uranium

	U PRESENT* (γ/ml)	U FOUND (γ/ml)	ORIGINAL H_3PO_4* CONCENTRATION	PERCENT ERROR
A	215	211	0.02 *M*	1.9
B	115	112	0.04 *M*	2.6
C	185	178	0.06 *M*	3.8
D	45	47	0.10 *M*	4.4
E	87	86	0.20 *M*	1.1
F	22	22	0.30 *M*	0

* The uranium and phosphoric acid concentration were not known to the authors.

POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF FERRIC IRON

F. L. Conover G. R. Wilson

In some common supporting electrolytes the $Fe^{+3} - Fe^{+2}$ wave overlaps the $UO_2^{++} - UO_2^{+}$ wave. It was observed, however, that in the presence of H_2SO_4, the $Fe^{+3} - Fe^{+2}$ wave was shifted away from the uranium wave.

To study the effect of H_2SO_4 in varying concentrations on the polarographic wave height of uranium, a series of samples was prepared containing a constant concentration of 50 γ/ml of uranium and a concentration of H_2SO_4 varying from

0.1 *N* to 6.0 *N*. The uranium polarographic wave heights obtained were plotted against the H_2SO_4 concentrations, and a curve similar to the corresponding H_3PO_4 concentration curve (Fig. 1) with a well defined plateau extending from the concentration of 0.9 *N* to beyond that of 2.0 *N* was obtained.

The possible development of a procedure for the polarographic determination of uranium in the presence of both orthophosphate and ferric ions is now being investigated.

RADIOCHEMICAL ANALYSIS—RESEARCH AND DEVELOPMENT

MEASUREMENT OF RADIOACTIVITY

X-Ray Counting (W. S. Lyon and S. A. Reynolds). Because of the increase in the number of K-capturing isotopes now being processed at ORNL, a program has been instituted to determine the efficiency of Krypton-filled G-M counter tubes for electromagnetic radiations of low energy. The construction of an X-ray counter specifically for this purpose is being planned.

The procedure used in this work has been to determine the absolute disintegration rate of an X-ray source and then count this source on the X-ray counter. One then sets

$$\frac{(C/M)\ \text{abs.}}{E} = d/M,$$

where E is defined as an empirical efficiency, including fluorescent yield, counter geometry, and intrinsic efficiency.

To date, points have been obtained for characteristic X radiation from K-capture in Mn, Fe, Co, Zn, and Xe. As more K-capturing nuclides of known disintegration schemes become available, additional points will be obtained.

Coincidence Counting (W. S. Lyon, T. H. Handley, and S. A. Reynolds). The coincidence counter with tubes of various types operating in the proportional region, as well as an anthracene crystal with photomultiplier, is being used for routine radioisotope assays.

4 π Counter (T. H. Handley). In collaboration with C. J. Borkowski of the Chemistry Division, an investigation is being made on the use of a 4 π proportional counter in radioisotope assay work.

Use of "rhm" Unit (T. H. Handley). J. A. Cox (Operations Division) and his group have agreed that certain gamma-activity radioisotopes will be assayed by measurement of their gamma radiations in roentgens per hour at one meter distance, as recommended by Curtiss *et al.*[1]

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(1) Curtiss, L. F., Evans, R. D., Johnson, W., and Seaborg, G. T., "Units of Radioactivity," *Phys. Rev.* 77, 142 (1950).

ACTIVATION ANALYSIS

G. W. Leddicotte and W. H. Beamer*

Analyses are in progress on various types of samples, including resin, nickel, chromium, magnesium, and iron alloys, etc.

A method for the analysis of Li^6 will be attempted in which the activity of tritium produced by the reaction

$$Li^6 (n, \alpha) H^3$$

will be measured by means of an ionization chamber and a vibrating reed electrometer.

Chlorine in organic compounds will be determined by measurement of the activity of 38-minute Cl^{38}. Highly concentrated samples will be assayed by means of the gamma ionization chamber, while less concentrated samples in benzene solution will be measured in a jacketed counter.

TITANIUM DIOXIDE

G. W. Leddicotte

It is apparent from recent studies that the approximately 72-day activity assigned to titanium[2] is not a titanium activity, but appears to be Ta^{182}. Details will be reported when work now in progress is completed.

MERCURY

W. S. Lyon

Hg^{203}. Assignment of the 43-day Hg activity to the Hg^{203} nuclide has been reported by Slatis and Siegbahn.[3] Using electromagnetically separated Hg^{202} (97% enrichment), this mass assignment has been checked and the thermal neutron cross section has been determined.

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(2) Seaborg, G. T. and Perlman, I., "Table of Isotopes," *Rev. Mod. Phys.* 20, 585-667 (1948).

(3) Slatis, H. and Siegbahn, K., "Disintegration of Hg^{203}," *Phys. Rev.* 75, 318 (1949).

* Dow Chemical Co., working here for a short period time.

Procedure. 2.372 mg of the enriched Hg^{202} was irradiated in the ORNL reactor with a cobalt monitor. At the end of three weeks, the sample was removed and the decay followed on both a high pressure gamma chamber and a conventional thin end-window bell-type G-M counter. These decay data indicate the activity to be all of approximately 43-day half-life, thus confirming the mass assignment of 203.

Aluminum absorption curve data, obtained on a helium filled G-M counter which minimized the effect of X rays from the conversion of the 0.28 Mev gamma ray, indicate the presence of a large amount (about 30%) of conversion electrons which is substantial agreement with the spectrometer data of Saxon.[4] The beta ray component, after subtraction of the conversion electrons was observed to exhibit a half-thickness of about 3 mg/cm^2. Beta-gamma coincidences as a function of aluminum absorber placed before the beta tube were taken. The coincidence rate also showed a half-thickness of about 3 mg/cm^2. These data are in accord with the accepted disintegration scheme of 0.20 Mev beta followed by a single gamma ray of 0.280 Mev energy.

Using a total conversion coefficient of 25% for the 0.280 Mev gamma,[5] the activity of the source has been determined using the high pressure ion chamber and method described by Overman and Jones.[6] The agreement between the value so determined and that obtained using absolute beta counting techiques is within 5%.

Using the value of the average flux calculated from the activity of the cobalt monitor, the isotopic cross section for the reaction

$$Hg^{202}\ (n, \gamma)\ Hg^{203}$$

with pile neutrons has been determined. σ isotopic was found to be 3.8 barns. σ atomic is, therefore, 1.1 barns. The only previously published value is that reported by Way and Haines[7] who list σ isotopic as 2.4 barns.

Hg^{205}. Hg^{205} produced by the n, γ reaction on Hg^{204} has been reported in the literature[8] as being a pure beta emitter of 5.5 minute half-life.

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(4) Saxon, D., "The Beta Spectrum of $Hg^{(203)}_{(205)}$," *Phys. Rev.* 74, 849 (1948).

(5) *Ibid.*

(6) Jones, J. W. and Overmann, R. T., *The Use and Calibration of a 100% Geometry Ion Chamber*, AEC-2367 (1948).

(7) Way, K. and Haines, G., *Table of Neutron Cross-Sections*, MonP-405 (1947).

(8) Curtiss L. F. *et al.*, *op. cit.*

Using electromagnetically separated Hg^{204} (89% enrichment), the half-life, β_{max}, and thermal neutron cross section for the production of Hg^{205} have been determined.

Procedure. 23.8 mg of metallic Hg^{204} were dissolved in dilute HNO_3, and suitable aliquots of this material were taken for pile bombardment. After exposure in the ORNL reactor, portions of the irradiated samples were evaporated on watch glasses and the decay was followed for several days on a conventional thin-end-window G-M counter equipped with a scaler and an Esterline-Angus continuous recorder. After plotting the data and subtraction of the longer-lived weak activities due to contamination in the dissolving medium, the Hg^{205} was found to exhibit a half-life of 5.66 min.

Another aliquot of the Hg^{204} solution together with a known weight of Mn metal for a monitor was exposed in the ORNL reactor for 1190 seconds. At the end of this time, the Mn was placed in an ion chamber and its decay followed using a Brown recorder. A known aliquot of the Hg solution was then evaporated, and an aluminum absorption curve was run on a counter of known geometry. The absorption curve data when corrected for decay (Fig. 2), was utilized in the method of absolute β counting to determine the total Hg^{205} activity produced per known weight of Hg^{204} bombarded. From the decay data of the Mn^{56} on the high-pressure gamma chamber and the known efficiency for Mn^{56}, the total Mn^{56} produced by the activation was determined. From this value, the average neutron flux during bombardment was obtained from the expression

$$A = N f \sigma \left[1 - \exp\left(- \frac{.693\ t}{t_{1/2}} \right) \right],$$

where N, the number of target Mn atoms, and σ, the cross section for production of Mn^{56}, are known. The isotopic cross section for the reaction Hg^{204} (n,γ) Hg^{205} with pile neutrons was calculated using this value of the neutron flux, the activity of the Hg^{205} produced as determined from absolute β counting, and the weight of Hg^{204} which this activity represented. This value was found to be

$$\sigma \text{ (isotopic)} = .47 \text{ barns},$$

$$\sigma \text{ (atomic)} = .032 \text{ barns}.$$

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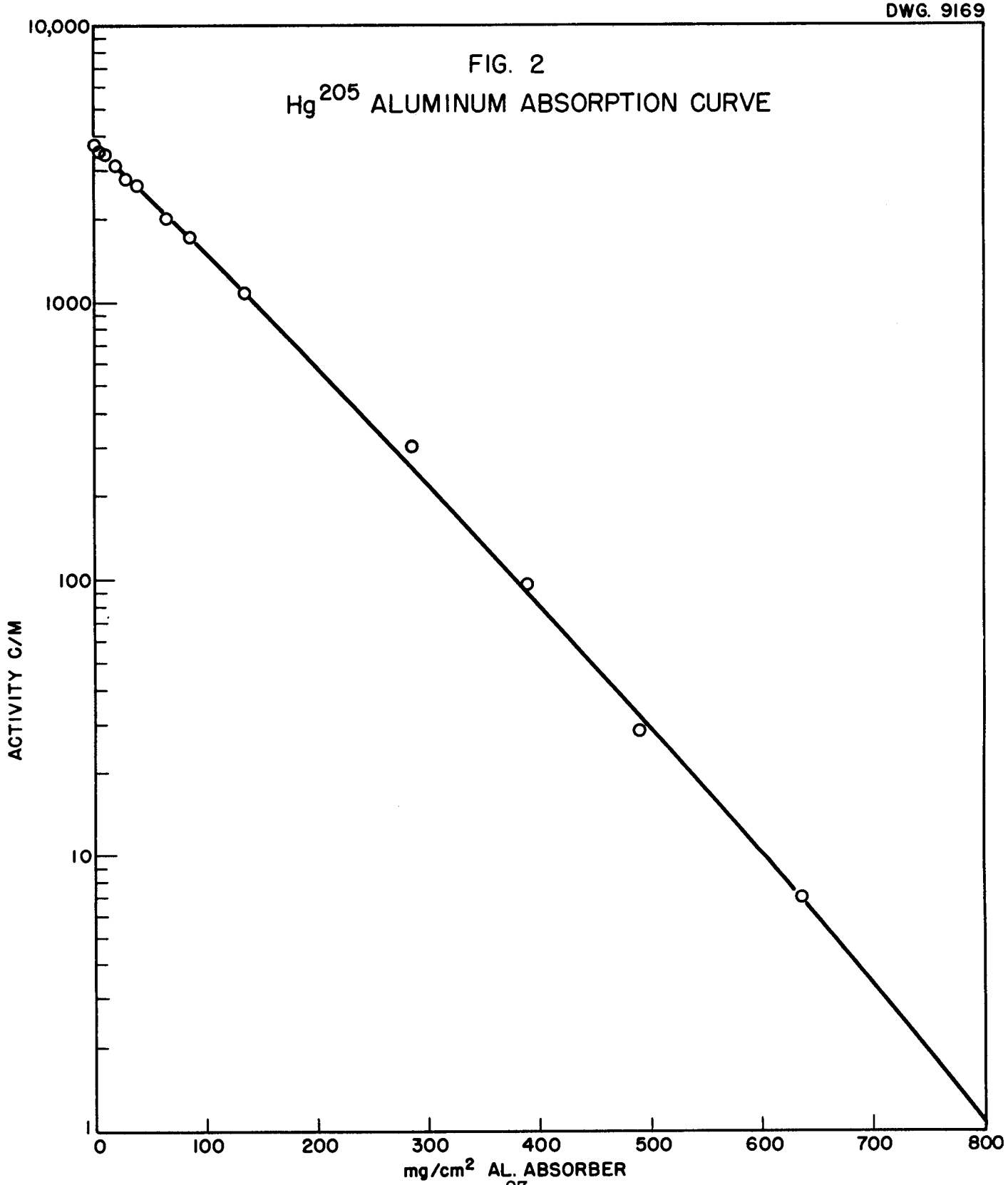

FIG. 2
Hg^{205} ALUMINUM ABSORPTION CURVE

The only other published data for this constant is 0.023 barns.[9]

Using P^{32} as a comparator, the absorption data mentioned above was treated by Feather analysis. The range of the simple β spectrum was found to be 813 mg/cm^2 of Al, corresponding to a maximum β energy of 1.75 Mev. Previously reported work of Kirshman and Nahum[10] lists 1.62 as the β end point.

PROBLEMS OF C^{14} ASSAY

W. S. Lyon

A survey has been made of the methods of production and assay of $BaC^{14}O_3$. On the basis of this work, recommendations have been made in a memorandum, adoption of which, it is felt, will result in a better product, more accurately assayed.

