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ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director

C. D. Susano, Associate Director

QUARTERLY PROGRESS REPORT

for Period Ending October 10, 1950

DATE ISSUED: DEC 28 1950

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ABSTRACT

ANALYTICAL CHEMISTRY DIVISION—X-10 SITE

Ionic Analyses—Research and Development. Microgram quantities of cobalt have been determined volumetrically using the automatic titrimeter. A microtitration method has been used to analyze Chalk River plutonium solutions. The lanthanum fluoride-carrier-precipitation method has been applied to the separation of U(IV) and U(VI).

An indirect polarographic method for the determination of sulfites and thiosulfates is proposed. Preliminary tests made with the redesigned Sargent polarograph model XX indicate that a more useful and versatile instrument has been built. A method for the polarographic determination of uranium in concentrated plutonium solutions has been tested.

Radiochemical Analyses—Research and Development. Activation cross sections for Ge^{70}, Ge^{74}, and Ge^{76} are reported here. A procedure for the determination of trace amounts of lithium by activation analysis is described. Activation-analysis procedures for sodium, potassium, copper, and manganese are also given.

A discussion of disintegration rates of I^{131} as determined by the end-window G-M counter (Radioisotope Control Laboratory), the coincidence counter, and the 4π proportional counter is included. A rapid method for the determination of I^{131} and I^{133} in process solutions is described. An evaluation of the zirconium phenylarsonate-carrier method for the determination of Pu(IV) has been made.

An ion-exchange method for the determination of small amounts of certain alkali metals in the presence of others has been tested. A study of the sorption of radionuclides by Arco soil is included.

Spectrochemical Analyses—Research and Development. Completed sections for the publication on photographic photometry of the American Society of Testing Materials are listed. A list of the new working curves which were prepared during this quarter is also given.

Service Analyses. A total of 39,924 analyses have been performed during this quarter.

[redacted]

Inorganic Preparations. A method for the preparation of the anhydrous chlorides and fluorides of Fe^{++}, Co^{++}, Ni^{++}, and Mn^{++} is given. A procedure for the preparation of three series of lithium compounds is included.

Analytical Chemical Control of Homogeneous Reactor Solution. A description of the further development of the two most feasible methods for the analytical chemical control of the homogeneous reactor solution is given.

Optical and Electron Microscopy. Further microscopic studies of Bureau of Mines zirconium are discussed. A panoramic cross section of a length of tantalum tubing welded in an argon atmosphere by a method using tungsten electrodes which do not contact the tubing is included.

ANALYTICAL CHEMISTRY DIVISION—Y-12 SITE

Ionic Analyses—Research and Development. A comparative study of three precipitating agents—phenylarsonic acid, mandelic acid, and cupferron—for the gravimetric determination of zirconium has been made.

Service Analyses. During this quarter 3475 analyses have been completed.

Inorganic Preparations. A method for the preparation of $U^{235}Cl_5$ is proposed.

ANALYTICAL CHEMISTRY DIVISION
X-10 SITE

IONIC ANALYSES—RESEARCH AND DEVELOPMENT

AUTOMATIC POTENTIOMETRIC TITRATION OF MICROGRAM QUANTITIES OF COBALT

P. F. Thomason

A number of nickel samples were submitted to the Spectrographic Laboratory for determination of the cobalt content. As a check method, it was decided by apply the semimicro automatic-titration apparatus to this problem, using $K_3Fe(CN)_6$ as the titrant. The $K_3Fe(CN)_6$ volumetric method has been used previously for the determination of milligram quantities of cobalt in the presence of nickel.(1) Since the amount of available sample was limited, microgram quantities of cobalt were titrated.

The semimicro automatic titration apparatus has been described previously.(2) The titrant, 0.02 *M* $K_3Fe(CN)_6$, was made from reagent-grade chemical and was standardized against two solutions of cobalt, one prepared by dissolving pure cobalt metal and the other prepared from reagent-grade cobaltous chloride.

Aliquots containing 100 γ of cobalt were pipetted into 20-ml beakers, 5 ml of 28% NH_4OH was added, and the volume was adjusted to 7 to 8 ml with distilled water. A magnetic stirring bar was placed in the beaker, and the solution was titrated with 0.02 *M* $K_3Fe(CN)_6$, using a platinum-wire indicating electrode and a calomel reference electrode as the electrode assembly. The calibration curve is shown in Fig. 1.

When the submitted samples were titrated, it was found that a break in the potential similar to the calibration curve could not be obtained. This was attributed to the manganese present in the samples. Zvenigorodskaya(3) has described a macro method for titrating cobalt with $K_3Fe(CN)_6$ in the presence of manganese, in which the cobalt is back-titrated after oxidation of the manganese. It was decided that a simple separation could be effected by oxidizing the Mn to MnO_2 with $(NH_4)_2S_2O_8$ in the presence of $AgNO_3$. The

(1) Dickens, P., and Maassen, G., "Application of Potentiometric Volumetric Analysis in the Steel-Plant Laboratory. VII," *Mitt. Kaiser-Wilhelm-Inst. Eisenforschung, Düsseldorf* 17, 191 (1935); Chem. Abs. 30, 695.

(2) Thomason, P.F., and Kelley, M. T., *Determination of Chloride in Zirconium Metal*, ORNL-747 (Aug. 3, 1950).

(3) Zvenigorodskaya, V. M., "*Potentiometric Determination of Cobalt in the Presence of Manganese*," *Zavodskaya Lab.* 11, 1010 (1945); *Chem. Abs.* 40, 7052.

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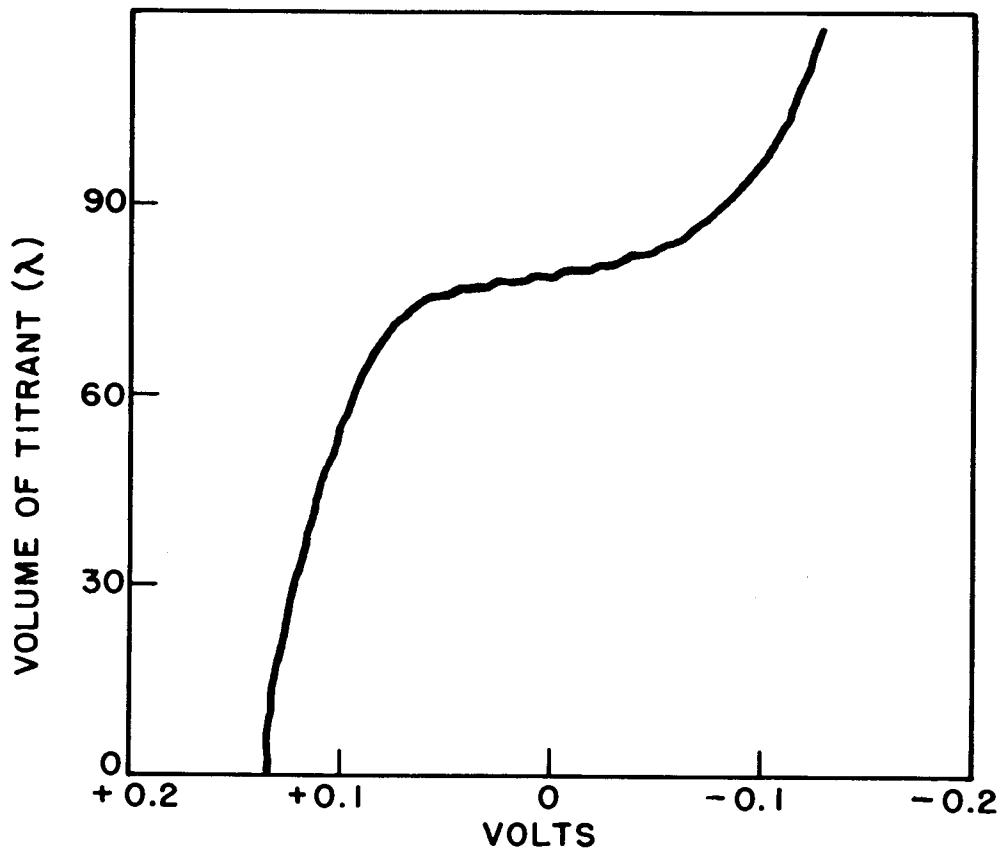

FIG. 1
TITRATION OF 100 γ OF Co WITH 0.02 M $K_3Fe(CN)_6$

MnO_2 was filtered off, and then the Ag was precipitated with HCl and filtered off. The filtrate, containing nickel and cobalt, was titrated in the usual manner after making the solution ammoniacal. The titration curves thus obtained were the typical Co^{++} to Co^{+++} oxidation curves using $K_3Fe(CN)_6$ as the oxidant.

AUTOMATIC POTENTIOMETRIC TITRATION OF MICROGRAM QUANTITIES OF PLUTONIUM

F. J. Miller

Previously described work[4] on microtitrations has been continued, directed toward the estimation of plutonium. A number of titrations have been made by the standard method of fuming the sample with sulfuric acid, diluting in 9 *N* H_2SO_4, reducing with 20% titanous chloride under a CO_2 atmosphere, and titrating.

The best value obtained by a number of titrations of a plutonium solution was higher than that obtained by alpha counting of the solution. In an effort to reconcile the difference, a gravimetric check was made. The gravimetric result is, apparently, in excellent agreement with the value obtained by titration.