The following is quoted from the memorandum: "This summarizes a series of discussions with E. I. Wyatt of the Radioisotope Analytical Control Lab, E. M. King of Operations and in charge of C^{14} production, and C. J. Collins of the Radio-Organic Chemistry Group together with members of Dr. Collins' organization. The survey was undertaken in an effort to evaluate the present methods of C^{14} assay and at the same time to disseminate information about, and understanding of, the various problems and procedures involved in the production, analysis, and radio-organic chemical use of $BaC^{14}O_3$. Experimental evidence obtained by Collins' group indicates that $BaCO_3$ produced by operations is inhomogeneous. Some statistical data lend evidence to this view. Accurate assay of C^{14} products as now received appears to be difficult, if not impossible. The Radioisotope Analytical Lab in 706-D Building assays all C^{14} products. The routine method consists of packing ~ 125 mg $BaC^{14}O_3$ into a small uniform hole centered in a stainless-steel plate, and comparing the counting rate with that obtained by packing a similar plate with $BaC^{14}O_3$ of known composition. A primary standard is used to check the packing standards at the commencement of each C^{14} run, and over a period of several years no loss of activity has been observed. Comparisons have been made between the Bureau of Standards and D Bldg. and, in general, results have agreed quite well.

(9) Taylor, I. T. and Havens, W. W., Jr., "Neutron Spectroscopy for Chemical Analysis. III. Thermal Neutron Flux Applications," *Nucleonics* 6, No. 4, 54 (1950).

(10) Kirshman, R. S. and Nahum, E. A., "Deutron Bombardment of the Heavy Elements. I. Mercury and Lead," *Proc. Camb. Phil. Soc.* 36, 490 (1940).

"The primary uncertainty in all analytical methods at the present time is the lack of homogeneity of the product. Results from Dr. Collins' group indicate that the product is not homogeneous, and recently Dr. Beamer of Dow Chemical Company reported the same conclusion. Attempts to determine the precision of routine or gas analysis methods using inhomogeneous material thus appear to be of rather doubtful value. It is suggested that homogeneous $BaC^{14}O_3$ be used for a series of inter-comparisons for both precision and accuracy. It would also allow an evaluation of the routine method on an equitable and reliable basis. If the method is then indicated to be unsatisfactory, a change over to gas counting might profitably be made."

Mn^{52} and Mn^{54}

T. H. Handley S. A. Reynolds
W. S. Lyon

A 6.5 d Mn^{52} preparation has been assayed by means of the gamma ionization chamber, assuming the decay scheme of Peacock and Deutsch(11) to be valid. A determination has been made of 310 d Mn^{54} in a pure sample by gamma measurement and coincidence counting, employing the simple decay scheme, K-capture followed by 0.84 Mev gamma, of Deutsch and Elliott.(12) Mn^{54} in a Mn^{52} preparation is being determined by following the gamma decay.

Ni^{63} and Ni^{59}

T. H. Handley

The solubility of nickel (II) dimethylglyoxime in chloroform(13) provides a convenient means of separating Ni activity from other activities. With proper care, 100% recovery of Ni is obtained eliminating yield corrections which are troublesome when dealing with micrograms of material. Satisfactory separations have been made from a mixture of Fe, Co, and Zn activities. After separation, the Ni is electroplated on a platinum disk for counting. A self-absorption graph for Ni^{63} beta (Fig. 3) has been constructed since self-absorption is a large factor when dealing with the weak radiations of Ni^{63}.

(11) Peacock, W. C. and Deutsch, M., "Disintegration Schemes of Radioactive Substances IX. Mn^{52} and V^{48}," *Phys. Rev.* 69, 306 (1945).

(12) Deutsch, M., "Disintegration Schemes of Radioactive Substances. VII. Mn^{54} and Co^{58}," *Phys. Rev.* 65, 211 (1944).

(13) Sandell, E. B., *Colorimetric Determination of Traces of Metals*, New York: Interscience Publishers, Inc., pp. 342-3 (1944).

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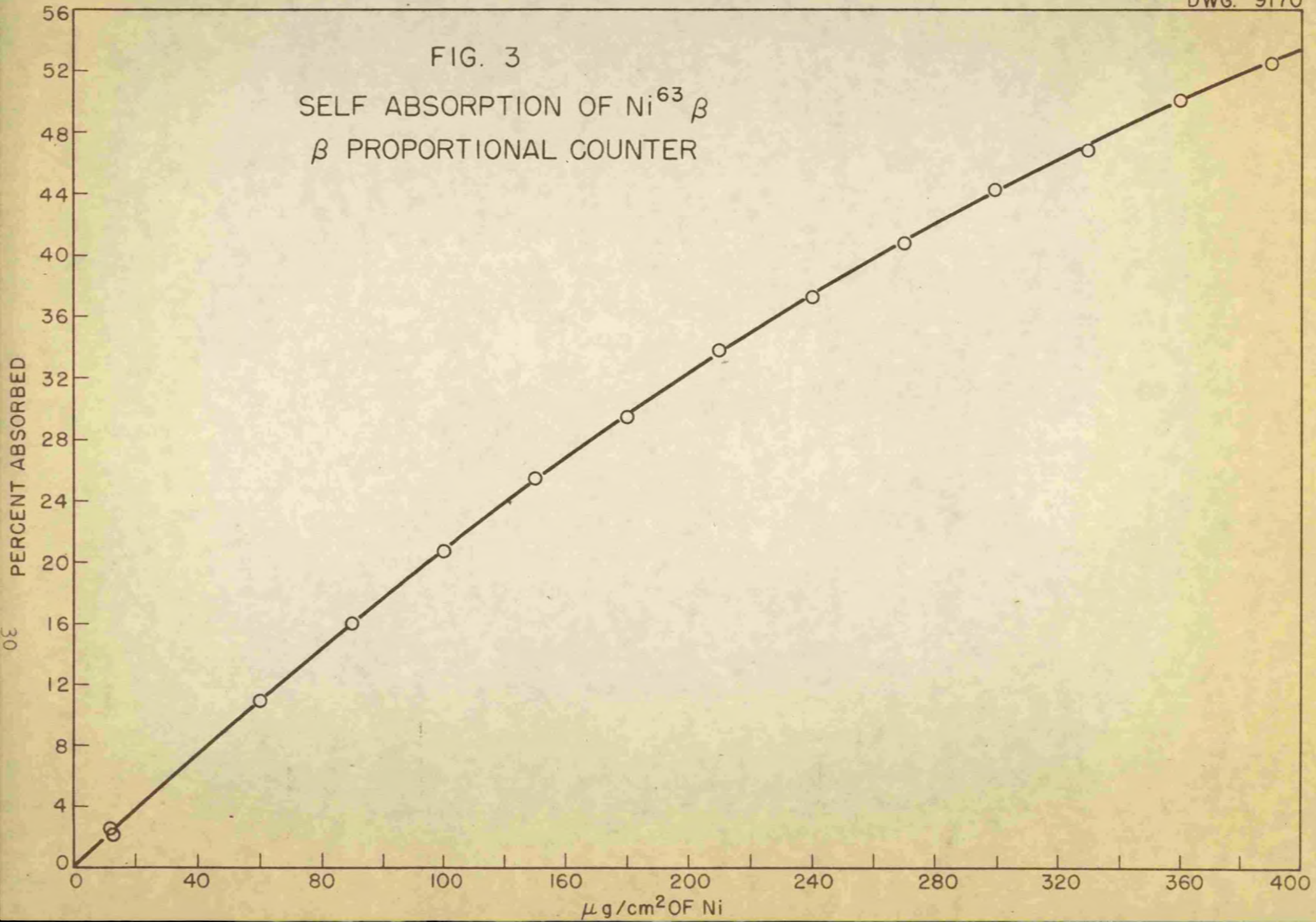

Using proper counting techniques Ni^{63} and Ni^{59} are determined from the same mount.

Procedure. Special solutions: Dimethylglyoxime, 1% in ethyl alcohol; sodium citrate, 10% in water; chloroform, reagent quality. To an aliquot of of the sample in slightly acid solution, add 100 to 200 micrograms of nickel carrier. Should the sample already contain inactive nickel, this must be determined by a colorimetric method and a proper aliquot taken. If the sample contains large amounts of contaminating activities and no carrier for these activities, separation will be enhanced by addition of holdback carriers for these activities. If large amounts of Mn are present, add a small amount of hydroxylamine hydrochloride to keep Ni reduced. Add 5 ml of sodium citrate or enough to keep iron (III), aluminum, etc. from precipitating and make slightly ammoniacal by adding a few drops of concentrated ammonia in excess. Add 2 ml of dimethylglyoxime solution and extract in a small separatory funnel with three 2-3 ml portions of chloroform, shaking for one minute each time. Allow the solutions to stand from five to ten minutes before attempting to separate the aqueous layer from the chloroform. Combine the extracts, shake with 5 ml of 1:50 ammonia, and transfer the chloroform into another separatory funnel; extract the water layer with 1 - 2 ml of chloroform and combine the latter with the washed extract. Remove the nickel from the chloroform by shaking for one minute with three portions of 0.5 *N* hydrochloric acid, each portion having a volume of 2 ml. Transfer the nickel solution to a special micro electroplating cell, add an excess of ammonia, and a small amount of ammonium sulfate.[14] A platinum disk one inch in diameter forms the cathode and a similar disk slightly smaller forms the anode. A wire gauze may be used, but it should have the same area as the area on the plate on which the Ni will be deposited. This is to insure a uniform current and prevent piling up of the nickel on the cathode which will materially affect the self absorption. The electroplating requires 15 to 20 minutes; care must be exercised to prevent spattering by raising the current too fast. The proper technique is to raise the current slowly toward the end of the period to a maximum of about two or three amperes. The cell is dismantled and the disk is washed with alcohol and dried. The area of the nickel film must be determined and the micrograms per cm^2 calculated. Percent of self-absorption may then be read from the graphs and corrections made on the counting rate. This graph is

(14) Sand, H. J. S., *Electrochemistry and Electrochemical Analysis*, New York: Chemical Publishing Co., Co., p. 75 (1946).

drawn from data of Brosi and Griess.[15]

To determine Ni^{63} content, the mount is counted on a slide chamber proportional counter using methane gas. A correction is made for a counting efficiency of 56%. This has been previously determined for betas of this energy.[16] The disintegration rate may be calculated with correction for aliquot taken or dilution made.

To determine Ni^{59} the sample is counted on an end-window Geiger-Muller tube. If sufficient time has been allowed for decay of Ni^{65} and Ni^{57}, only an X-ray component is observed. To obtain an absolute value, the counting efficiency of the tube for Co K X-rays must be determined from a known source. Also a correction for a fluorescent yield of ~ 0.33 for Co K X-rays must be be made. From these data, the disintegration rate is calculated.

The recovery of Ni carrier and its contamination by activities which might be present in a sample was determined. The procedure as previously outlined was used. Co, Zn, and Fe activities were added—total 1.5×10^6 cts/min. After separation, the Ni was checked for the sum total of contamination from these activities. Results are shown in Table VI.

TABLE VI

Yield of Ni and Contaminants

Ni TAKEN (γ)	Ni FOUND (γ)	TOTAL CONTAMINATING ACTIVITY (cts/min)
75.0	75	49
75.0	77	80
87	86	48
87	87	106

Ni was determined colorimetrically using dimethylglyoxime. In each case, a control was run under identical conditions and gave identical results. Due to the complete recovery of the nickel, this determination on each sample

(15) Brosi, A. R. and Griess, J. C., "Decay Constants of Ni^{59} and Ni^{63}," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1949*, ORNL 499 (Dec. 6, 1949).

(16) Griess, J. C., Brosi, A. R., and Zeldes, H., "Counting Yields of Low Energy Beta Emitters," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1949*, ORNL 286, 104 (Sept. 14, 1949).

can be eliminated and final calculations are simplified. Contamination from those activities tested, which are most likely to give trouble, is negligible.

Se^{75}

T. H. Handley

Two samples of Se^{75} were submitted for analysis. Aliquots of the submitted samples were placed in distillation flasks. Se, As, Sn, Sb, and Ge carriers and HBr were added. Heat was applied. The distillate containing Se, As, and Ge was caught in a hydrochloric acid solution and Se was then precipitated with sulfur dioxide. Examination of the residue after distillation and of the liquid residue after precipitation did not show the presence of radioactive impurities.

MEASUREMENT OF A PURE SAMPLE OF Se^{75}

T. H. Handley

Procedure. The activity of a pure sample of Se^{75} was measured with a coincidence counter and the gamma ion chamber. Coincidences were counted between the X ray and the stronger gamma radiation. (All the other gammas were absorbed by placing 3.0 g/cm^2 of Pb in front of the crystal on the gamma side.) The gamma-ion chamber calculations were made on the basis of the stronger gamma also. Checks were obtained between these methods.

Of course, this method is probably in error because Se^{75} probably does not decay 100% by the stronger gamma and no corrections were made for the internal conversion of the weaker gammas when measuring the X rays. Other errors may also be present, but until more is known about the decay scheme this method is recommended.

Nb^{95} IN SOLUTION CONTAINING ORTHOPHOSPHATE

R. B. Hahn

Difficulties were encountered in determining the Nb activity in a solution containing phosphoric acid. When the usual procedure[17] was followed, yields

(17) Hume, D. N. *et al.*, *Radiochemical Determination of Fission Product Activities*, CN-2815 (1945).

greater than 100% were obtained. A spectrographic analysis of the final precipitate showed it to be contaminated with phosphorus (probably in the form of $PO_4^{\equiv}$ or P_2O_5). The presence of the phosphate also caused some zirconium to be carried down in the final precipitate.

A study of the coprecipitation of phosphates with Nb showed that approximately 1 mole of P_2O_5 is carried down with 1 mole of Nb_2O_5. This suggests the possibility of the formation of a compound of niobium and phosphate. Since no such compound has been reported in the literature, a further investigation will be made.

The following methods were tried in an attempt to remove the phosphate from the niobium:

Method	Results
1. Precipitation of niobium hydroxide by addition of NaOH or NH_4OH	Phosphate coprecipitated with niobium
2. Precipitation of ferric phosphate in slightly acid solution (Niobium present in solution as perniobic acid)	Niobium was carried down with ferric phosphate
3. Precipitation of phosphate with $ZrO(NO_3)_2$ (Niobium present as perniobic acid)	Niobium was carried down with zirconium phosphate. 10 - 20% recovery of the niobium tracer used was obtained
4. Precipitation of phosphate in alkaline solution as $MgNH_4PO_4$	Low yields were obtained as in (3)
5. Precipitation of niobium with an an excess of iodic acid, HIO_3	This precipitate does not carry down as much phosphate as other niobium precipitates. The method will be further investigated to determine whether sufficient decontamination from other fission materials can be obtained

I^{125}

E. K. Wilson* and S. A. Reynolds

I^{125} samples were submitted for the determination of I^{125}, I^{126}, and I^{131}. The samples, which had been radiochemically separated, were counted on an

* Née E. V. Kazlauskis.