Samples of Chalk River plutonium solutions were then run, and these results were also higher than those obtained by alpha counting. Colorimetric analysis for iron and polarographic analysis for uranium showed only a small amount of these ions present. After corrections were made for the U and Fe present, the results were still high.

Synthetic samples, using standard iron solutions instead of plutonium solutions, were titrated with high accuracy and precision.

Titration of Plutonium Solution with Ceric Sulfate. Five titrations of a plutonium solution were made with ceric sulfate as titrant.

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

Pu ALIQUOT (λ)	NORMALITY OF CERIC SULFATE SOLUTION	CHART TRAVEL (in.)	CALCULATION
100	0.0971	5.75	$\frac{5.6 \times 1.02^* \times 0.0971 \times 239}{100}$
100	0.0971	5.50	
100	0.0971	5.35	= 1.325 mg of Pu per ml
100	0.0971	5.70	
100	0.0971	5.60	
		5.58 (Avg.)	

* Calibration factor for buret.

Average deviation = 0.134 in.
Standard deviation = 0.153 in.
Probable deviation = 0.117 in.

Titration of Iron with Ceric Sulfate. Two 10-ml aliquots of $FeSO_4$ solution were titrated with ceric sulfate, using eriochrome blue as an indicator.

Fe ALIQUOT (ml)	NORMALITY OF CERIC SULFATE SOLUTION	TITER (ml)	CALCULATION
10	0.0976	8.2	$\frac{0.0976 \times 8.2}{10}$
10	0.0976	8.2	
			= 0.0800 *N* $FeSO_4$ solution

Five 10-λ aliquots of $FeSO_4$ solution were titrated manually to a colorimetric end point, using eriochrome blue as indicator.

Fe ALIQUOT (λ)	NORMALITY OF CERIC SULFATE SOLUTION	TITER (λ)	CALCULATION
10	0.0976	7.59	$\frac{7.29 \times 1.02^* \times 0.0976}{10}$
10	0.0976	7.61	
10	0.0976	7.00	= 0.0728 *N* $FeSO_4$ solution
10	0.0976	7.23	
10	0.0976	7.04	
		7.29 (Avg.)	

* Calibration factor for buret.

Six 10-λ aliquots of $FeSO_4$ solution were titrated using the same buret coupled to the automatic titration mechanism.

Fe ALIQUOT (λ)	NORMALITY OF CERIC SULFATE SOLUTION	CHART TRAVEL (in.)	CALCULATION
10	0.0976	7.30	$\frac{7.23 \times 1.02^* \times 0.0976}{10}$
10	0.0976	7.38	
10	0.0976	7.27	= 0.0719 *N* $FeSO_4$ solution
10	0.0976	7.45	
10	0.0976	6.98	
10	0.0976	7.40	
10	0.0976	6.85	
		7.23 (Avg.)	

* Calibration factor for buret.

If the value 6.85 is eliminated, the following value is obtained:

$$\frac{7.29 \times 1.02 \times 0.0976}{10} = 0.0726\ N\ FeSO_4 \text{ solution}$$

The normality of the $FeSO_4$ solution as obtained by these three methods is:

Macro	0.0800
Micro colorimetric	0.0728
Micro automatic potentiometric	0.0726, 0.0719

A series of eight titrations of 0.210 *N* ferrous sulfate solution against 0.0971 *N* ceric sulfate solution was run potentiometrically using a microburet coupled to the automatic titration mechanism. The results are given below:

TITRATION	CHART TRAVEL (in.)	DEVIATION	+ DEVIATION	- DEVIATION	SQUARE OF DEVIATION
1	20.40	-0.28		-0.28	0.0784
2	21.25	+0.57	+0.57		0.3249
3	20.80	+0.12	+0.12		0.0144
4	20.28	-0.40		-0.40	0.1600
5	20.75	+0.07	+0.07		0.0049
6	20.15	-0.53		-0.53	0.2809
7	20.75	+0.09	+0.09		0.0081
8	21.05	+0.37	+0.37		0.1369
	20.68 (Avg.)	0.30 (Avg.)			

Average error of a single determination = 2.43/8 = 0.30

Average error of n determinations = $2.43/8\sqrt{8}$ = 2.43/23.2 = 0.18

Standard deviation of a single determination = $\sqrt{1.0085/7} = \sqrt{0.144}$ = 0.38

Standard deviation of n determinations = $\sqrt{1.0085/56} = \sqrt{0.018}$ = 0.136

Probable error of n measurements = 0.6745 × 0.135 = 0.091

Probable error of a single measurement = 0.6745 × 0.38 = 0.25

SEPARATION OF U(IV) FROM U(VI) BY THE LANTHANUM FLUORIDE-CARRIER METHOD

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

The procedure for separating U(IV) from U(VI) has been adapted from a standard procedure for separating Pu(IV) from U(VI) in which the Pu(IV) is carried, as a precipitate of PuF_4, by lanthanum fluoride. The precipitate is washed successively with 1 *N* HF–1 *N* HCl and 1 *N* HF–1 *N* HNO_3. After each washing the solution is centrifuged and the supernatant is decanted. The precipitate thus treated is filtered onto a polished platinum plate, and the plutonium is determined by alpha counting. To permit the polarographic determination of the U(IV) as U(VI) the procedure is modified as follows:

U(IV) is precipitated as UF_4 with lanthanum fluoride carrier. After complete washing and centrifugation, it is dissolved in 75 λ of concentrated HNO_3 and 1 drop of saturated H_3BO_3 solution. The U(IV) is oxidized to U(VI) with a small crystal of $KMnO_4$, and the excess permanganate is reduced with 1 drop of 10% $NH_2OH \cdot HCl$ solution. The solution is diluted to 2 ml, and the U(VI) is determined polarographically.

Procedure. A standard U(IV) solution containing 10 mg of total U per milliliter is prepared by digesting 0.1179 g of U_3O_8 in concentrated H_2SO_4 and reducing the U(VI) to U(IV) in a Jones reductor. Any U(III) that may be present is oxidized to U(IV) by bubbling air through the solution. The solution is diluted to 10 ml.

Residual U(VI) is determined by diluting a 20-λ aliquot of the standard U(IV) solution to 2 ml and analyzing polarographically for U(VI). The total uranium is determined by oxidizing a 20-λ aliquot with $KMnO_4$, reducing excess $KMnO_4$ with $NH_2OH \cdot HCl$, diluting to 2 ml, and analyzing polarographically.

$$\text{Total U} - \text{U(VI)} = \text{U(IV)}$$

The values obtained from the standard solution were checked by carrying out the lanthanum fluoride separation of U(IV) from U(VI).

Table 1 shows the results obtained when standard U(IV) solutions were analyzed both directly for U(IV) and after lanthanum carrier precipitation.

TABLE 1

Separation of U(IV) from U(VI) in Standard U(IV) Solutions

TOTAL U IN STANDARD (γ)	U(VI) IN STANDARD (γ)	U(IV) IN STANDARD (γ)	
		BY DIFFERENCE	BY LaF SEPARATION
200	21.4	178.6	185.5
200	21.4	178.6	183.6
194.6	26.6	168.0	168.8

Table 2 shows the results obtained from samples submitted by A. R. Olsen and J. L. English of the Reactor Technology Division.

TABLE 2

Separation of U(IV) from U(VI) in UO_2SO_4 Samples Submitted by the Reactor Technology Division

SAMPLE	U(IV) (γ/ml)
D8-1a	12.5
D8-1b	9.3
D10-1a	65.4
D10-1b	65.4
D13-1	438.0
139-2Fa	8.2
139-2Fb	8.4
139-3F	12.8

SPECTROPHOTOMETRIC DETERMINATION OF INORGANIC FLUORIDES

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

A detailed report of the completed experimental work is to be issued soon as ORNL-839.

INDIRECT POLAROGRAPHIC DETERMINATION OF SULFITES AND THIOSULFATES

A. D. Horton M. T. Kelley
P. F. Thomason

A number of UO_2SO_4 solutions which have been subjected to high pressure and radiation in the ORNL reactor have been submitted to this laboratory for determination of the decomposition products of SO_4^-. It was believed that any sulfites or thiosulfates present in these solutions could be determined by a modification of an indirect sulfate polarographic method which has already been developed.(5) Sulfites, thiosulfates, or any easily reducible sulfur complex can be reduced to H_2S with pure aluminum strips in the presence of HCl. Sulfate would not be reduced by the aluminum.

Several synthetic samples containing known amounts of sodium thiosulfate were analyzed by this procedure. The H_2S was collected in a cadmium chloride solution. The CdS precipitate was washed, dissolved in HCl, and diluted to a final volume of 5 ml, and polarograms of the cadmium were obtained. The data are shown in Fig. 2. The abscissa is plotted as micrograms of sulfide, although in reality it is the cadmium polarogram that is measured.

The analyses of the submitted samples have not been completed. Results will be reported later.

MODIFICATION OF THE SARGENT POLAROGRAPH MODEL XX

H. H. Miller

Owing to the need for a more sensitive instrument, it was decided to redesign the Sargent polarograph model XX and make an instrument very similar to that designed by Kelley.(6)

By the new design the sensitivity of the instrument was increased from 50 to 0.05 μa per full scale deflection; a compensator for condenser current

(5) Horton, A. D., and Thomason, P. F., *Polarographic Determination of Sulfates*, ORNL-755, to be issued.