X-ray counter with a 0.99 gram beryllium absorber. The aluminum absorption curve data showed the X-ray component to exhibit a half thickness of ~ 500 mg/cm^2 Al (Fig. 4). The X-ray counter was calibrated with I^{129}. After the disintegration rate of I^{129} was determined on a coincidence counter,[18] a count was obtained on the X-ray counter and suitable corrections were made for the difference in the type of X rays emitted.

Aluminum absorption data were obtained on a helium filled G-M counter which minimized the effect of X rays. The curve was resolved into three components—gamma and two betas whose half-thicknesses were approximately those expected for I^{126} and I^{131} on the basis of their beta energies. The apparent ratio was 1:1.

A sample volume of 1 ml was sealed into a pyrex tube and the decay was followed for twenty-seven days with a gamma chamber. The decay curve could not be resolved into component parts. The apparent half-life was ten days (Fig. 5).

By means of the simultaneous equations

$$A = A^{\circ}_{126} + A^{\circ}_{131}$$

$$A^{1} = A^{\circ}_{126} \exp(-\lambda\ 126\ t) + A^{\circ}_{131} \exp(-\lambda_{131}\ t)$$

the activities due to I^{126} and I^{131} were calculated to be present in a ratio of approximately 1:1.

ANALYSIS FOR TRANSURANIUM ELEMENTS—Np^{237}

F. L. Moore

Procedure for Np^{237}. Development of the following routine procedure will be described in detail in a separate report:

1. Take a 1 ml aliquot of sample in a 5 ml test tube. Add 1 ml of HCl to make a total acidity of ~ 4 *M*.
2. Add 0.4 ml of NH_2O-HCl (1 *M*); warm in boiling H_2O bath ~ 1 min. Add 2-3 drops of $SnCl_2$ (1 *M*) and 1.6 ml of KI (5 *M*). Allow to

(18) Jones, J. W. and Overman, R. T., *op. cit.*

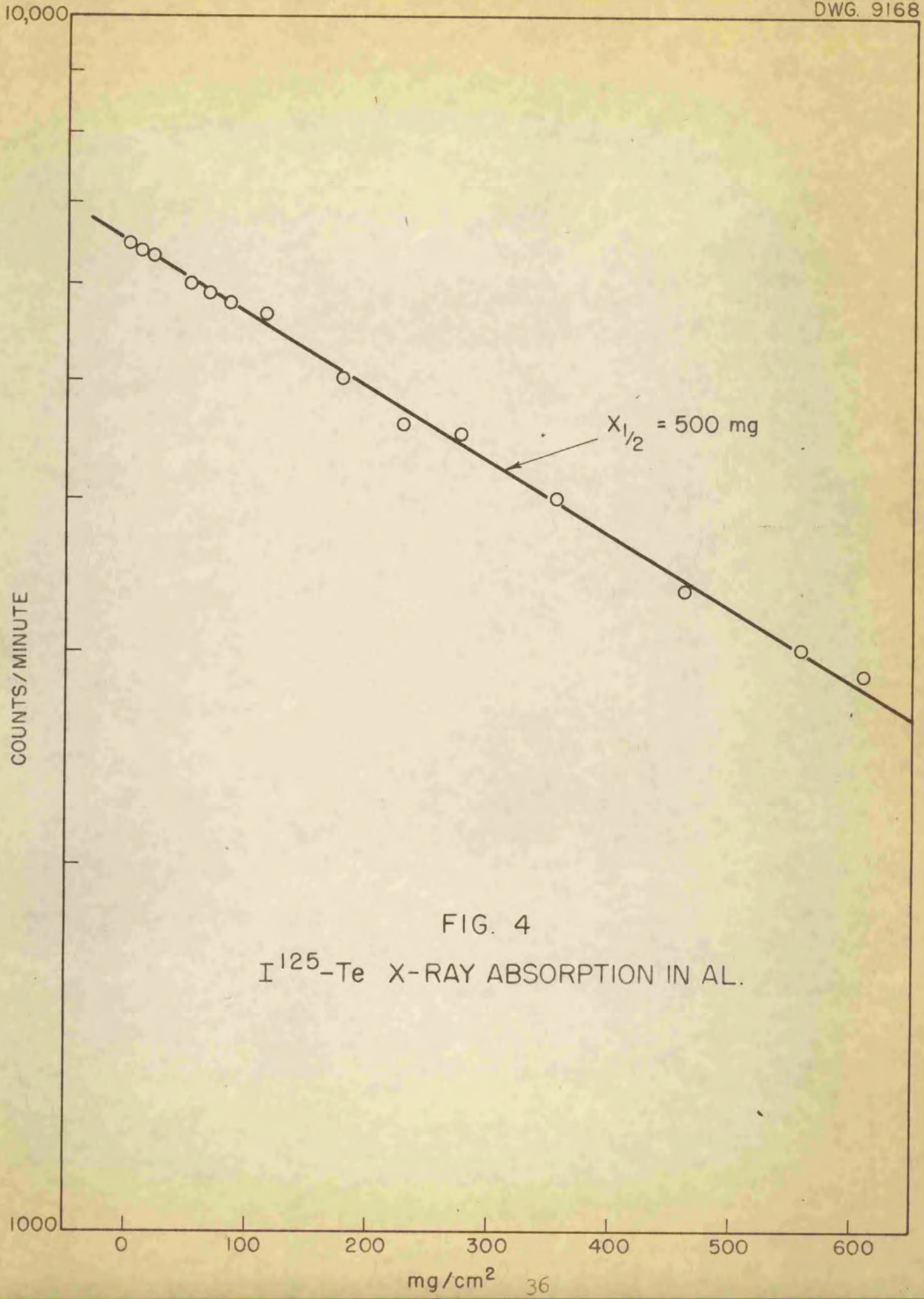

FIG. 4

I^{125}-Te X-RAY ABSORPTION IN AL.

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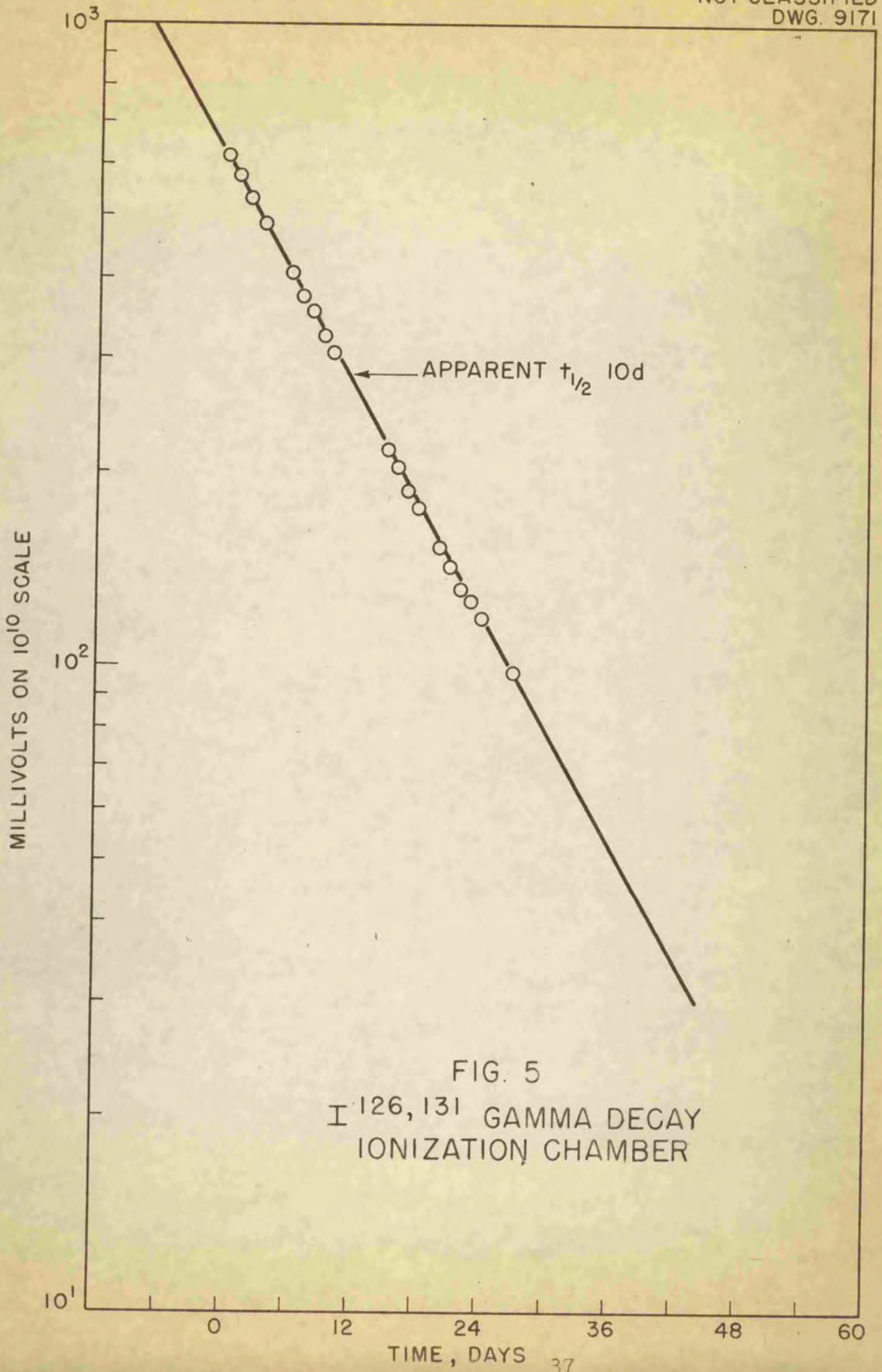


FIG. 5
$I^{126,131}$ GAMMA DECAY
IONIZATION CHAMBER

sit in a boiling H_2O bath for ten minutes.

3. Transfer quantitatively to a separatory funnel or other extraction vessel with several drops of 1 *M* HCl.

4. Extract ten minutes with 2 ml of 0.5 *M* TTA-xylene. Drain off the aqueous phase carefully and discard. Wash the organic phase three minutes with 2 ml of 1 *M* HCl. Discard the aqueous wash and transfer the organic phase into a 3 ml centrifuge cone. Centrifuge three minutes. Take an aliquot of the organic phase, mount on a stainless steel plate, dry under infra-red heat lamp, count alpha.

Note. If the solution to be analyzed contains $Hg(NO_3)_2$, *simply omit the* $SnCl_2$ *and allow the KI reduction to go twenty minutes in the boiling* H_2O *bath.*

IDENTIFICATION OF RADIOELEMENTS

T. H. Handley and W. A. Brooksbank, Jr.

A fraction of an eluent from an ion-exchange column was submitted for identification of the constituent. When a qualitative separation by groups was made using carriers, it was found that all the activity was carried by the third group. Further separation indicated that it was not a rare earth activity. The absorption curve when resolved, showed two components with half-thickness of ~ 2 mg/cm^2, 18 mg/cm^2, and a gamma component. The decay curve run for 60 days showed a single component of ~ 53 day half-life. Hf^{181} was suspected. A delayed coincidence count confirmed the presence of Hf^{181}. No other activities were detected.

Identification of long-lived components on four bombarded samples of rare earths will be made by ion-exchange methods.

APPLICATION OF ION-EXCHANGE METHODS TO RADIOCHEMICAL ANALYSIS

W. A. Brooksbank, Jr. and E. K. Wilson

Ion Exchange Separation of Rare Earths. Two identical columns have been set up which will be fed from a common reservoir at the same flow rate. Equal aliquots of a sample of pure rare earth will be placed on each column. On one column will be placed an aliquot of the rare earth to be analyzed.

Activity will be measured with standard ORNL pipette counters, recorded by two scalers and an Esterline-Angus 5 pen recorder. Each scaler actuates two pens, one of which records units of 64, the other, tens of 64. The fifth pen records the turn of the collecting table.

The eluants will be collected in receivers aligned in two concentric rings on a common turn table. The elution curves will be plotted. If the unknown is pure, there will be two peaks on one column, one peak on the other. If more peaks are present, the areas under the peaks will be evaluated as impurities.

Runs will be made on synthetic rare earth solutions before the analysis of unknown samples is attempted.

Separation of P^{32} from Cation Activities. A cation exchange column was used to separate P^{32} from other possible activities present in phosphorus-bakelite plaques.

MISCELLANEOUS ACTIVITIES

Decontamination Studies (T. H. Handley). This material will be reported in ORNL-732, soon to be issued.

Rainwater Radiochemical Analysis (W. A. Brooksbank, Jr., A. H. Emmons*, J. W. Gost*, and S. A. Reynolds). Results of this investigation are given in a report now undergoing final reviewing, prior to issuing.

ANALYSIS OF PHOSPHORUS-BAKELITE PLAQUES

E. K. Wilson

A phosphorus-bakelite plaque which had been activiated by neutron bombardment in the pile was submitted to this laboratory for the radiochemical determination of suspected cobalt, iron and nickel impurities. To use similar plaques for high intensity beta radiation sources, it is necessary that the material be free of impurities which would contribute a significant amount of undesirable radiation after activation.

The problem was one of developing a suitable quantitative method for readily separating the P^{32} activity from other possible activities. Although various procedures including carrier precipitation, liquid-liquid extraction

* Health Physics Division

and ion exchangers were considered, only the latter two were investigated because of the ease with which separation could be obtained.

Liquid-liquid extraction was the first method experimentally investigated. An attempt was made to adapt a standard colorimetric procedure for the determination of phosphate to allow for the amount of phosphate present in a 2 gram sample of the phosphorus-bakelite plaque. (This sample size is necessary to insure reasonable counting rates of the impurities.) A sample of unirradiated plaque was oxidized with nitric acid reacted with ammonium molybdate and a butyl alcohol-chloroform extraction was attempted on the heteropoly acid. An emulsion formed with the solvent mixture which could not be broken readily. Since a thorough investigation of the conditions under which this extraction could be made would require considerable time, this method was filed for future reference to be used only if no other satisfactory method could be found.

The use of a cation exchange column as the decontamination mechanism was next investigated. Dowex 50 (100-200 mesh) was used for this study.

The resin was conditioned by alternate treatment with 6 *N* nitric acid and 0.5 *M* sodium nitrate. After three cycles, the resin was washed with water until the water decanted from the resin was neutral. Nitric acid was then passed through the resin until the effluent had the same normality (0.2 *N*) as the solution being put through the column.

Synthetic solutions were then prepared containing a P^{32} tracer activity comparable to that contained in a two gram sample of the activated phosphorus-bakelite plaque and a concentration of Fe^{59} and Co^{60} which would give a convenient counting rate. The total activity of P^{32}, Fe^{59} and Co^{60} was of the order of 3×10^5. Of this total activity, 1×10^5 was due to P^{32}. Sample preparation involved oxidizing the phosphorus to phosphoric acid with fuming nitric and adjusting the normality to approximately 0.2 *N* acid (*p*H 3).

The conditions for column operation were as follows:

1. Resin bed of approximately 5 ml.
2. Volume containing the sample was about 100 ml.
3. Flow rate 1 ml per minute.

Samples of the effluent were collected at convenient intervals. Gross beta counts were made. An absorption curve showed only one constituent passing through the column which had a half thickness corresponding to that of P^{32}.

When no further counts were obtained, the column was inverted to facilitate the elution of the absorbed cation activities. Two possible methods for stripping the column were considered: (1) preferential stripping with complexing agents, or (2) stripping of all activities with 6 *M* HCl and chemical separation of the constituents.

A 50 ml volume of 0.5 *M* tartaric acid which had been neutralized to *p*H 3 with sodium hydroxide was used to elute the Fe^{59} activity. Aliquots were taken and subjected to nitric acid—peroxide treatment before gross beta counts were made. Coatings appeared on all of the plates. It seemed reasonable to assume that the apparent loss of activity was due to the inability of the low energy particles being emitted to count through the coating. It was also difficult to wash the column free of tartrate.

It was decided to strip all activities with 6 *M* HCl and to chemically separate the constituents. A volume of 50 ml of 6 *M* HCl was found to be sufficient to give 93% recovery.

The design of the box for breaking the phosphorus-bakelite plaques suggested in ORNL-263 was modified (Figs. 6 and 7). One and one-half inch lucite was used to construct the box. The stainless steel cup in the bottom of the well can be removed with the sample and stored or it can be emptied and readily decontaminated. Broken pieces are removed by sliding the lid ajar far enough to allow a pair of long laboratory tongs to be used.

ORNL-263 includes a discussion of the solution of samples of the phosphorus-bakelite plaques. It was found that the solution of a two gram sample was not easily accomplished. Unless the solid was subjected to a prolonged treatment with fuming nitric acid (the temperature being maintained at 70 - 80°C) and 30% hydrogen peroxide carefully added, the following occurred: upon concentration a carbonaceous precipitate formed, while on dilution a cloudy precipitate of polymerized resin formed; in both instances, the solution could not be used for column work.

ELECTRODEPOSITION OF U^{233} TRACER

W. A. Brooksbank, Jr.

U^{233} can be plated from a solution of ammonium oxalate at a *p*H of 6-8 with a current of 1.6 amperes per cell.[19,20]

(19) Bizzell, O. M., Notebook CL-1151.

(20) Hull, D. E., *The Counting Method of Isotopic Analysis of Uranium*, MDDC-387 (Oct. 18, 1946).

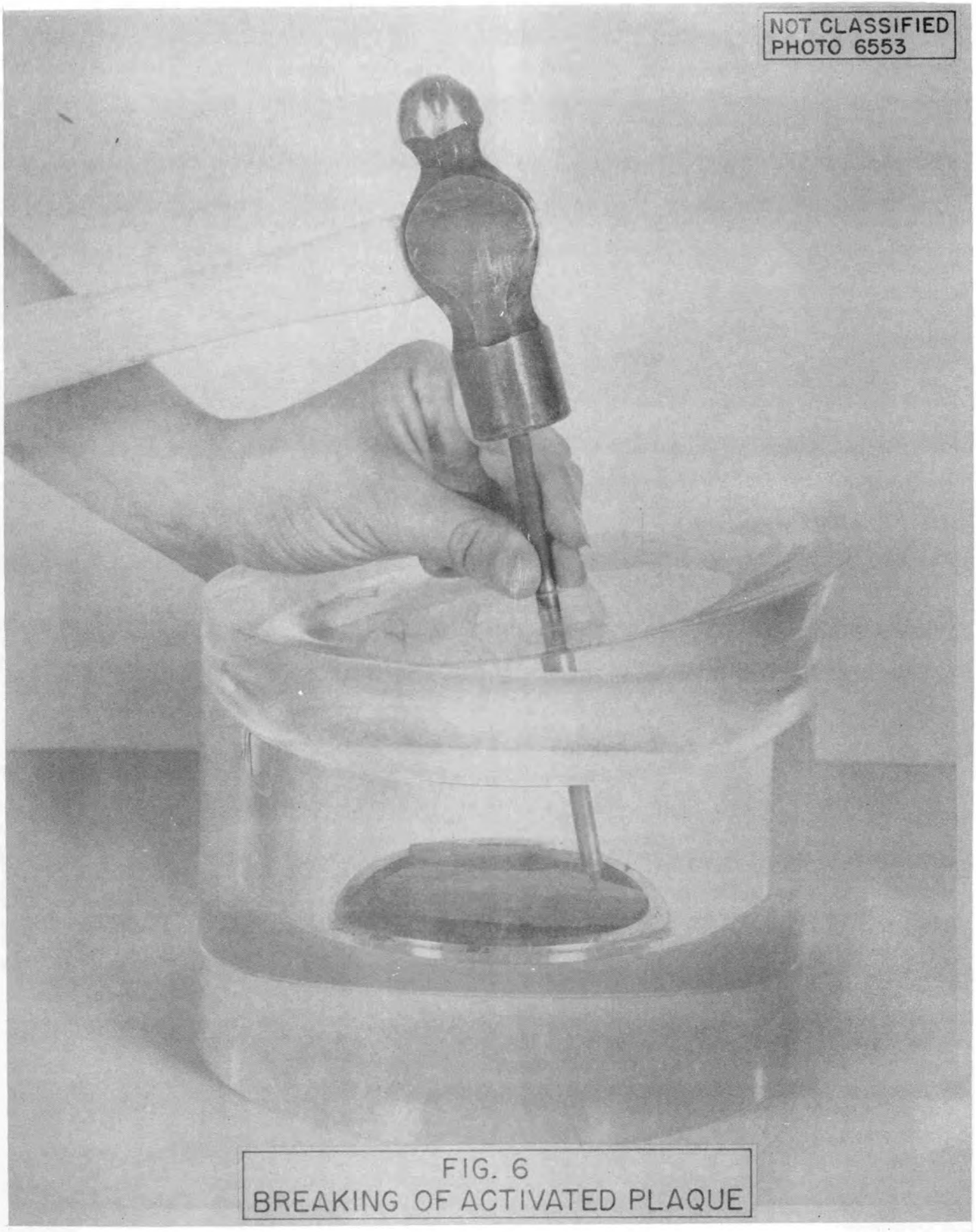


FIG. 6
BREAKING OF ACTIVATED PLAQUE

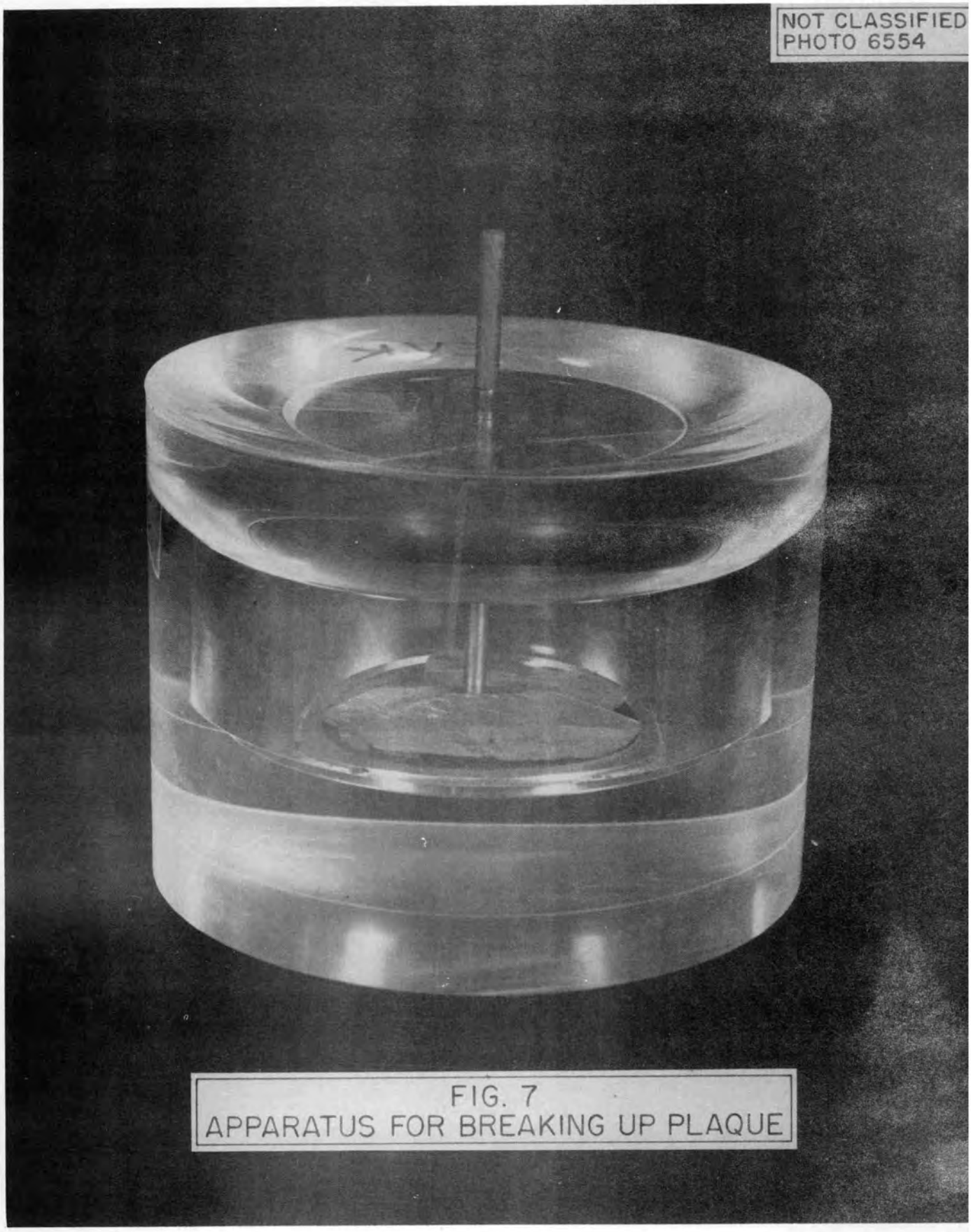


FIG. 7
APPARATUS FOR BREAKING UP PLAQUE

NOT CLASSIFIED
DWG. 9182

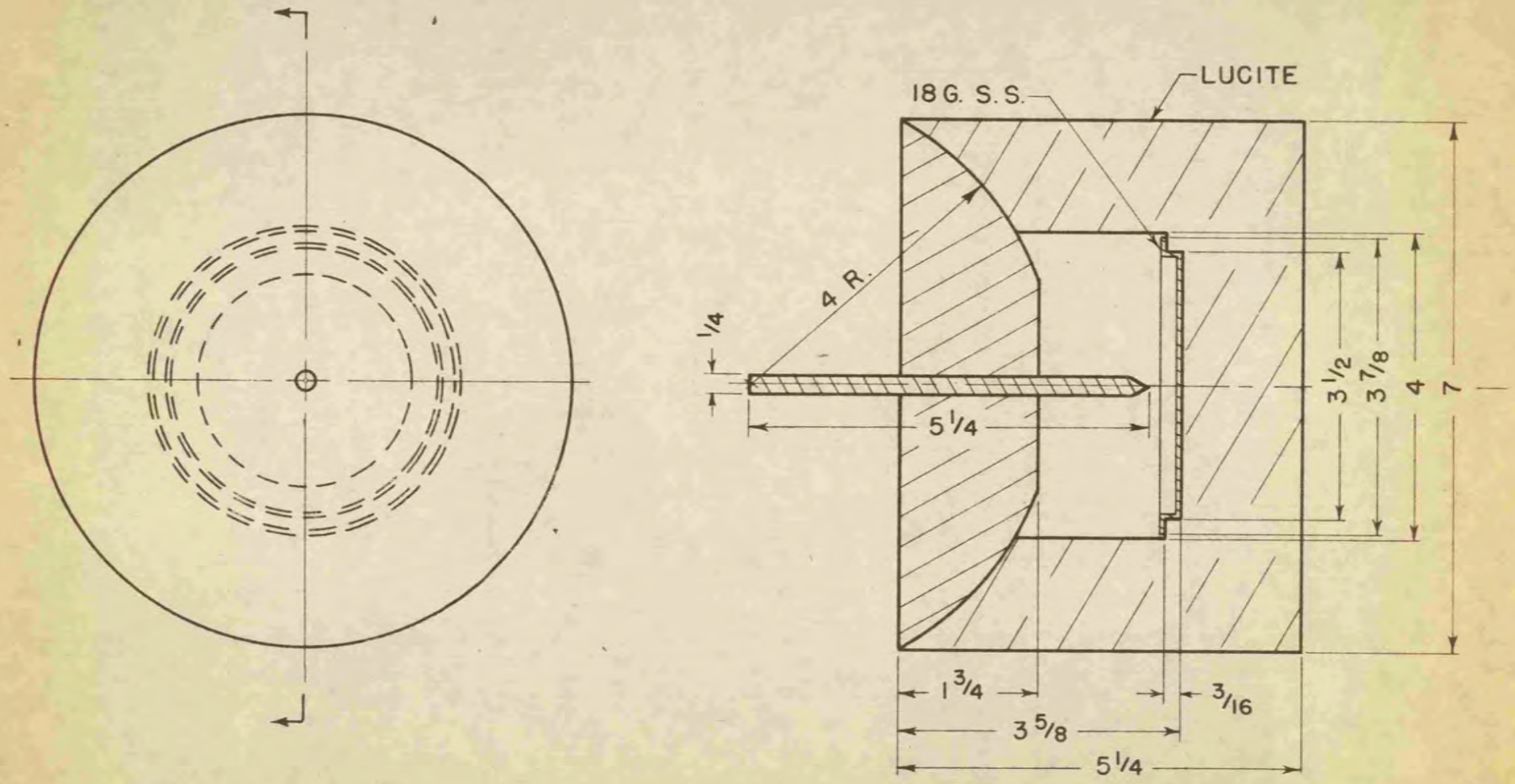


FIG. 8
APPARATUS FOR BREAKING UP AN ACTIVATED PLAQUE

The electrolysis cell consisted of a glass cylinder, 6.3 cm high and 2 cm ID, encircled by an external shoulder midway along its length (Fig. 9).