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

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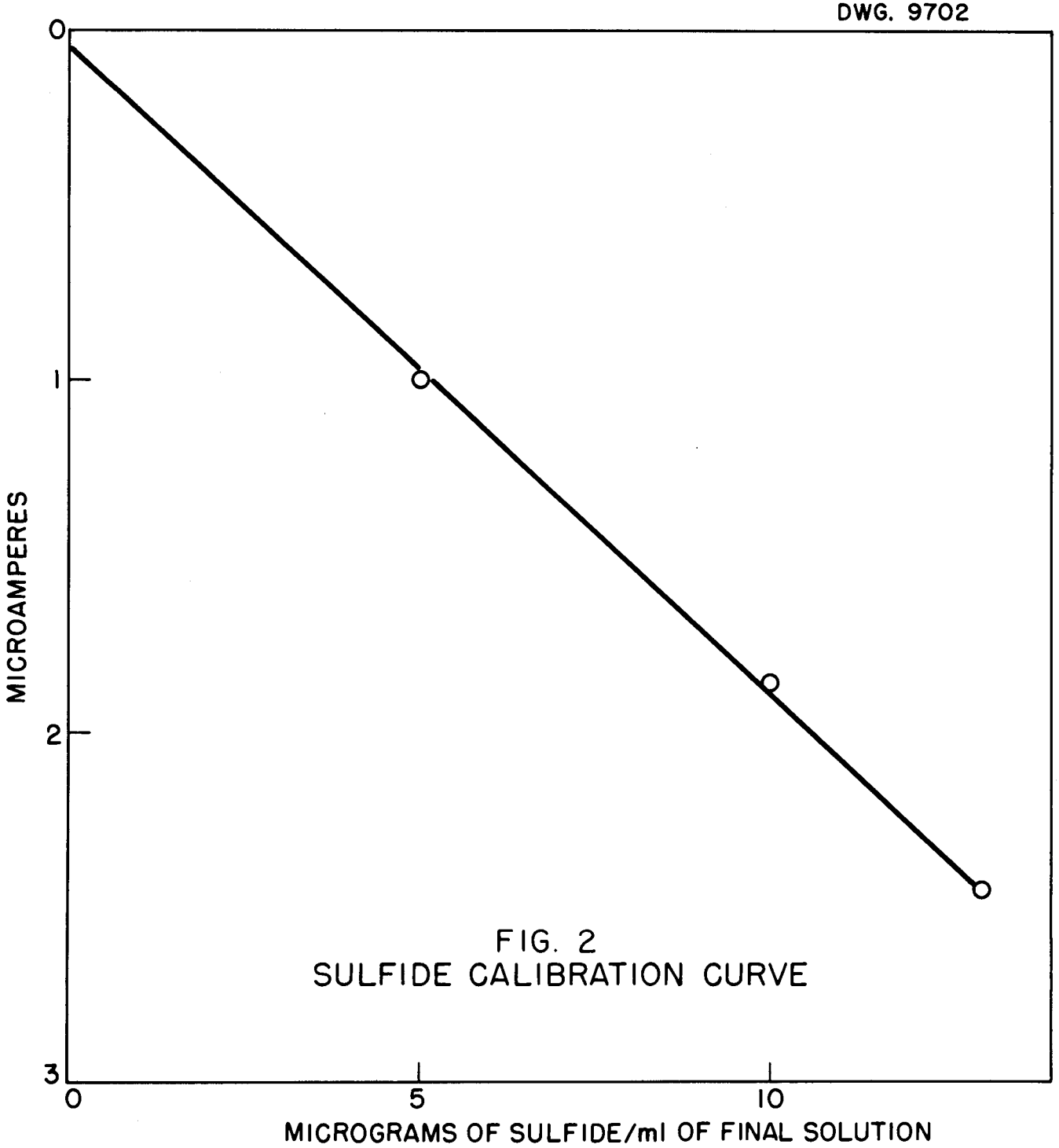

FIG. 2
SULFIDE CALIBRATION CURVE

was included. The panel of the instrument was completely redesigned to eliminate a-c pickup. This modification eliminated certain inherent limitations of the original instrument such as poor sensitivity, dead space in the recording circuit, and poor damping control. Preliminary tests indicate that it is more useful and versatile than the original Sargent polarograph model XX.

POLAROGRAPHY OF VERY DILUTE SOLUTIONS USING THE CURVE FOLLOWER

H. H. Miller

The polarographic determination of constituents present in concentrations of 10^{-6} *M* or lower using the curve follower has been continued. Calibration curves were run on lead solutions, and new techniques have been developed. This work is described in ORNL-942, *A High-sensitivity Recording Polarograph,* which is to be issued soon.

POLAROGRAPHIC DETERMINATION OF URANIUM IN CONCENTRATED PLUTONIUM SOLUTIONS

H. H. Miller

Previous work has shown that uranium can be determined polarographically in the presence of plutonium.[7] The determinations were made on solutions that had a fairly high uranium-to-plutonium ratio, but by using large dilution factors it was possible to obtain a final solution that had a low plutonium concentration.

It has become necessary to analyze concentrated plutonium solutions for uranium impurity. The plutonium-to-uranium ratio, in this case, limits the degree of dilution that can be made, and the final solution, therefore, is relatively high in plutonium.

In previous samples, containing approximately 0.2 to 0.3 mg of Pu per milliliter, the Pu(VI) was reduced to Pu(III) with hydroxylamine hydrochloride while the solution was deaerating. When the plutonium is increased to about 2.6 to 15 mg/ml, a longer reduction period is necessary. Excess hydrazine

(7) Miller, H. H., "Polargraphic Determination of Uranium in Plutonium Solutions," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part II. Analytical Chemistry,* ORNL 686, p. 21 (May 18, 1950).

nitrate, which has been found to be a more effective reducing agent than hydroxylamine hydrochloride, is added, and the solutions are heated for 1 to 2 hr at 65°C to 70°C.

In a solution containing 54 mg of Pu per milliliter, 0.3% uranium was determined, but this does not appear to be the lower limit of the analysis.

POLAROGRAPHIC DETERMINATION OF CADMIUM IN VINYLITE

H. H. Miller

The polarographic method for determining cadmium in vinylite has been reported previously.[8] Results of polarographic determinations are shown in Table 3.

TABLE 3

Polarographic Determination of Cadmium in Vinylite

SAMPLE NO.	CADMIUM CONCENTRATION (ppm)	
	ESTIMATED BY MANUFACTURER	POLAROGRAPHIC
15A		228
15B		None found
15C	980	344
15D	225	67
15E	45	15
15F	175	116

POLAROGRAPHIC DETERMINATION OF COBALT IN THE PRESENCE OF LARGE AMOUNTS OF NICKEL

H. H. Miller

Polarographic determination of small amounts of cobalt in the presence of large amounts of nickel is complicated by the fact that the half-wave potential of nickel directly precedes that of cobalt. In most media it would be impossible to get the two waves on the same scale since the nickel would

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

give a very large wave and the cobalt a very small one. If the ratio of nickel to cobalt does not exceed about 100 to 1, it would be possible to shift the nickel wave off scale and obtain only the cobalt wave. However, methods for the polarographic determination of cobalt when the 100-to-1 nickel-to-cobalt ratio is exceeded were desired.

It was thought that a complexing agent might be found which would either increase the half-wave potential of nickel beyond that of cobalt or tie it up so that no nickel wave would be obtained. Kolthoff and Lingane[9] report that in 1 *M* tartrate medium cobalt will give a wave with a half-wave potential at -1.6 volts vs. S.C.E. while the nickel shows no reaction. It was found, however, that under these conditions the cobalt wave was poorly defined and could not be used for analytical purposes.

It has also been reported[10] that the cobaltic ion gives a useful wave with a half-wave potential of approximately -0.15 volt vs. S.C.E. It should be possible to selectively oxidize a solution containing cobalt and nickel and obtain a wave for the cobaltic ion at approximately -0.15 volt. In this case, the nickel wave would come at a more negative potential and would not interfere. In order to check this observation a pure cobaltic compound, cobaltic hexammine chloride $[Co(NH_3)_6Cl_3]$, was prepared according to the method of Biltz.[11] It was found that in a neutral solution the cobaltic ion gave a fairly well-defined wave with a half-wave potential at approximately -0.15 volt.

Several methods of oxidizing Co^{++} to Co^{+++} have been tried. It has been reported[12] that Co^{++} can be oxidized to Co^{+++} in an ammoniacal chloride solution by bubbling air through the solution. However, this method failed to produce any Co^{+++} after an aerating period of 1 hr. Since longer aerating periods are not feasible, the method was not investigated further.

It was possible to oxidize Co^{++} to Co^{+++} with $Ag(NH_3)^{+}$ in an ammoniacal chloride solution, and a fairly well-defined curve was obtained with a half-wave potential at approximately -0.35 volt. The wave height was, however, much less than calculated, indicating incomplete oxidation.

(9) Kolthoff, I. M., and Lingane, J. J., *Polarography*, p. 286, Interscience, New York, 1941.
(10) *Ibid.*
(11) Biltz, W., "Ueber den thermischen Abbau der Kobaltiake," *Z. anorg. Chem.* 83, 177 (1914).
(12) Kolthoff, I. M., and Lingane, J. J., *op. cit.*, p. 285.