The cell mount consists of a 4 in. square × 1/4 in. brass plate tapped to receive 6 cm long studs placed equidistant from each corner. The studs pass through an upper plate bored to slip over the glass cell down to the shoulder.

A one inch diameter cathode of stainless steel or platinum is centered on the bottom plate and a ring shaped gasket of cellophane is placed on top of it. The glass cell is then placed on the gasket, a rubber ring placed above the shoulder on the cell and the upper plate is secured to the bottom plate with thumbscrews. The cell is watertight.

The rotating anode is a platinum gauze 1.5 cm in diameter and fitted with a platinum rod down the axis. It should extend into the solution about 2 cm.

Power was supplied by a Fisher "Powerhouse."

Two ml of $(NH_4)_2C_2O_4$ are added to the cell, then the sample (not more than 500 λ), one drop of 6 *N* HNO_3, one drop of phenol red, and the solution brought to the endpoint with 6 *N* NH_4OH. One drop 6 *N* HNO_3 is added, and the electrolysis begun.

The amperage should remain constant at 1.6 amps and the voltage between 8.8 - 9.8 v d-c. Forty-five minutes is sufficient to plate all the U^{233}.

The cell is dismantled, and the cathode washed well with distilled water, dried with an infra-red lamp and counted.

This method can be used to plate as little as 2000 c/m (52% geometry) with a precision of better than 5%.

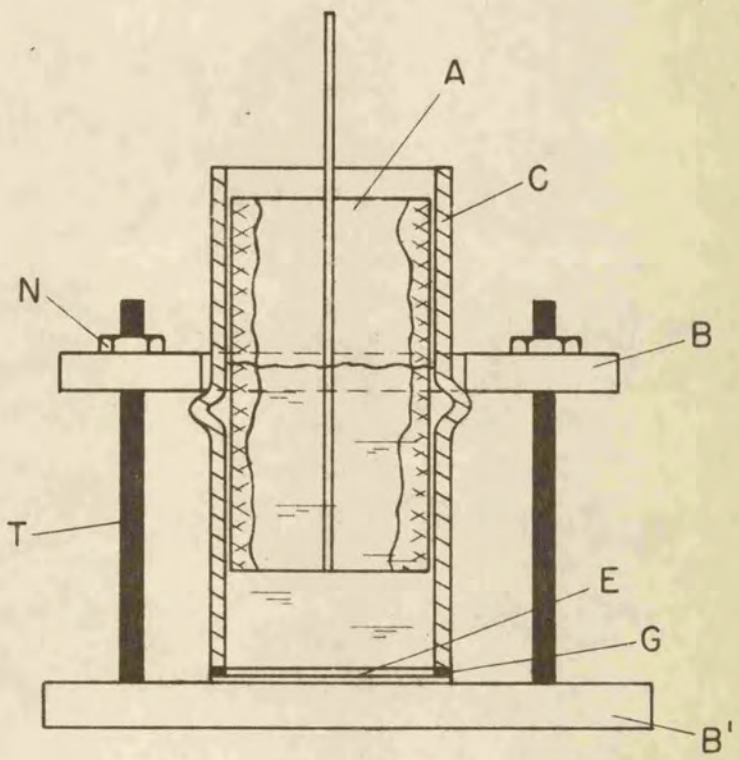
TABLE VII

Efficiency and Reproducibility of U^{233} Plating

SAMPLE NO.	C/M PLATED	C/M REMAINING
Sample 1	8389	52
	8390	64
	8314	80
Sample 2	9134	67
	9181	41
	9028	69
Sample 1.248	13462	--
	13249	--
Sample 2.496	26114	--
	26223	--
Sample 4.992	53683	--
	55186	--
	53475	--
	54306	--
	54724	--
	54895	--
Sample 4	2204	Less than
	2350	Background
	2118	

NOT CLASSIFIED
DWG. 9184

FIG. 9
ELECTRODEPOSITION CELL



A ROTATING ANODE (PLATINUM GAUZE)
B BRASS COLLAR
B' BRASS BASE
E CATHODE (SAMPLE PLATE)
G GASKET
N BRASS NUT
T THREADED BRASS BOLT

PREPARATION OF COCKROFT-WALTON TARGETS

R. A. Bolomey

A tritium-zirconium target has been prepared for bombardment in the Cockroft-Walton accelerator.

RECOVERY OF TRITIUM FROM TRITIUM WATER

The following procedure is being used to recover tritium from tritium water: tritium water is passed over magnesium heated to 525°C and the tritium is collected as uranium triteride in powdered metallic uranium. A more comprehensive report will appear at a later date.

SPECTROCHEMICAL ANALYSIS—RESEARCH AND DEVELOPMENT

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

REVIEW OF PHOTOGRAPHIC PHOTOMETRY

A review of photographic photometry is being written for Committee E-2 of the American Society for Testing Materials.

The first of the sections completed so far discusses intensity ratios in spectra of mixtures as a function of time, and brings out implications of the behavior discussed for exposure techniques and photometry.

The second section describes several intensity scale methods for calibrating emulsions. Primary methods included are as follows:

(a) The inverse square law: necessity for using diffusing screen as source with fixed geometry; line shape; slit width; criteria for judging practical range of validity of inverse square law.

(b) The neutral stepped filter: precautions for selecting and mounting filters; direct photometric and photographic methods for calibrating filters.

(c) The step-wedge diaphragm: construction; accuracy required; theory of mounting; optical conditions to prevent vignetting and light scattering within instrument.

(d) The biprism: theory; advantages over other two-line methods; illumination requirements.

The homologous line-group method is described as a secondary method (*i.e.*, one in which the values of the intensity standards are measured by a primary method). Topics covered include the reasons for using homologous line groups; effect of source variables on relative intensities; selection of lines for such groups; self-reversal, how to minimize it and how to select lines least subject to it; tables of lines in selected wave length ranges between 2600 and 4300 Å suitable for use in emulsion calibration.

WORKING CURVES

New working curves were developed for the following analyses by the porous cup method.

(1) 0.3 - 12.0% Na in Li metal

(2) 0.08 - 1.00% Ta in Zr metal

(3) 15-125 ppm Gd in 10% H_2SO_4

(4) 30-500 ppm Sm in 10% H_2SO_4

(5) 1.3 - 20 ppm Eu in 10% H_2SO_4

Analysis of Gasoline. One volume of gasoline was mixed with one part of mineral oil (Nujol) and the mixture gently heated on a hot plate until its temperature reached ~140°C. This liquid was then analyzed by the porous cup technique.

EXPERIMENTAL HOMOGENEOUS REACTOR CHEMICAL CONTROL

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

The problem of chemical control of the "soup" solution of the experimental homogeneous reactor includes the separate problems of the determination of total uranium, reduced uranium, acidity, suspended particles and their nature, and oxidizing power. The presence of the following factors further complicates these determinations:

1. *Temperature.* An experimental operating range of 200°C - 250°C is achieved by the initial application of external heat to the system.

   An internal heat of 250°C within the system is due to the resultant power of the reactor and the constant heat released from the radioactive decay of the fission product.

2. *Pressure.* Any apparatus used in measuring any of the desired properties of the "soup" must be capable of withstanding sudden pressure changes from 1000 psi to 10 psi. The system will be under a total operating pressure of 1000 psi of which 580 psi will be contributed by water at 250°C and the balance by a pressurizer operating at 285°C.

3. *Radioactivity.* The radioactive level of the "soup" has been calculated to be about 30 curies per ml as fission products at 1000 kw.

Severe limitations in the type of apparatus to be used in the measurement of any of the properties of the "soup" are imposed by the requirements inherent in the construction, design, and fabrication materials of the experimental homogeneous reactor as well as the resultant high level of radiation of the solution. In general, all optical methods are inoperative for routine control. Remote control is mandatory for any conceivable method of making any determinations.

Three methods by which chemical control would be possible have been investigated and are discussed below.

DETERMINATION OF URANIUM CONCENTRATIONS

The total uranium content of the "soup" appears to be the most important analytical determination to be made. The accuracy required is 0.1 g/liter.[1]

(1) Winters, C. E., to Secoy, C. H., private communication, May 16, 1950.

Direct Methods.

X ray: The possibility of using a modification of the General Electric X-Ray Photometer was considered. It was found that absolute errors in excess of 0.1 g U/liter occur in the calibration of the instrument.[2] The following factors were also to be noted:

1. Using the usual X-ray targets, it is impossible to operate at the K-edge for uranium, where the greatest "jump" in absorption is observed.
2. The presence of foreign elements of atomic number up to element 42 and above element 53 in concentrations as low as 1% would rapidly increase the apparent uranium content of the "soup."
3. It would be necessary to have a sample container of low absorption characteristic which would provide a sufficiently thin wall thickness to effectively transmit the X rays and at the same time withstand the changes or pressure before noted.

The possibility of measuring with a discriminator pulse analyzer and a proportional beta counter the energy of a photon ejected by an X-ray emanating from uranium induced by an external gamma source or other means was also eliminated. Mr. Borkowski[3] stated that even with the use of a pulse technique of introducing gamma rays, the method would not have sufficient sensitivity due to the high level of gamma and X-ray background.

Nuclear Induction: It is possible that a specific method for the determination of U^{235} concentration may be found in the measurement of the nuclear inductance of the solution. Mr. Walchli and Mr. Zimmerman of Y-12 are attempting to find a resonance peak for U^{235}. It appears that if such a peak is found, the application of this measurement to the accurate determination of the U^{235} concentration will still remain a major problem.

Conventional Chemical Methods: In general, the use of standard chemical methods are highly undesirable because of the problem of sample removal and fission product separation before analysis.

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(2) Barlett, T. W., *The General Electric X-Ray Photometer and Its Application to the Determination of Uranium, Part II*, AECD-2766 (Oct. 28, 1949).

(3) Borkowski, C. J., private communication, May 18, 1950.

Indirect Methods.

Conductivity: Indication of changes of the uranium concentration in the reactor solution could be obtained by following the conductivity of the solution. If the contribution of the other ions in the solution of the total conductivity is known, then a direct measure of the uranium concentration is available.

The simplest means of measuring conductivity would be to insert two electrodes, probably platinum, of known area into the solution at a known distance apart and measure either the resistance or the conductance of the solution between the electrodes.

This method is not readily adaptable to the homogeneous reactor system since the conditions require that at least one lead be insulated from the steel pipe and that both the insulating material and the electrodes be stable to radiation and pressure. The Instrument Department has been giving consideration to this phase of the problem and may be able to develop suitable insulators and electrodes.

K. Kline of the Instrument Department is working on another method for measuring conductivity which might be adapted to the reactor problem. It consists of placing a coil inside the pipe, applying a predetermined frequency on the coil and measuring the conductivity in terms of the change in Q of the coil.

Early results do indicate a dependence of Q upon the uranium concentration. This method, however, is in the early stages of development and no conclusive results have been obtained.

Density: Density is another property of the reactor solution which is affected by uranium concentration. The accurate determination of density within the system itself is difficult but one method which appears feasible makes use of an electromagnetic densitometer.

The measurement of density in this way has been reported by Lamb and Lee[4] and by Richards.[5] In principle, a submerged float containing an

(4) Lamb, A. B. and Lee, R. E., "The Densities of Certain Dilute Aqueous Solutions by a New and Precise Method," *Am. Chem. Soc. J.* 35, 1666 (1913).

(5) Richards, A. R., "An Electromagnetic Densitometer," *Ind. and Eng. Chem., Anal. Ed.* 14, 595 (1942).

iron core is moved through a liquid by the effect of the magnetic field of d-c or a-c coil exterior to the liquid. The force produced in the coil which is necessary to move the float to or from a given position is proportional to the density of the liquid. The force is measured in milliamperes passing through the coil. Since density is dependent upon temperature, changes in temperature must be either controlled or known. Under favorable conditions the methods can be extremely accurate. The sensitivity, however, decreases as the range is increased.

Here again the development of this method for use in the homogeneous reactor is in the early stages. Aspects to be investigated include (a) the dimensions of the float and coil required, (b) the material to be used for the float which of necessity must be thin-walled and yet be able to withstand pressure and corrosion, (c) a method for the precise automatic recording of the float movement, (d) the effect of high temperature and pressure, and (e) the control of the temperature.

Density and/or Adiabatic Compressibility by Sonic Interferometer: Bachem and Falkenhagen[6] have shown that the velocity of sound is dependent on the concentration (over the range of 0.1 *M* to 0.6 *M*) of KBr, $BaCl_2$, NaCl, $MgSO_4$, $K_3[Fe(CN)_6]$, Na_2CO_3, and $K_4[Fe(CN)_6]$ in aqueous media. Since the velocity, v, equals $\sqrt{1/p\ B_{ad}}$, it seems that a means might be devised to measure p, the density, or at least the product of the density, and B_{ad}, the adiabatic compressibility as per the above relationship.