In the potentiometric titration of Co^{++} with $K_3Fe(CN)_6$ a good break is found, the reaction being oxidation of Co^{++} to Co^{+++}. A polarographic solution of Co^{++} was titrated until a slight excess of $K_3Fe(CN)_6$ was present, as indicated by the break in the curve, and the solution was analyzed polarographically; no Co^{+++} wave was obtained. When Co^{+++} was added to this solution, a wave was found at approximately -0.15 volt, indicating that the Co^{++} in the original solution had either been precipitated or had not been completely oxidized.

Further work on this procedure will be done using a controlled potential regulator to attempt electrolytic oxidation of the cobalt.

RADIOCHEMICAL ANALYSES—RESEARCH AND DEVELOPMENT

NUCLEAR PROPERTIES

Germanium Cross Sections (S. A. Reynolds). At the request of Dr. K. Lark-Horovitz, activation cross sections have been determined for Ge^{70}, Ge^{74}, and Ge^{76}, the three Ge isotopes producing activities upon neutron bombardment. The values found show reasonable agreement with the capture cross-section values found by H. S. Pomerance of the ORNL Physics Division.

The initial bombardment targets were separated Ge isotopes obtained from Y-12. Some runs were later made with normal GeO_2. Cobalt and manganese monitors were used to determine the flux.

It was found that only an 11-day K-capture activity was produced on bombarding $Ge^{70}O_2$, verifying the observation of McCown *et al.*[1] that there is only a single isomer of Ge^{71}. A cross-section value of 3.9 barns has been obtained using proportional and G-M counters calibrated with a Ni^{59} standard (C. J. Borkowski and A. R. Brosi) and a Zn^{65} sample that had been standardized by ion-chamber measurement of the intensity of the 1.1-Mev gamma, assuming the decay scheme of Good and Peacock.[2] Uncertainties in fluorescence yields and counter efficiencies account for most of the large discrepancy (Table 4). The cadmium ratio, defined as

$$\frac{\text{activity/mg in unshielded sample}}{\text{activity/mg in Cd-shielded sample}}$$

was normal (~30).

The short-lived Ge^{75} was produced in bombardment of $Ge^{74}O_2$. The half-life of Ge^{75} was found to be 79 min, somewhat lower than the value reported by Seaborg *et al.*[3] but approximating closely that of McCown *et al.*[4] Results are

(1) McCown, D. A., Woodward, L. L., and Pool, M. L., "Radioactive Isotopes of Ga and Ge," *Phys. Rev.* 74, 1311 (1948).

(2) Good, W. M., and Peacock, W. C., "Positron Emission, Electron Capture Competition in Zn^{65}," (abstract), *Phys. Rev.* 69, 680 (1946).

(3) Seaborg, G. T., Livingood, J. J., and Friedlander, G., "Radioactive Isotopes of Germanium," *Phys. Rev.* 59, 320 (1941).

(4) *Op. cit.*

TABLE 4

Germanium Activities Produced by Neutron Capture

TARGET	CROSS SECTION* (barns)			Cd RATIO	PRODUCT	HALF-LIFE	RADIATION**	E_β	E_γ
	PILE	THERMAL	PILE OSCILLATOR						
Ge^{70}	~4.2	3.9 ± 1.2	3.26	30	Ge^{71}	11 d	K		
Ge^{74}	0.5	0.53 ± 0.1	0.60	20	Ge^{75}	79 ± 4 m	β^-, γ(?)	1.3	~0.25(?)
Ge^{76}	~0.46	0.015 ± 0.006 0.30 ± 0.06	0.35	3.2	Ge^{77} Ge^{77}	0.95 ± 0.1 m 12 ± 1 h	β^- β^-, γ	1.8	~0.3, ~0.6

* "Pile" refers to apparent cross section for pile neutrons, where apparent thermal flux is determined by Co monitor; "thermal" refers to thermal cross sections; "pile oscillator" refers to determination by means of pile oscillator.

**Only properties determined or checked in the work reported here are given.

given in Table 5. The decay scheme appears to consist of a beta particle of energy about 1.3 Mev (Fig. 3) with about 10% of an approximately 0.25-Mev gamma. The presence of this gamma and the facts of its ~80-min half-life and possible coincidence with a fraction of the Ge^{75} beta have been demonstrated by means of G-M counters, the gamma-ray ionization chamber, and the coincidence instrument using proportional beta counters with a gold-window tube on the "gamma side." However, this half-life assignment is uncertain because the low efficiency for measuring the gamma and the short half-life made coincidence counting inaccurate. From coincidence data an approximate value for the Ge^{74} cross section was calculated which agreed with the reliable value obtained by spreading a weighed sample of bombarded GeO_2 on a polystyrene film and counting with a calibrated G-M counter (Table 4).

TABLE 5

Half-life of Ge^{75}

INSTRUMENT	HALF-LIFE (min)
β proportional counter	83
Automatic decay counter (Fig. 4)	77.5
G-M with E-A	81
γ ionization chamber	75
	79 ± 4 (Avg.)

Ge^{76} produces two isomers by neutron capture. The upper state decays to As^{77} through a 2.8-Mev beta path with a half-life of about 1 min.[5] The cross section for its production was determined by a technique similar to that used for Ge^{75} except that the counting rates of the sample were determined by recording every 640th count for the scaler on an Esterline-Angus chart traveling at constant known speed, then measuring the distance between successive

(5) Arnold, J. R., and Sugarman, N., *Short-lived Isomeric States of Se^{83} and Ge^{77}*, Argonne Report CC-3785 (Mar. 17, 1947).

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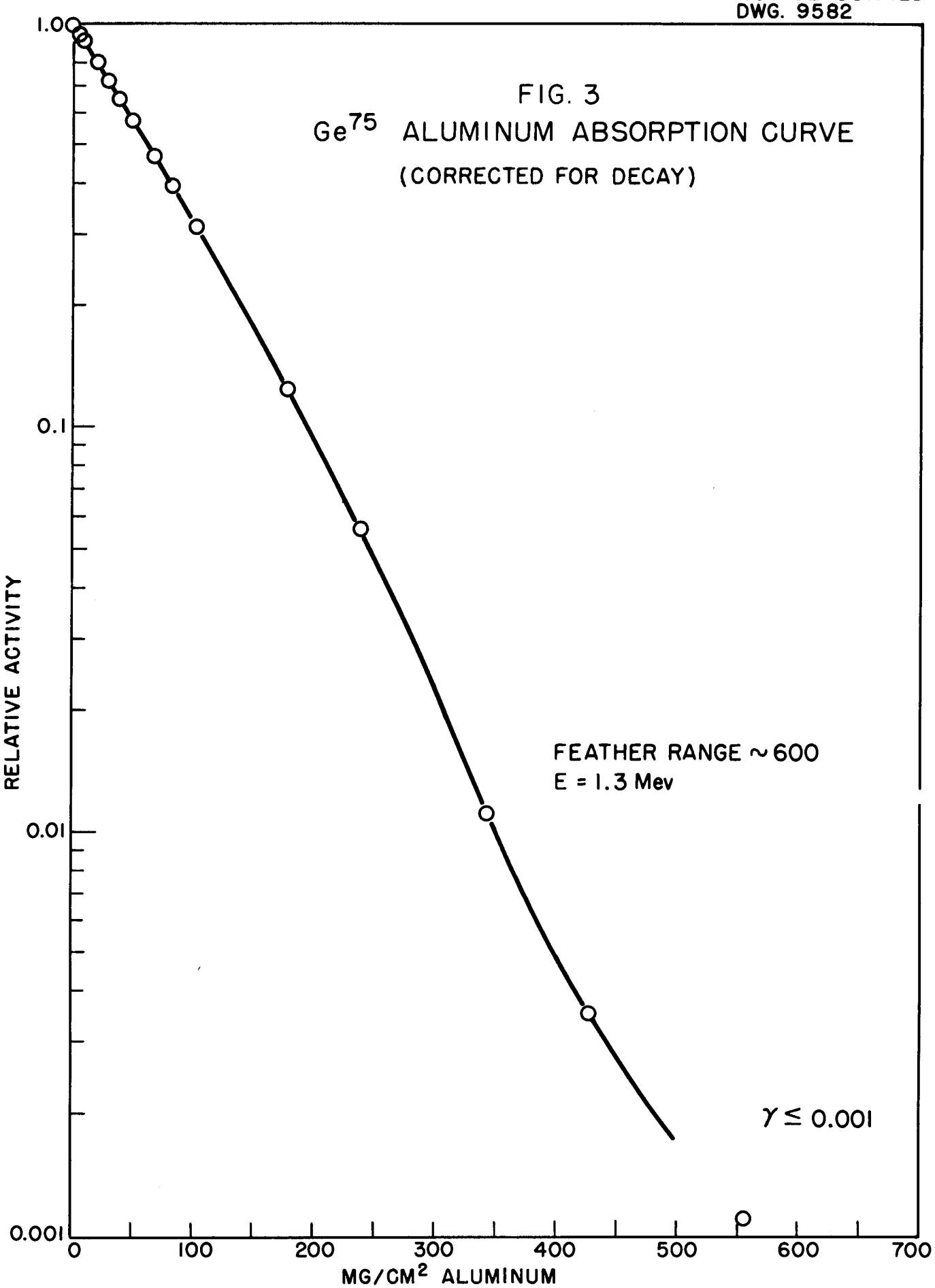