The major problems are as follows:

1. Accurately measuring the temperature of the "soup" or controlling the temperature of the "soup" by a bath thermostated to the small temperature variation permissible. It is to be remembered that the "soup" heats itself by virtue of its own radiation about 30 calories/ml/hr.

2. Possible radiation damage to the source of the sound generator, the piezoquartz or the magnetostriction material.

3. Probable presence of gas bubbles which cannot be tolerated in a sonic interferometer.

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(6) Falkenhagen, H. H. and Bachem, Ch. "Zur Kompressibilitat Starker Elektrolyte," *Z. Electrochem.* 41, 570 (1935).

DETERMINATION OF OXIDIZING POWER

If chromic acid is used as the holding oxidant in the reactor solution, it is expected that some reduction of chromium will take place. If this reduction is appreciable more chromic acid would be required. Rather than attempt to determine the rate of reduction, the possibility of a continuous regeneration of the chromic acid was investigated. This would also prevent the build-up of chromium in solution.

It was found that on a laboratory scale (1.5 liters of 0.005 *M* $Cr_2(SO_4)_2$ and 0.01 *M* CrO_3) chromic acid could be regenerated electrolytically. The chromic acid solution was circulated (using a circulating pump) at a rate of 1-12 gals/min past two platinum electrodes sealed in a glass tube. The anode was a platinum gauze cylinder 5 cm long and 1.3 cm in diameter. A platinum wire 1 mm in diameter and 3 mm long was used as the cathode. This anode to cathode size ratio favored the oxidation reaction at the anode.

Samples were taken periodically and analyzed colorimetrically for Cr^{+6} and Cr^{+3}. The *p*H and temperature were also determined.

The results of four laboratory runs are summarized below:

1. Essentially all of a 0.005 *M* chromic sulfate solution can be reoxidized at room temperature with an average current efficiency of 24%.
2. If the anode is first plated with lead dioxide the current efficiency is increased to 35%.
3. Heating the solution to 95°C results in an increase in current but a decrease in current efficiency. The net effect is a slight increase in the rate of oxidation.

On the basis of the tests conducted on a laboratory scale, the electrolytic regeneration of chromic acid in the homogeneous reactor solution seems possible, providing the required rate of oxidation is not too high. Using the laboratory results as a guide, a reasonable estimate of the time required to completely reoxidize 50 liters of 0.001 *M* Cr would be three to four hours.

No further work on the regeneration of chromic acid is contemplated unless the need for such regeneration becomes apparent.

DETERMINATION OF OTHER PROPERTIES

Less time has been devoted to development work on the chemical control of other properties of the reactor solution such as reduced uranium, acidity, etc., due to the primary importance of analytically determining total uranium concentration.

OPTICAL AND ELECTRON MICROSCOPY

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

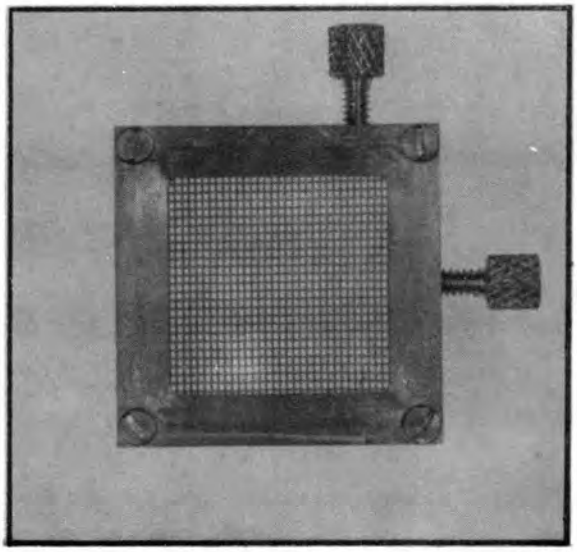
METALLOGRAPHY OF CORROSION SAMPLES

Mapping of Inclusions in Metals Prior to Corrosion Tests. A study of the relationship of inclusions to the corrosion attack on QRM Beryllium and Bureau of Mines Zirconium was undertaken to obtain pertinent information for the Reactor Program. It was suggested that samples of these metals be submitted to the Optical and Electron Microscopy Section for a metallographic polishing and a systematic mapping of various areas containing inclusions prior to corrosion tests. These samples would then be subjected to corrosion attack and returned to this section for relocation of areas previously mapped, and for the study of the nature of the attack, structural changes, or corrosion products formed on or near inclusions. The following method has been developed to this end.

Samples submitted by the corrosion section of the Reactor Technology Division for mapping were approximately 1 in. (2.5 cm) square. To hold these securely and permit subsequent mapping, a holder design was submitted to the machine shop for fabrication. The completed holder is shown in Fig. 10-A.

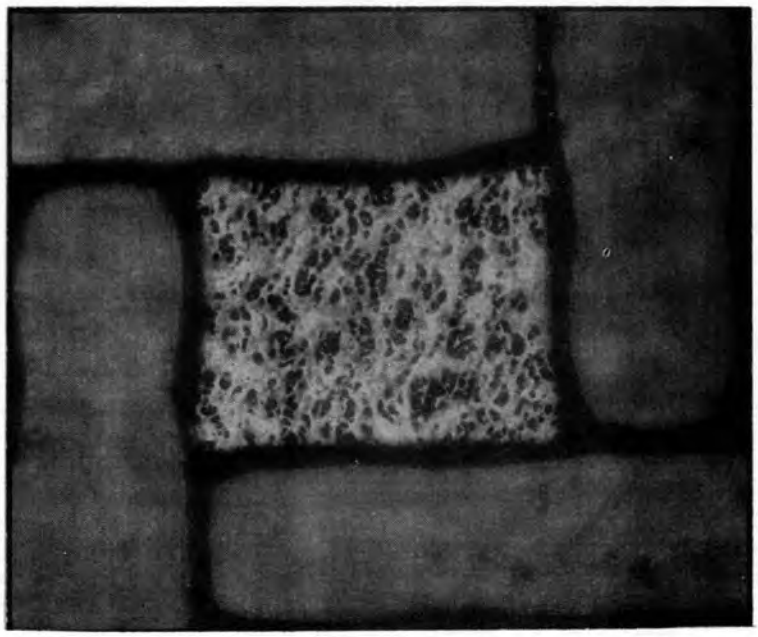
The holder is made of 6.5 mm thick brass stock machined to a 3.8 cm square with a square hole slightly larger than the size of the sample cut in it. Over this opening is fastened, by means of a 1.5 mm thick bevelled brass plate, secured by screws, a piece of 100 mesh screen rolled so that the dimensions of the holes are approximately 0.7 mm × 0.5 mm. These dimensions allow for the viewing of one opening when a 16 mm objective is used in conjunction with a 10X ocular. This gives an approximate magnification of 100X of the metal surface bordered by the wire lands of the screen. Figure 10-B shows the appearance of a field as observed in the microscope. Two set screws in the holder block are provided to anchor the sample securely in place and assure that is will always be tight against two edges of the holder.

In use, the samples which had been polished and etched are inserted in the holder. The unit is then placed on the stage of the metallograph so that the opening in the upper left hand corner is in the field. Starting from this first opening and counting the openings as they pass through the field of view



10 A.-Sample Holder for Metallographic Mapping of Inclusions

T-105



10 B.-Field as Observed at Low Power Thru One Opening In Screen

ME-578

FIG. 10

and recording as over and down, for example (over 4 down 6), a succession of photomicrographs may be taken of various fields containing inclusions. This gives a permanent picture record for use in comparing pictures of identical fields taken after corrosion tests.

In practice, this method has proved to be simpler and more time saving than making use of the graduated scales provided on the object stage of the metallograph. High power, dry objectives as short as 4 mm focal length can be used if more detailed studies of certain inclusions are necessary. For use with objectives of short working distance, fields should be selected about 8 screen openings over and down, and the location indexed with an objective of lower power and recorded.

Carbide Inclusions in U. S. Bureau of Mines Zirconium—An Electron Microscope Study. It was previously suggested from microscopic observations that some relationship existed between the site of carbide inclusions and the areas where corrosion attack has taken place. It was previously noted that localized attack in acid solution[1] had taken place around carbide inclusions.

In an effort to learn more about the nature of this attack, replicas of metallographically polished zirconium samples, which have been lightly etched with a solution of six parts glycerine, two parts HF, and one part HNO_3, were made. Areas at or adjacent to carbide inclusions were photographed using the electron microscope. It was expected that the electron microscope, with its greater depth of field and better resolving power, would reveal details unobserved with the optical microscope. A study of the resulting photographs might explain why more intense corrosion attack takes place at the embedded carbides.

Plates EM-673(2) and 673(5) (Figs. 11-12), two of a series of electron micrographs taken of zirconium, show the carbide inclusions and the adjacent areas. From these and similar pictures of other fields, it was noted that the condition observed at the zirconium metal-carbide interface was prevalent in all fields examined, *i.e.*, a spongy appearance in the structure of the zirconium metal at the interface and the presence of what appeared to be very small inclusions at the boundaries of the carbide inclusions.

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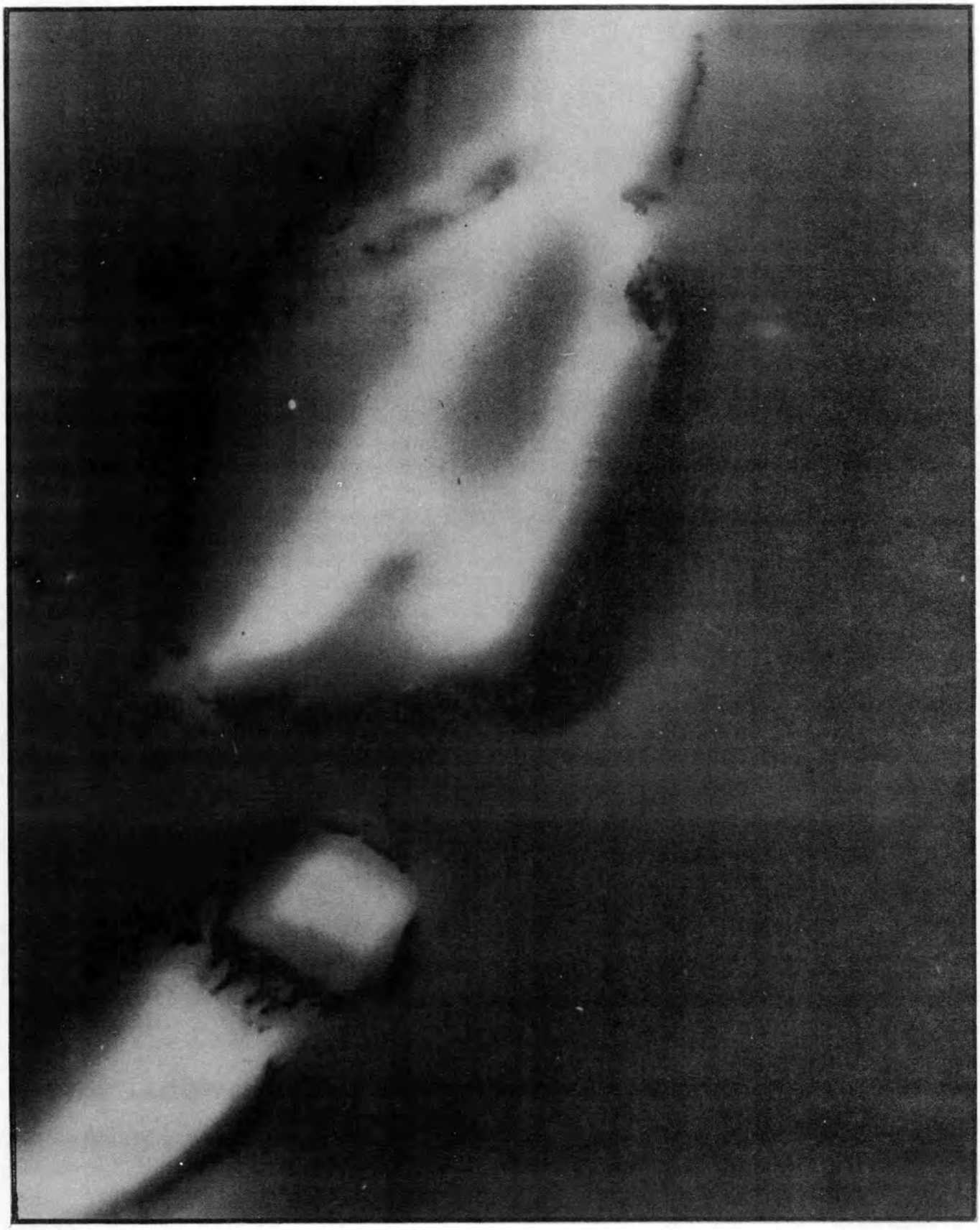
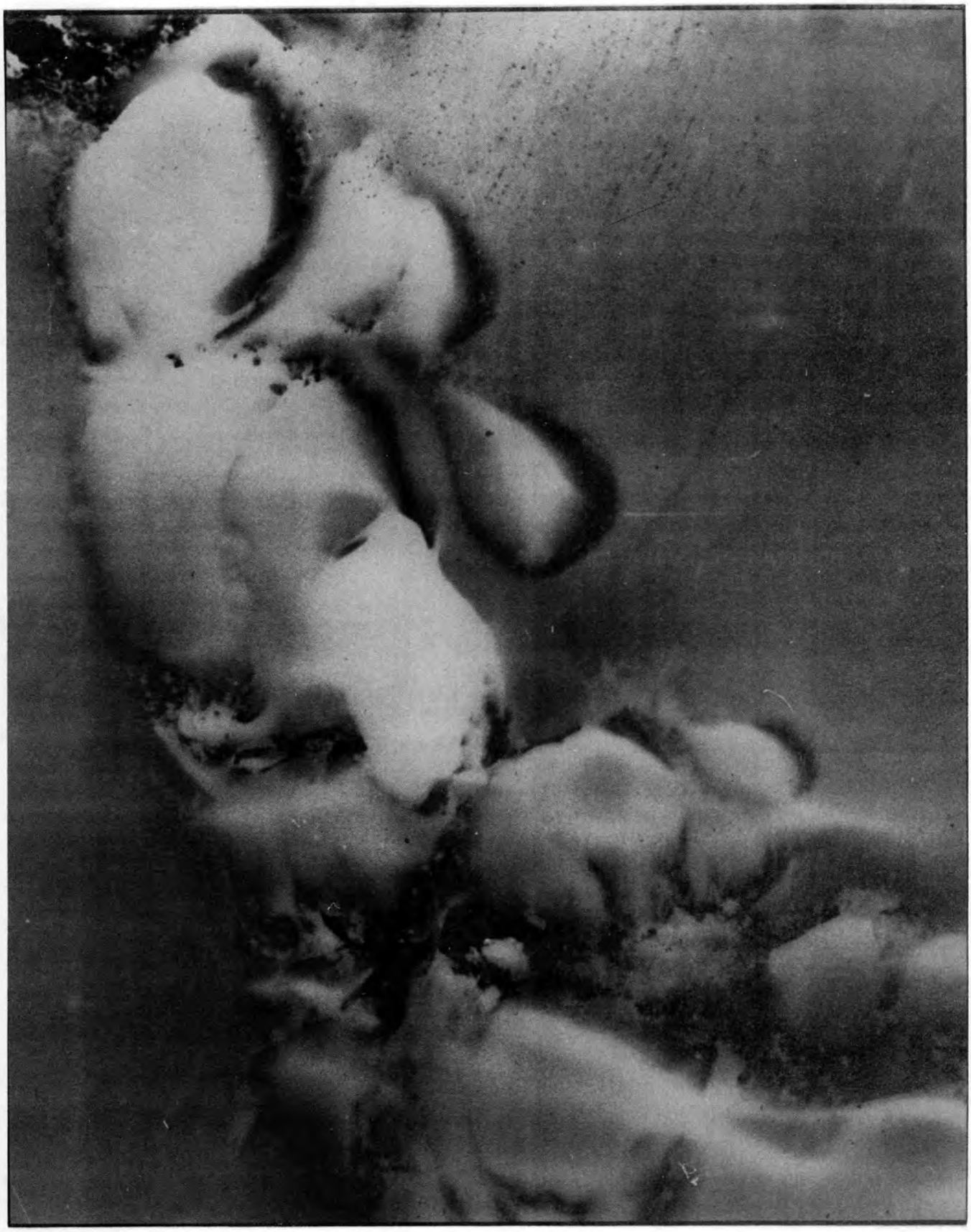
(1) Willmarth, T. E., McNeer, F. D. and Gary, B. I. "Microscopic Examination of the Structure and Corrosion of Samples 765, 766, 767 and 785" *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, 162 (June 16, 1950).