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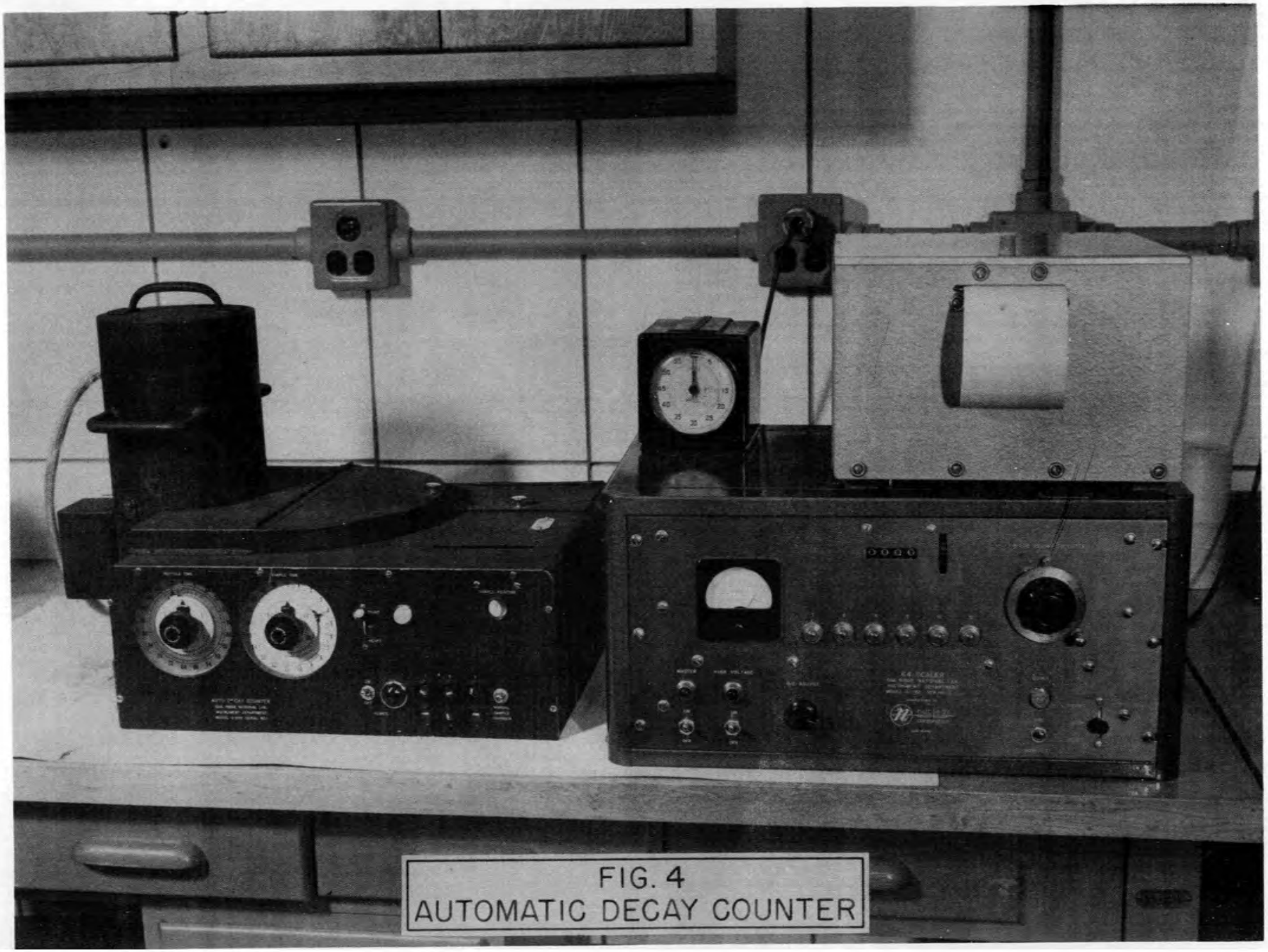

FIG. 4
AUTOMATIC DECAY COUNTER

marks (Fig. 5). The counting rates were extrapolated to zero absorber and zero time as usual.

The lower isomer has a half-life of 12 hr and a beta energy of approximately 1.8 Mev. The As^{77} daughter has a 40-hr half-life and decays by beta emission with maximum energy of 0.8 Mev. By lead absorption curves there was demonstrated the presence of at least two gamma components, one of low intensity of energy about 0.6 Mev and one of higher intensity of energy about 0.3 Mev. By coincidence absorption curves in lead it was shown that hard gamma—soft gamma coincidences are absent, but soft gamma—soft gamma coincidences were found. Also, the ratio of beta-gamma coincidences to gamma counts as a function of lead absorber was constant, indicating that both hard and soft gammas are coincident with the beta. Thus a decay scheme consisting of one beta followed by decay through alternate one-gamma or two-gamma paths is not illogical.

The disintegration rate of Ge^{77} in a bombarded GeO_2 sample was determined by coincidence counting, using sufficient aluminum absorber to stop the 0.8-Mev As^{77} beta. The cross section for the production of Ge^{77} given in Table 4 was calculated from this information after correction for the cadmium ratio.

Arnold and Sugarman[6] report that the cross section of Ge^{76} for production of Ge^{77} is about 10% higher than for Ge^{77}. This obviously is not consistent with the present work. On the basis of cross sections given in Table 4, it was calculated that after a 64-hr bombardment of GeO_2 slightly over half the gross beta activity would be due to As^{77}. By decay study it was found that about three-fourths of the activity had a half-life of approximately 40 hr, perhaps indicating a somewhat higher cross section for Ge^{77}. However, it is thought that 17-sec Se^{77} may be present as a result of its formation from As^{77}. The conversion electrons from this nuclide would cause an apparent increase in the amount of 40-hr activity. Since the "atomic" cross section for production of Ge^{77} and Ge^{77} is only about 0.02 barn, no further investigation is planned.

(6) Arnold, J. R., and Sugarman, N., *op. cit.*

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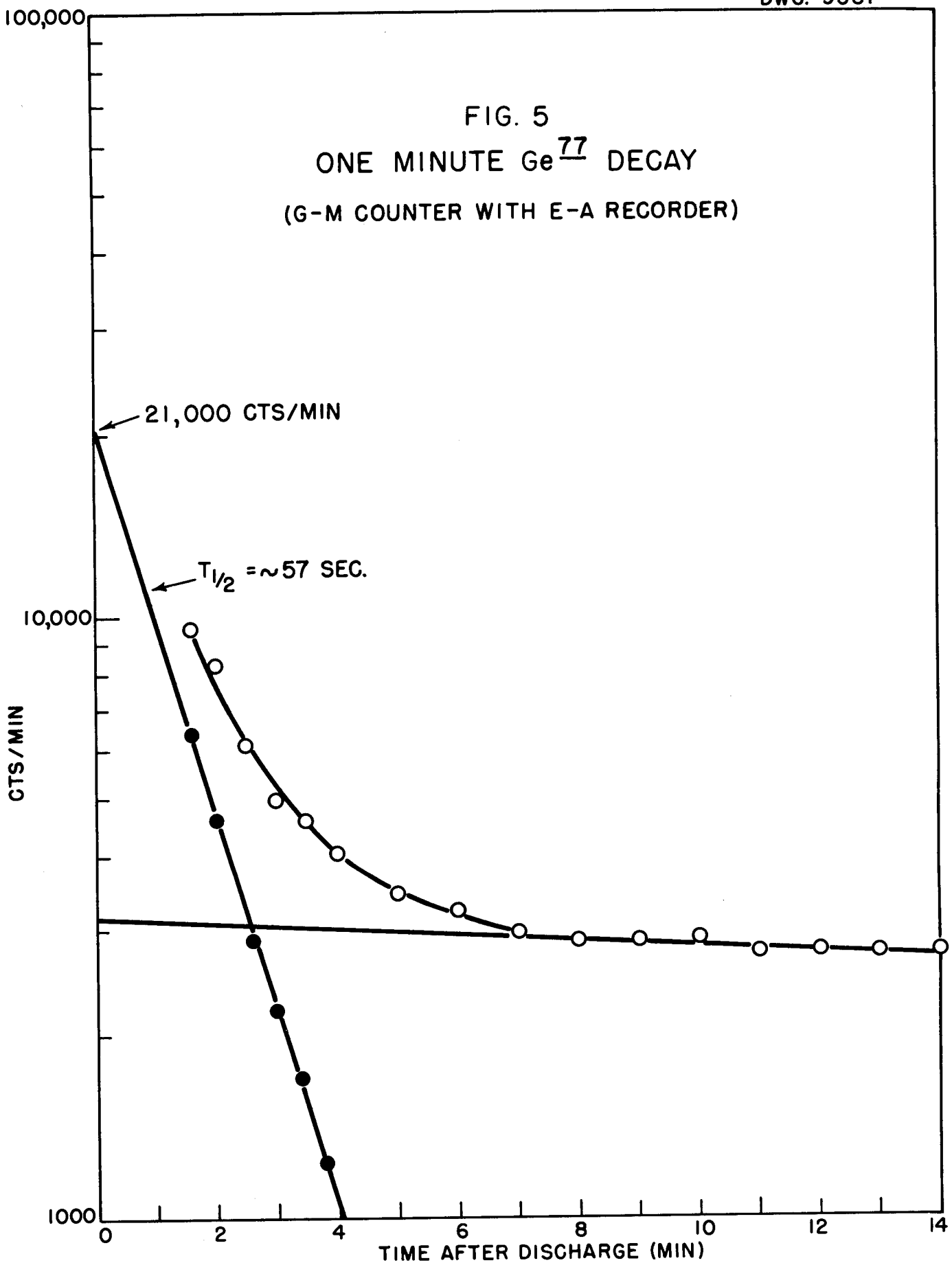

FIG. 5
ONE MINUTE Ge^{77} DECAY
(G-M COUNTER WITH E-A RECORDER)

Hf^{181} Half-life (S. A. Reynolds). The half-life of Hf^{181} (Fig. 6) has been determined by means of the gamma-ray ionization chamber.