Electron Micrograph Showing Area Adjacent to Carbide Inclusions in U. S. Bureau of Mines Zirconium.
Plate 673(2) - 5000X

FIG. 11



Electron Micrograph Showing Area Adjacent to Carbide Inclusions in U. S. Bureau of Mines Zirconium.
Plate 673(5) - 5000X

FIG. 12

Some of the possibilities which may account for attack at these areas are as follows:

1. The zirconium at the zirconium carbide interface is less passive to corrosion attack than the zirconium farther removed, *i.e.*, the formation of the zirconium carbide impoverishes the metal immediately adjacent to a point where it cannot withstand corrosion attack. This is similar to the impoverishment of chromium in some stainless steels.

2. The possible precipitation, at present, of an undetermined impurity at the zirconium carbide boundaries. The impurity is a material that is more readily attacked in acid solution.

3. The segregation of an impurity at these sites would establish electro-chemical action in acid solution.

Further work on this problem is contemplated.

RADIOGRAPHY

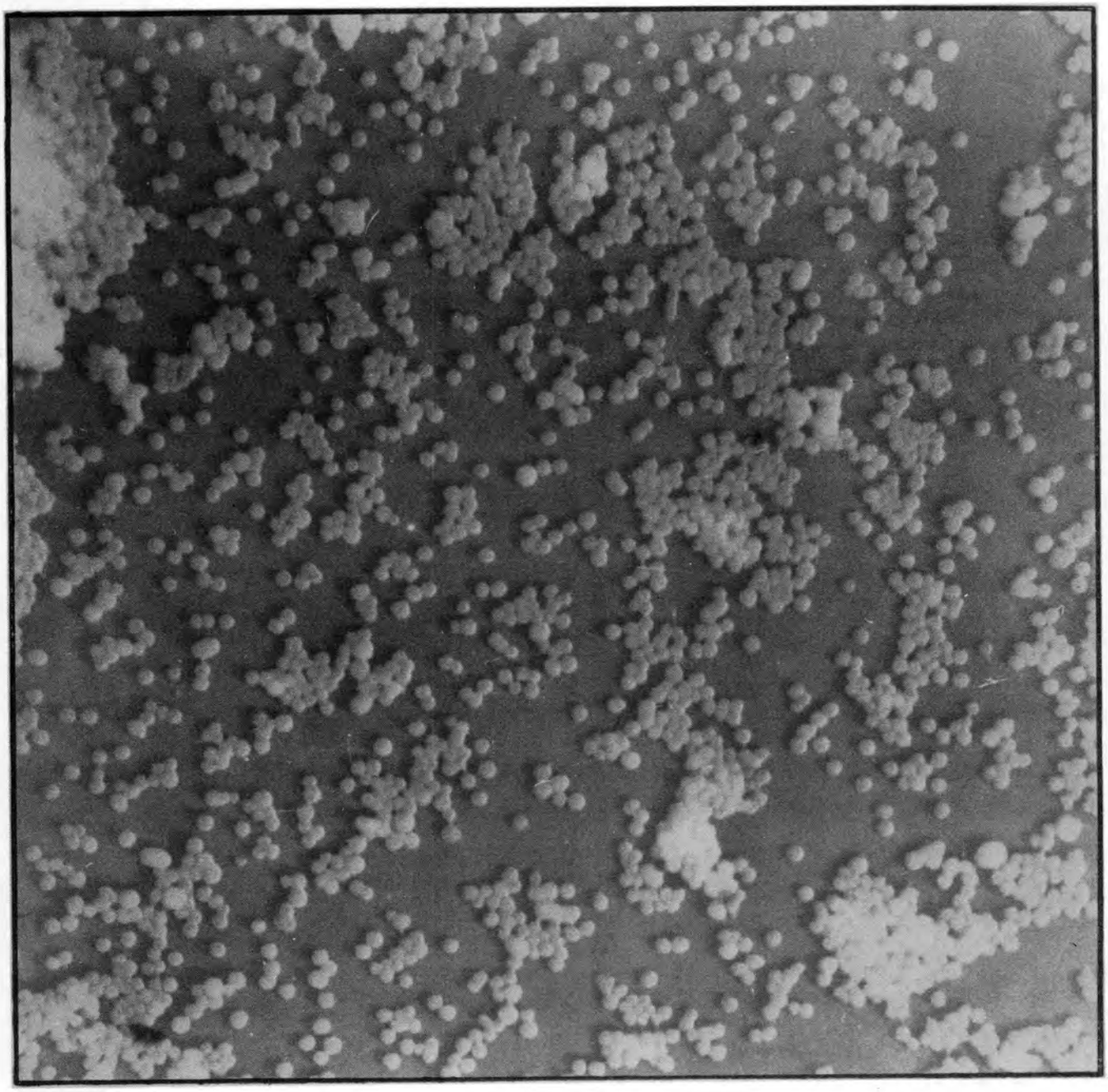
Radiography of Gas Welded Tantalum Tubing Using Isotopes as a Ray Source. The possible need for an easily portable ray source was suggested by E. Wischhusen of the Chemical Technology Section. Experiments are being conducted to determine the best isotope to use in radiographing in one exposure a weld on a tube of small diameter (approximately ½ in.) with a wall thickness of 0.5 mm where intra-surface defections or impurities would be in the micro range.

RESINOGRAPHY

An electron micrograph of colloidal Dowex is shown in EM plate 707 (Fig. 13). This is included for its possible interest to people working with exchange resins.

REPORT OF WORK DONE IN THE OPTICAL AND ELECTRON MICROSCOPY SECTION

During the period from March 20, 1950 to June 20, 1950, the following samples were received, microscopic work done, photographs taken, and prints made:



COLLOIDAL DOWEX - PLATE 707 - 25000X

FIG. 13

Samples received	74	
Metallographs taken	75	
Photomicrographs taken	30	
Electron micrographs taken	60	plates of 5 frames each - 300
Copy negatives	8	
Lantern slides made	18	
Total pictures taken	431	
Prints made	1250	(approximately)

Other services included some 60 jobs done on the evaporator for various personnel of the laboratory, radioautographs of precipitated material from corrosion tests, and the spot microscopic observations of various materials. Assistance and advice was also rendered various people in using our equipment and materials.

Considerable work had to be done on the electron microscope vacuum system which entailed leak testing and replacement of sylphon bellows. It was also necessary to replace some of the wiring, a regulator tube, and the thermocouple plug in the electron circuit. The high voltage circuit of the electron gun was rendered inoperative on several occasions by the high humidity resulting from the failure of the air conditioning system.

Information obtained from the service work done for the members of the laboratory is best reported by them in connection with their individual problems and is not, therefore, included in this report.

TABLE VIII

Summary of Service Analytical Work for Period

(April 1 - June 30, 1950, Number of Analyses Reported)

PERSONNEL	RADIOCHEMICAL DEV.	IONIC DEV.	SPECTRO-CHEMICAL GROUP	GENERAL RADIOCHEMICAL GROUP	GENERAL IONIC GROUP	WATER ANALYSES	LAB AND SEMI-WORKS CONTROL	PILOT PLANT	PRODUCTION CONTROL	TOTALS
Tech.	10	5	4	4	4	1	2	5	7	42
Non-Tech.	2	1	0	7	1	4	12	19	18	64
Biology	-	-	24	-	-	-	-	-	-	24
Physics	-	4	72	-	10	-	-	-	-	86
Chemistry	19	155	179	27	67	56	334	10	619	1466
Chem. Tech.	58	69	17	6378	88	577	9969	5207	2242	24605
Metallurgy	-	-	72	-	86	-	239	-	-	397
Reactor-Tech.	-	14	243	-	24	493	-	-	-	774
Operations	542	25	171	-	1	13	-	-	8295	9047
Health-Physics	-	-	52	78	-	-	-	-	-	130
Miscellaneous	156	-	3	-	-	-	-	-	-	159
TOTALS	775	267	833	6483	276	1139	10542	5217	11156	36688

ANALYTICAL CHEMISTRY DIVISION

Y-12 SITE

SERVICE ANALYSES

ANALYTICAL WORK FOR THE NEPA PLANT

L. J. Brady

Both spectrographic and chemical analyses of samples for the NEPA plant are being done in increasing volume. The spectrographic work is concerned mainly with the analysis of bismuth metal and bismuth-lead alloys for minor constituents (Fe, Cr, Ni, Mn, Mo, Nb, Ti, W, and Ta) which were picked up from contact of molten metals with stainless steels. Spectrographic standard solutions of all metals tested both with Bi and Bi-Pb matrices were prepared in the chemical laboratories.

The preparation of samples for spectrographic analyses includes melting the samples from stainless steel capsules under vacuum, dissolution in suitable solvents and addition of platinum to the solutions as an internal spectrographic standard.

Some difficulty was encountered in dissolving Bi-Pb alloys, particularly those containing Cr, Ta, or Nb. HNO_3-HCl in addition to perchloric acid has proven an effective solvent for the high-chromium samples. The dissolution difficulties have been overcome and the chemical preparation methods have been fairly well established.

Chemical analyses include the determination of oxygen in Bi and Bi-Pb alloys, the complete analyses of stainless steels, and other miscellaneous samples varied in chemical nature.

A small laboratory has been equipped specifically for the analysis of stainless steels so that this type of work can be carried out rapidly and efficiently.

In the earlier stages of this work, progress was rather slow because of the necessity of establishing satisfactory techniques both in the chemical preparation and subsequent spectrographic examination. Earlier difficulties have been largely overcome and the work is progressing satisfactorily.

A summary of the analytical work carried out for the NEPA plant during this period is as follows:

Summary of NEPA Analytical Work

For period, March 26 to June 26, 1950, inclusive

		NUMBER OF SAMPLES
Backlog, March 26, 1950		226
Received, March 26 - June 25, 1950, incl.		163
	TOTAL	389
Reported, March 26 - June 25, 1950, incl.		343
Backlog, June 26, 1950		46

ANALYTICAL SERVICES FOR Y-12 PLANT

J. W. Robinson

During the past quarter, the major part of the analyses of this group was performed for various groups of the Y-12 Chemical Research Division. A large number of samples of zirconium tetrafluoride from the Isotope Chemistry Division were analyzed. Miscellaneous zirconium compounds were also analyzed. Manganese determinations were made on samples of calcium metal which were submitted by the Production Chemical Department. The work for the Health Physics and Hygiene Department includes the analyses of air and water samples. Zirconium metal was analyzed for the Materials Laboratory. Of the various materials which were analyzed for the Chemical Development Division, the samples derived from the study of the uranium-carbonate and uranium-carbonate-fluoride systems contributed a large part of the load. Samples from experimental work with lithium amalgams, and solutions and solids from the phosphate rock program have also contributed a large share. In addition, miscellaneous samples such as lead phthalates, sodium uranyl arsenates, other uranium compounds, miscellaneous residues and solutions, samples of distilled water, etc., were analyzed.

Other services that are increasing in volume are the preparation of standard solutions and samples for spectrographic analysis.

TABLE IX

Summary of Y-12 Analytical Work

TYPE OF MATERIAL	NUMBER OF SAMPLES REPORTED
Zirconium compounds	382
Calcium metal	254
Carbonate solutions	191
Water	74
Transformer oils	63
Amalgams and lithium mixtures	53
Fluoride solutions	44
Uranium compounds	37
Resins	31
Organic solvent solutions	30
Phosphate rock, solids and solutions	24
Air samples	33
Miscellaneous residues	22
Lead phthalates and leach solutions	16
Zirconium metal	5
Other	71
Total number of samples reported	1330
Total number of determinations made	3607
Average number of laboratory personnel	12

METHODS DEVELOPMENT

The development of analytical methods falls principally into two categories, (1) work on problems encountered in service analysis, and (2) a development program, somewhat broader in scope, which is concerned chiefly with current and anticipated analytical requirements of the NEPA research and development work.

ANALYSIS OF LITHIUM WITH THE FLAME PHOTOMETER

H. P. House and Samuel Blumkin

A systematic study is being made of the applicability of the Beckman Flame Photometer to the determination of Na, K, Ca, and Mg in lithium metal and lithium salts.

No lithium metal or lithium compound sufficiently free of sodium to serve satisfactorily as a standard material has been located. The best material so far tested contains ~80 parts per million of sodium. (This value is in question since a sodium-free reference standard for comparison is not available.) The effects of variables on sensitivity and apparent interferences are being studied for Na, K, Li, and Na plus Li with the Beckman Flame Photometer. At present, the effective limit of sensitivity for sodium in a lithium matrix appears to be of the order of 20 - 50 parts per million.

OXYGEN IN ZIRCONIUM METAL

H. P. House and Roberta McCutchen

It was necessary to develop or adapt a method for determining the oxygen content of the zirconium metal. It was assumed that upon volatilization of the metal, the oxygen would remain in the residue in the form of zirconium oxide. On the basis of this assumption, a method proposed by Dr. E. B. Read[1] was investigated.

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(1) Rodden, C. J., *Minutes of Zirconium Conference, January 9 and 10, 1950*, NYDO-2005 (n.d.).

The method consisted of three steps: volatilization of the metal in a quartz combustion tube with HCl gas at 500 - 850°C, ignition of the residue at 1000°C in air to convert the materials to the oxides, and the analysis of the ignited residue for zirconium.

It was found necessary to modify both the apparatus and procedure proposed by Dr. Read in order to obtain more accurate results. Originally, air was driven from the volatilization tube by dry, oxygen-free argon gas, but this was later found to be unnecessary. Dry HCl gas has been substituted for argon. This eliminates changing from one gas to another and insured sufficient HCl gas to completely volatilize the zirconium. The zirconium content of the residue is determined and suitable corrections are made for any impurities which are non-volatile with HCl.

Initially calcium sulfate and concentrated H_2SO_4 were used as drying agents but calcium chloride was later substituted to eliminate the "carry-over" of sulfate into the volatilization tube.

From the oxygen values obtained for crystal bar zirconium metal, it is believed that the presence of sulfate inhibits the reaction of the HCl gas and zirconium metal. When calcium chloride was substituted for the sulfate drying agents, the apparent oxygen content of crystal bar decreased from about 3 percent to 0.6 percent. Since this latter value is more nearly consistent with the known physical properties of the crystal bar, it appears that the method as modified here is satisfactory for determining the oxygen content of zirconium metal.

COLORIMETRIC PERIODATE DETERMINATION OF MANGANESE

Roberta McCutchen

The determination of low concentrations of manganese in calcium metal by the periodate method has been in use for some time and satisfactory results have been obtained. When the determination of manganese in solutions of bismuth metal was attempted using this method, inconsistent results were obtained. Using a solution of Bureau of Standards manganese metal (No. 67), a study is being made to determine why this method is satisfactory for low concentrations of manganese but not for higher concentrations. Although this study has not

been completed, it appears that a break in the linear relationship of optical density to manganese concentration probably occurs at about 100 parts per million manganese. An attempt is being made to overcome this difficulty by using larger cells and a more sensitive instrument. A Beckman Model D. U spectrophotometer equipped with 10 cm cells is being substituted for the Coleman instrument with 3.8 cm cells.

NITROGEN IN ARGON

Helen Grady and Roberta McCutchen

Since nitrogen combines readily with zirconium metal (small amounts impart undesirable properties to the metal), the following method is being investigated for determination of traces of nitrogen in the argon to be used to maintain an inert atmosphere during the refining operations. Known volumes of the argon are passed over heated calcium. The micro Kjeldahl method is then used for the determination of the nitrogen content of the calcium.

HEXONE IN AIR SAMPLES

H. P. House and Mary Barnes

Possible methods for the determination of low concentrations of hexone in air samples submitted by the Health-Physics and Hygiene Department are being investigated. The method proposed by Jacobs[2] which depends on the reaction of a ketone with I_2 to form iodoform and subsequent titration of the excess iodine has not given consistent or quantitative results, when standard solutions of hexone were analyzed.

DETERMINATION OF AIR-BORNE THALLIUM

Mary Barnes

Colorimetric methods for the thallium collected in air samples proved to be too insensitive for micro concentrations. It was found, however, that

(2) Jacobs, M. B., *Analytical Chemistry of Industrial Poisons, Hazards and Solvents*, New York: Interscience Publishers, Inc., Vol. 1, p. 543 (1941).

the thallium could be removed from the absorbent by coprecipitation with aluminum hydroxide as a carrier, the precipitate ignited and then analyzed spectrographically. Using this method, as little as one microgram of thallium per four milligrams of aluminum oxide can be determined.

ANALYSIS OF LITHIUM HYDRIDE

H. P. House and C. K. Talbott

Comparative tests were made of the gas evolution and combustion method for determining hydrogen in lithium hydride. Although the precision of the combustion method was considerably better than that of the gas evolution method, the gas evolution method can be used satisfactorily, where errors of the order of one percent may be tolerated.

ANALYSIS OF ZIRCONIUM TETRAFLUORIDE

J. W. Robinson

The complete removal of fluoride from zirconium fluoride by the Willard and Winters distillation process requires ~ 2-3 hours. If the fluoride is not completely removed prior to the determination of zirconium in the residual solution, the recovery of zirconium by precipitation will be incomplete. In order to decrease the time, and simplify the analysis, it is proposed to hydrolyze ZrF_4 with steam at 1000°C. This technique is used successfully in the K-25 plant laboratories for decomposing UF_4. It is anticipated that the distillate can then be analyzed for fluoride in the usual manner (titration with thorium nitrate), the residual solution evaporated and the residue ignited as zirconium oxide.

Experimental work on this method of analysis will be carried out as soon as a special platinum reaction tube and accessories, which have been ordered, are available.

QUALITY CONTROL

During this period a system of quality control somewhat more comprehensive than that which was previously used was placed in operation. Standard samples are analyzed under exactly the same conditions as are regular samples. The test results for standard samples are evaluated statistically, and limit charts constructed. When the results indicate the necessity, methods and techniques are studied and such corrections are applied as may be necessary to insure satisfactory precision and accuracy. In addition to indicating trouble spots in service analysis, the quality control work also defines the limits of error which may be anticipated. A summary of quality control data setting forth limits of error for the most commonly required determinations is tabulated in Tables X and XI. The precision given in the "Reported Values" column is twice the standard deviation for the series in question, which is equal to the 95% confidence interval for a single determination. The column headed "Limit of Error of One Analysis, in Percent" expresses the same figure in terms of a percentage of the value determined.

CHEMICAL ANALYSIS

Roberta McCutchen

The test results obtained for sodium and carbonate in the standard carbonate solution, as given in the following table, are not as precise or accurate as had been anticipated. A new standard solution of Mallinckrodt Na_2CO_3 (Primary Standard) has been prepared and will be used to determine those steps necessary to achieve maximum accuracy and precision.

The concentration of zirconium in zirconium fluoride is expected to be 54.5 percent. The value obtained by the analysis of ZrF_4 for zirconium is 54.9 ± 0.1 percent with a limit of error in one analysis of 3 percent. Since the error of the zirconium analysis is greater than is normally expected for a constituent present in the amount of 50 percent or greater, it appears that the method is not completely satisfactory.

TABLE X

Quality Control Summary
Chemical Analyses

SAMPLE TYPE	DETERMINED	METHOD		CONTROL SAMPLES ANALYZED	ACCEPTED VALUE	REPORTED VALUES (Av. Mean ± 2)	UNITS	PERCENT LIMIT OF ERROR OF ONE ANALYSIS
Na_2CO_3	Na	Flame Photometer		27	3.4	3.2 ± 0.1	mg/ml	8
Na_2CO_3	CO_3	Gas Evolution		26	4.4	4.4 ± 0.6	mg/ml	4
ZrF_4	Zr	Gravimetric, phenyl arsonic acid pptn.		44		54.9 ± 0.1	percent	3
ZrF_4	H_2O	Karl Fischer		44		0.2 ± 0.2	percent	100
Calcium	Mn	Periodate, Colorimetric	Std. #1	8		4.8 ± 0.9	ppm	38
				5		8.9 ± 2.5	ppm	20*
			Std. #2	7		3.9 ± 0.9	ppm	22

*The method was modified (after eight controls had been processed) to eliminate chloride interference. Therefore, the test results for the last five control samples are believed to be more accurate and the method more precise.

The limit of error determined for the analysis of water in zirconium fluoride is exceptionally large. However, since the amount of water present is very small, about 0.2 percent, an error of this magnitude may be unavoidable. An investigation of the method will be carried out in order to determine whether the precision can be improved.

A modification of the method used for determining manganese in calcium metal has resulted in considerable improvement in the precision of the test results, the limit of error having decreased from about 40 to 20 percent. A 20 percent limit of error for this analysis is satisfactory when the low concentration of manganese in the calcium metal is taken into consideration.

An increase in the number of samples requiring the determination of chloride has indicated the necessity of starting a control program for this analysis. A solution of Merck, ACS, Reagent grade NaCl, has been secured and will be used for preparing a standard for control purposes.

A sample of fluoride phosphate rock slime is now being prepared for use as a control sample for the phosphate rock program.

SPECTROGRAPHIC ANALYSIS

Roberta McCutchen

A study was made of the precision and accuracy obtained in the spectrographic determination of traces Fe, Ni, Cr, Mo and Mn in metallic Bi and Pb-Bi alloys. Twenty percent solutions of Bi and 15 percent solutions of Pb-Bi alloy in 15 percent aqua regia were prepared, treated with known amounts of the above elements, and submitted for spectrographic analysis. The results are presented in Table XI. The limit of error (95 percent confidence interval) ranges from 14 to 65 percent, depending on the element determined and its concentration level. As these results were among the first obtained with the technique used, the figures obtained are regarded as quite satisfactory.

TABLE XI

Spectrographic Analyses

SAMPLE TYPE	DETERMINED	SERIES 1				SERIES 2			
		CONTROL SAMPLES ANALYZED	ACCEPTED VALUES (ppm)	REPORTED VALUES (Av. Mean ± 2σ) (ppm)	PERCENT LIMIT OF ERROR OF ONE ANALYSIS (95% conf. int.)	CONTROL SAMPLES ANALYZED	ACCEPTED VALUES (ppm)	REPORTED VALUES (Av. Mean ± 2σ) (ppm)	PERCENT LIMIT OF ERROR OF ONE ANALYSIS (95% conf. int.)
Bismuth	Fe	4	149	166 ± 24	14	3	178	190 ± 50	26
	Ni	4	109	*	*				
	Cr	4	39	44 ± 28	65	4	28	30 ± 18	60
	Mn	4	47	48 ± 28	60	4	<10	<10	*
Bismuth-Lead	Fe	6	150	143 ± 33	23				
	Ni	6	110	130 ± 26	20				
	Cr	6	39	47 ± 31	65				
	Mo	6	<10	<10	*				

* Insufficient data to determine limits of error.

SPECIAL PROBLEMS

A considerable number of special problems, non-analytical in nature, are continually being worked on. Projects of this type which are currently active or which were completed during this period are briefly reviewed below.

INHIBITING ACTION OF CHROMATE ON CORROSION OF ZIRCONIUM BY UO_2F_2 SOLUTION

Roberta McCutchen

Corrosion resistance tests of metallic zirconium in UO_2F_2 aqueous solutions, to which varying amount of potassium chromate were added, were completed during the period. A report of this work is now in preparation.

PURIFICATION OF ZIRCONIUM OXIDE

J. W. Robinson and S. R. Buxton

A successful laboratory-scale method[1] for the preparation of ZrO_2 of sufficiently high purity to be acceptable as a spectrographic standard was used to produce ~ 200 grams of this material. Since a larger stock of this material is desired, a large-scale purification of eight to nine pounds of ZrO_2 is now in progress.

A salicylic acid precipitation is made on the final product to remove the iron which is probably picked up from the reaction kettle.

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(1) Clewett, G. H., *Progress Report of Y-12 Chemical Research Division, January 1, 1550 to March 31, 1950*, Y-585 (April 20, 1950).

[redacted]

PREPARATION OF URANIUM TELLURIDE

L. J. Brady

Approximately 17 grams of a product which chemical analyses and X-ray diffraction studies indicated to be of the order of 35 percent UTe with NaCl, UCl_4, and a little UO_2 comprising the remainder was supplied to Argonne National Laboratories.

The following attempt was made to produce pure UTe: tellurium vapor was reacted directly with uranium metal at 980°C. The test results of chemical analyses and X-ray diffraction studies of the black residue indicated that approximately 25 percent of the uranium had undergone a reaction, assuming the product to be UTe. It seems reasonable to assume that a telluride surface layer formed which inhibited the further reaction of uranium with tellurium.

Attempts to isolate the UTe by subliming it under vacuum at 1200°C, the maximum temperature attainable in the apparatus used, were unsuccessful. No uranium telluride volatilized under these conditions, indicating that the vapor pressure of this compound is extremely low and that it is thermally quite stable.

SOLUBILITY TESTS OF CO_2 IN VARIOUS SOLUTIONS

H. P. House and Mary Barns

A suitable confining liquid is necessary for gases which are evolved when certain materials are subjected to pile irradiation. Tests were made of the solubility of CO_2 in aqueous solutions of Na_2CO_3, $NaHCO_3$, and $AgNO_3$ containing 5 percent of HNO_3. All of the solutions tested dissolved CO_2 to such an extent as to preclude their use for confining gas mixtures containing this component.

[redacted]