A sample of pure HfO_2 was bombarded to supply the activity. The result, 45 ± 2 days, agrees closely with that of Seren *et al.*[7]

Mn^{52} Half-life (T. H. Handley). The decay of a sample of Mn^{52} has been followed on the gamma ionization chamber for 120 days. By extrapolating Mn^{54} decay to zero time and subtracting this portion from the entire curve, a half-life of 6.0 ± 0.1 days was obtained from Mn^{52} (Fig. 7).

ACTIVATION ANALYSES

W. A. Brooksbank T. H. Handley
G. W. Leddicotte N. D. Lee*
C. W. Keenan**

Alkali Metals. Analysis by ion exchange for small amounts of certain alkali metals in the presence of others has been made (see p. 52).

Lithium. The problem of determining micro quantities of lithium in solution was first presented by J. C. Gross of the Chemistry Division. Since Li^6 is a stable isotope and Li^8 (from stable Li^7) has such a short half-life (0.89 sec), it was thought that trace amounts of lithium might be determined by activation analysis using the reaction of Chadwick and Goldhaber,[8]

$$3Li^6 + {}_0n^1 \longrightarrow 2He^4 + {}_1H^3$$

This reaction can also be utilized for the determination of Li^6 in isotope process solutions.

The most recent data on the half-life of H^3 indicate that its half-life is about 10.7 to 12.1 years.[9,10] The energy of the emitted beta particles is 0.0169 Mev.[11] The choice of this reaction for determining trace amounts of lithium seemed practical since it could be carried out in the ORNL reactor and since the feasibility of measuring the radioactivity of the hydrogen has been discussed in the literature.

*On loan.

**Part-time.

(7) Seren, L., Friedlander, H., and Turkel, S., "Activation Cross Sections," *Argonne Laboratory Report for Month Ending September 23, 1944*, CF-2161, p. 23 (Oct. 17, 1944).

(8) Chadwick, J., and Goldhaber, M., "Disintegration by Slow Neutrons," *Nature* 135, 65 (1935).

(9) Novick, A., "Half-life of Tritium," *Phys. Rev.* 72, 972 (1947).

(10) Goldblatt, M., Robinson, E. S., and Spence, R. W., "The Half-life of Tritium," *Phys. Rev.* 72, 973 (1947).

(11) Curran, S. C., Angus, J., and Cockcroft, A. L., "Beta Spectrum of Tritium," *Nature* 162, 302 (1948).

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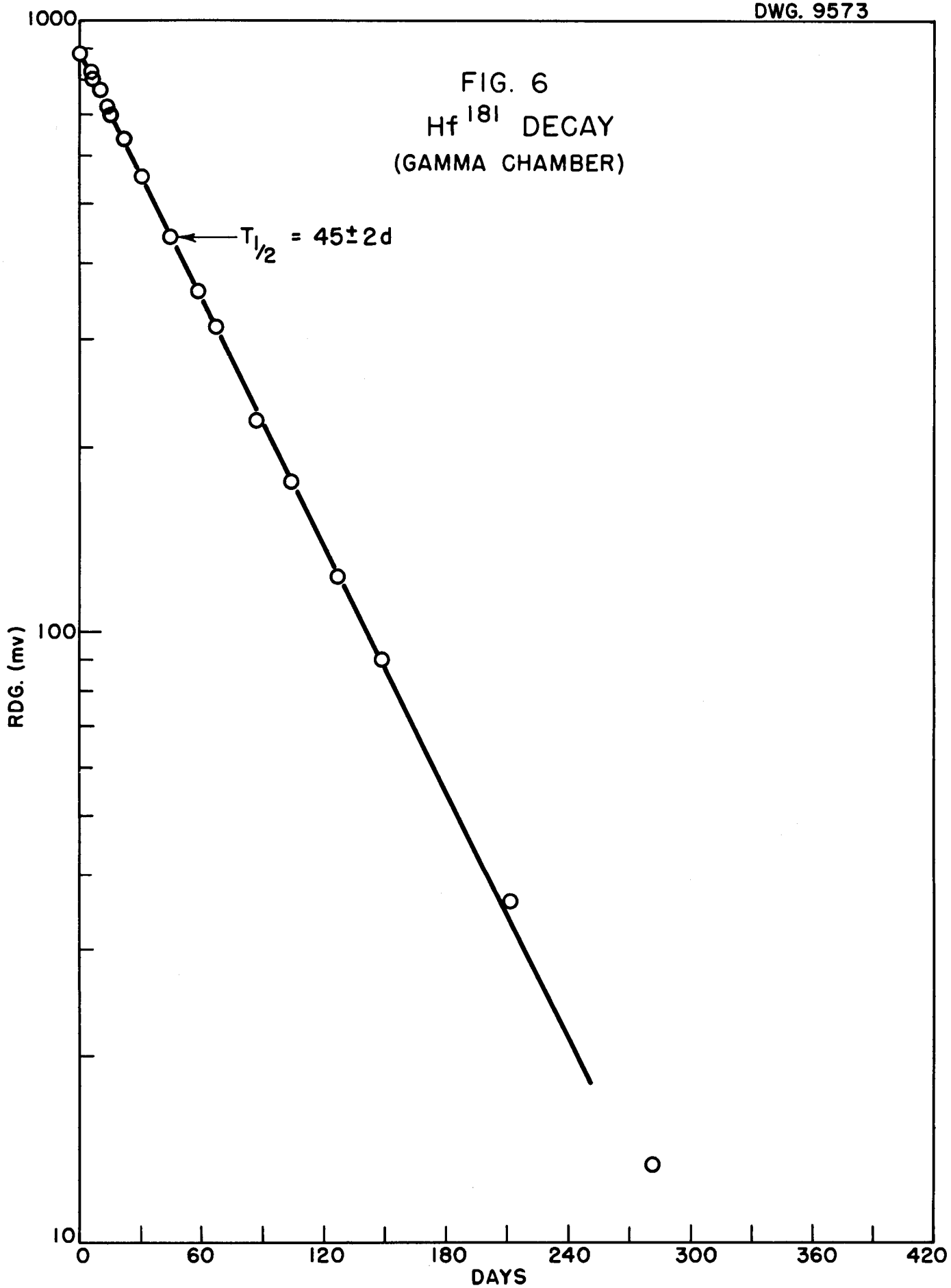

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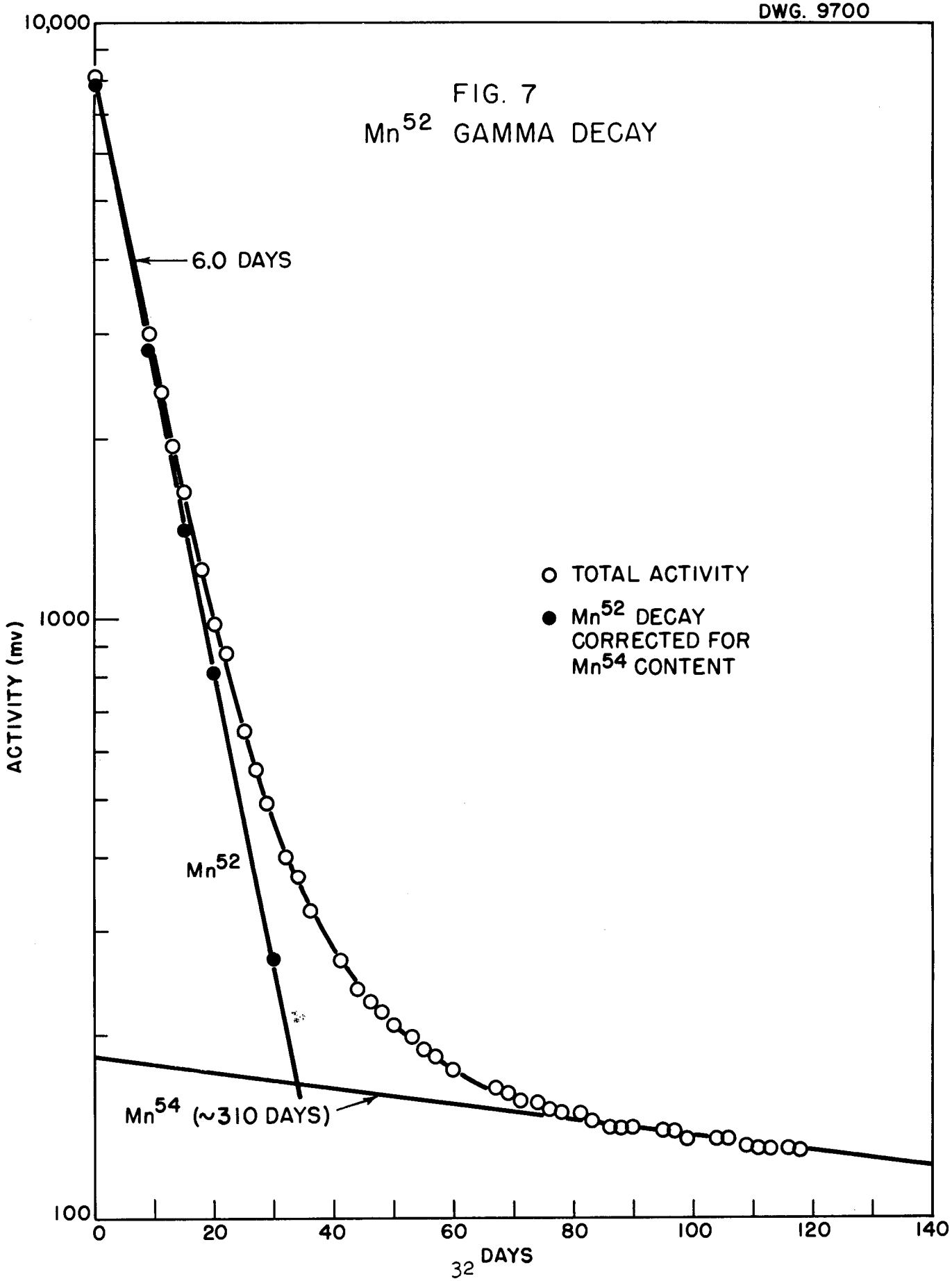

In determining trace amounts of lithium by means of the tritium produced in the nuclear reaction, the amount of high-cross-sectional material or of substances which might interfere strongly in the separation of the tritium should probably be almost negligible in the salt subjected to bombardment. Also, the material must be stable under bombardment and it should not react with the containing apparatus. It should be possible to prepare the source materials very pure with respect to hydrogen. Lithium sulfate is being used as the tritium source.

The number of tritium atoms formed by irradiation of a lithium salt was calculated from the equation

$$N = F\sigma g t$$

where N = number of H^3 atoms formed

F = flux of the reactor expressed as neutrons/sec/cm^2

σ = atomic cross section (cross section of the total element multiplied by the isotopic abundance of Li^6)

g = weight of lithium involved in the reaction

t = irradiation time in seconds

The number of atoms of tritium produced by bombarding 1 mg of lithium sulfate for 1 hr at the present neutron flux in the pneumatic tube in the pile was calculated to give a measurable ion current. It appears that it may be possible, by increasing the weight of the sample and the irradiation period, to obtain results within our present limits of accuracy.

The ionization-chamber measurement of tritium activity is felt to be superior to other methods because soft beta radiations of the type emitted by tritium make it difficult to obtain satisfactory results with thin-window G-M counters. The ionization chamber will give a reproducible geometry and is capable of a wide range of linear response. Also, possible self-absorption effects within a sample make it expedient to convert the radioactive substance into a volatile gas which can be introduced into an ionization chamber. The ion current is read on a vibrating-reed electrometer.

The lithium salt is placed in a small quartz ampoule which is sealed off and placed in a "rabbit" for bombardment in the reactor. After bombardment, the ampoule is transferred to the analytical apparatus before the tritium is released for collection.

The present apparatus (Fig. 8) was designed primarily for determination of the relative amount of tritium produced in a sample of unknown lithium content as compared to the amount of tritium produced in a sample of known lithium concentration. Although inactive hydrogen is used as a carrier gas, a quantitative determination of the amount of hydrogen put into the evacuated system is not necessary, since the volume of the ionization chamber and the final pressure are constant. Therefore, by using a similar technique on the known and the unknown sample, it is possible to achieve a degree of accuracy within the limits of error of the electrometer.

The apparatus is a continuous system of pyrex and quartz. The tritium is released into the system by introducing the sealed ampoule into the combustion tube, where it may be opened *in vacuo* by a magnetic breaking device. This portion of the system is separated from the collection side of the system by a fritted disk and a palladium valve. The fritted disk is placed in the system to catch any glass particles that might possibly be swept into other portions of the system when the carrier gas is introduced into the system. The palladium valve serves as the purifier of the released hydrogen since it is permeable to no gas except hydrogen at high temperatures.

The "collection" side of the system contains the ionization chamber and is kept at a low pressure behind the palladium valve to allow the purified hydrogen to pass into the chamber. Each part of the system includes a manometer for pressure measurements and a modified mercury pump for passing the hydrogen through the palladium valve. Each part of the system can be evacuated separately by means of a mechanical pump.

In effect, the present procedure allows evacuation of the system for at least 15 min after the ampoule is placed in the combustion tube. A charge of inactive hydrogen is introduced into the system, the system is evacuated, and then a new charge of hydrogen is introduced. This second charge of hydrogen is removed also, and another charge of hydrogen is passed into the part of the system before the palladium valve, while the collection side is maintained at a low pressure.

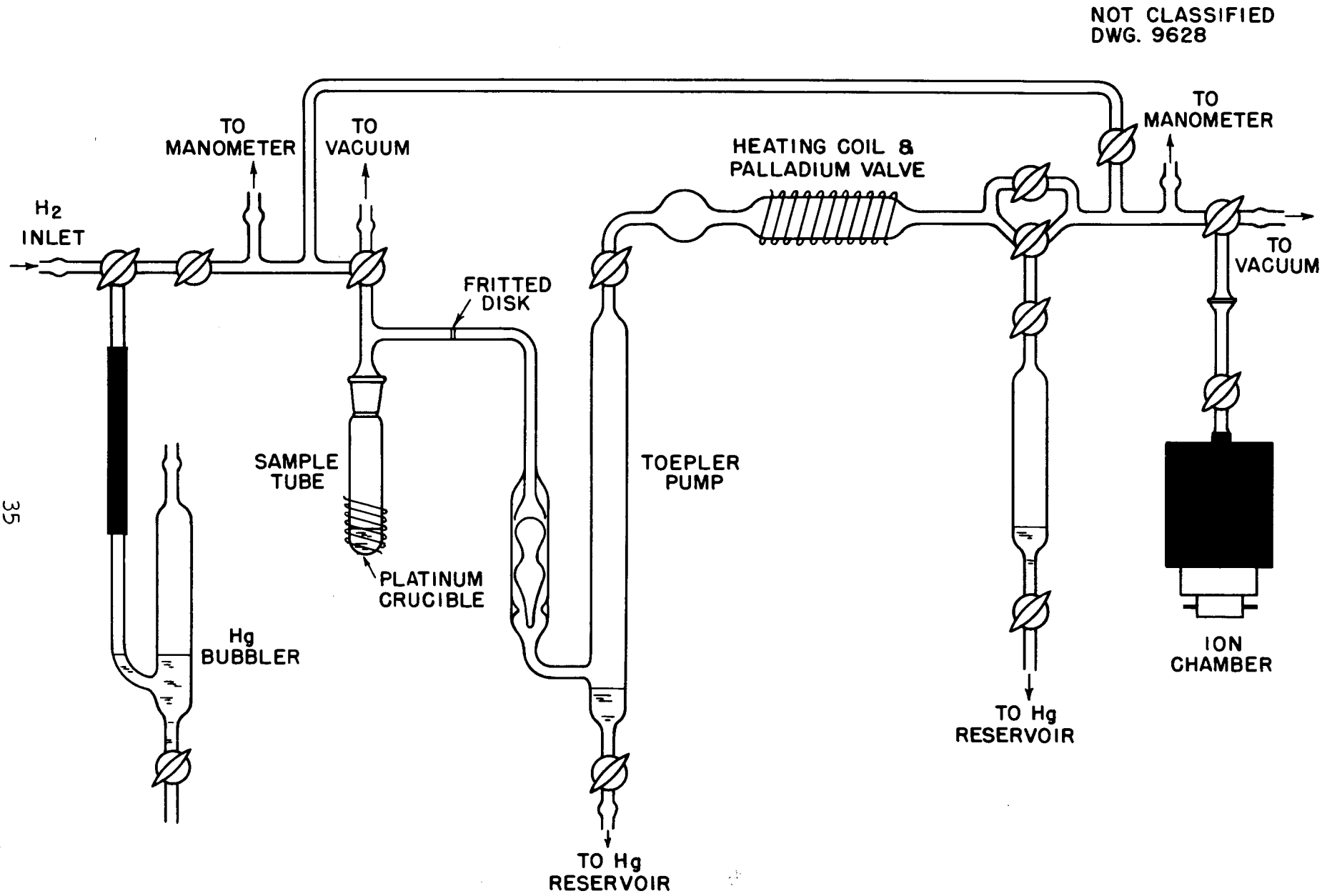

FIG. 8
APPARATUS FOR TRITIUM ANALYSES

The ampoule is broken, and heat is applied to the sample area by means of a coil heater. It has been recommended that the irradiated Li_2SO_4 be heated to at least 800°C in order to drive the tritium from the salt crystals.

This heating process is continued for at least 15 min. Then, by alternate raising and lowering of the mercury in the modified pump, the charge of inactive hydrogen plus tritium is passed through the palladium valve into the collection side of the system. When the manometer on the sample-introduction side indicates complete passage of the hydrogen through the palladium valve, a new charge of hydrogen is introduced; the alternate raising and lowering of the pressure is repeated until a positive atmospheric pressure is obtained in the ionization chamber. The ionization chamber is demounted from the apparatus and carried to the counting room, and the ion current obtained from the tritium radiations is measured with the vibrating-reed electrometer and recorded.

Preliminary work on the system has included a check on the performance of the palladium valve and a reproducibility study, *i.e.*, a comparison of samples of known lithium content which have been bombarded under the same conditions and processed in the apparatus under similar conditions. Also, a check of total recovery of the tritium is being made. The recovery of tritium could be seriously affected if the tritium were adsorbed on the walls of the apparatus or absorbed by water vapor arising from the sample. In addition, it is certain that some tritium could be retained in areas of the system beyond the valve if sufficient carrier gas is not introduced. However, this volume should be constant if the unknown and known samples are treated in the same way.

In view of the probability that the tritium activity which did not pass through the palladium valve is in the form of water vapor, it is planned to expose the crude gas to a heated tungsten filament in order to remove both free and combined oxygen. Replacement of portions of the apparatus, especially after the palladium valve, with capillary tubing should ensure a greater volume recovery of the gas.

A study is also being made of an apparatus without a palladium valve. If this proves satisfactory, the time for each analysis can be shortened.

Sodium. Furman[12] states that small amounts of sodium may be determined as sodium zinc uranyl acetate in the presence of moderate amounts of K, NH_3, Mg, Ca, and Ba and small amounts of Li and Sr, preferably present as chlorides; SO_4 does not interfere if the solution does not contain Ca, Ba, or Sr; PO_4, silicates, oxalates, and tartrates interfere.

The following procedure has been used to determine trace amounts of sodium in magnesium carbonate, potassium carbonate, and lithium salts after neutron activation: The sample is dissolved and Cu, Fe, Sr, PO_4, Na, and K carriers are added. The heavy metals are separated with H_2S, ammonia, and HCl. The solution is boiled, and SO_4 carrier is added and precipitated with $BaCl_2$. Ammonium carbonate and excess ammonia are added to separate strontium. The ammonium salts are removed by ignition.

The resulting solution is evaporated to a small volume, and an excess of zinc uranyl acetate reagent is added. The resulting mixture is allowed to digest 30 to 45 min, is filtered through a sintered-glass crucible, and is washed several times with small portions of dilute reagent, 95% ethyl alcohol, and ether. The final precipitate is weighed as

$$NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6H_2O$$

and is mounted and counted in the conventional manner.

The sodium standard, usually Na_2CO_3, is treated in the same manner as the unknown sample.

This procedure, however, has several serious limitations. The molecule resulting from the uranyl acetate reagent is larger than the molecules encountered in ordinary radiochemical procedures and, consequently, cannot be handled as easily. Also, the uranyl ions, upon separation as sodium zinc uranyl acetate, give rise to UX_1^{234} beta activity (from U^{238} alpha decay). The growth of the beta activity could be a serious factor if the time of counting of the separated sample should be several hours after the initial

(12) Furman, N. H., *Scott's Standard Methods of Chemical Analysis*, Van Nostrand, New York, 1944.

separation (which is not unlikely, if an analyst is handling a number of samples at one time). A growth curve for this activity indicates that, in 3 hr after separation of the sodium zinc uranyl acetate precipitate, it is possible to have at least 10% increase in the UX_1 activity. This could seriously affect analysis for sodium in concentrations of 0.01% or less.

In order to eliminate these possible serious effects, it is proposed to precipitate the sodium as NaCl.

Potassium. Trace amounts of potassium in magnesium metal and lithium salts have been determined. After irradiation, potassium is precipitated as potassium chloroplatinate by a standard procedure.[13] Na, Li, Mg, Ca, and Sr do not interfere since, in principle, the K_2PtCl_6 is practically insoluble in strong alcohol while the other chloroplatinates are readily soluble.

The sample is dissolved, and the following carriers are added: Cu, Fe, Sr, Na, and K. The heavy metals are separated by H_2S and NH_3 precipitations, followed by removal of H_2S by boiling. The solution is concentrated to a small volume and HCl is added. Then a slight excess of chloroplatinic acid (stock solution: 1 g of Pt per 10 ml) is added to convert all the chlorides present into the corresponding chloroplatinates. This solution is evaporated on the steam bath to a syrupy consistency, *i.e.*, until solidification occurs on cooling. The cooled residue is flooded with 95% alcohol, allowed to stand for about 30 min, and filtered through a tared paper and washed several times with small portions of alcohol until the wash liquid becomes colorless. The precipitate is dried at 110°C, cooled, weighed as K_2PtCl_6, and then mounted in the usual way for counting.

The standard sample, usually K_2CO_3, is treated in a similar manner.

Copper. Trace amounts of copper in beryllium metal have been determined by the following procedure: After bombardment, the sample is dissolved, carriers are added, and the copper is separated by H_2S precipitation. The precipitate is dissolved, additional carriers are added, and the copper in the purified solution is precipitated as CuCNS. This is mounted and counted in the usual manner.

(13) Furman, N. H., *op. cit.*

Manganese. A direct-reading method involving no prior chemical separation has been used effectively in determining trace amounts of manganese in beryllium metal (Table 6). After being bombarded for 2 hr, samples are read directly on the gamma-ray ionization chamber. Decay studies indicate that the manganese decays with a 2.59-hr half-life and that the possible contribution due to other contaminants such as sodium or copper is much less than 1%. Since this method of analysis is applicable only to samples that contain negligible concentrations of these contaminants, a precipitation method is also being developed.

MEASUREMENT OF RADIOACTIVITY

4π Proportional Counter (T. H. Handley). An investigation is being made of the applicability of the 4π proportional counter designed by C. J. Borkowski of the Chemistry Division to radioisotope assay work.

A special technique is used for mounting sources for this counter. The source mount is a circular stainless-steel disk with a 1-in. hole in the center. A thin Formvar-polystyrene film is placed over the hole, and both sides of the film are covered with gold or another metal by evaporation of the metal in a vacuum. The activity is evaporated on the metal-coated film.

The absolute disintegration rate of a number of isotopes has been determined with the 4π proportional counter. A comparison of these values with absolute disintegration rates obtained with other counters is given in Table 7. The results indicate that the values for absolute disintegration rates of weak beta emitters are consistently lower when determined on the 4π proportional counter.

To eliminate self-absorption due to foreign material, radioautographs of an evaporated source and a plated source of Co^{60} were made; these showed that the plated source was evenly distributed over a much larger area than the evaporated source, but no significant difference in the counting rates was observed. This indicates that self-absorption was not the sole source of the observed difference. Experiments with a Co^{60} source using absorbers equivalent to the backing of the source indicate that there may be absorption of weak emission by the backing.

TABLE 6

Manganese Determination by Direct Gamma Reading

(Beryllium Samples Submitted by F. W. Drosten of Metallurgy Division)

SAMPLE NO.	CONCENTRATION (ppm)	
	BY ACTIVATION ANALYSIS	BY SPECTROGRAPHIC ANALYSIS*
4521	242	292
4522	193	236-150
4523	170	205-180
4524	237	220
4525	114	88-100
4526	152	164-120
4527	166	184-130
4528	131	157
4529	111	152-100
4530	163	180-100
4531	120	160-96
4532	125	192-110
4533	121	152
4534	101	128-110
4535	128	
4536	116	136-99
4537	100	96-83
4538	98	
4542	102	126-100
4543	103	100

*Where more than one value is given for a sample, the first is the result of analyses at Brush Beryllium Corp. and the second is the result from the AEC New Brunswick Laboratory.

TABLE 7

Comparison of Determined Absolute Disintegration Rates

ACTIVITY	COUNTING METHOD	EVALUATION OF RESULTS OBTAINED ON THE 4π PROPORTIONAL COUNTER
P^{32}	End-window G-M counter (method described by Zumwalt[14])	7% low
Na^{24}	Coincidence counting	Good agreement
Co^{60}	Coincidence counting	19% low
I^{131}	Coincidence counting	13% low

Initially both sides of the Formvar-polystyrene film were covered with metal. Further experiments showed that reproducible results could be obtained if the metal is evaporated on only one side. It was observed also that a Formvar film can be prepared which is much thinner than the original Formvar-polystyrene film. The extent to which the backing absorption of sources mounted in this way will be diminished has not, as yet, been determined. If the absorption of the backing cannot be eliminated, a correction may be made for it.

Reproduction of the metal films has been difficult, and further work will be done along this line.

Calibration of a New Gamma Chamber (W. S. Lyon). The high-pressure ionization chamber in Building 902 (Radioisotope Analysis) has been calibrated in a manner similar to that described by Overman and Jones[15] and more recently by Cobble.[16] Resistance scales of 10^8, 10^9, 10^{10}, and 10^{11} ohms and open are provided, although it should be noted that these scales do not differ by an exact factor of 10. Calibration curves relating millivolt reading

(14) Zumwalt, L. R., *Absolute Beta Counting Using End-window Geiger-Mueller Counters and Experimental Data on Beta-particle Scattering Effects*, AECU-567 (Sept. 14, 1949).

(15) Overman, R. T., and Jones, J. W., *The Use and Calibration of a 100% Geometry Ion Chamber*, MonC-399 (Mar. 20, 1948).

(16) Cobble, J. W., "Calibration of a High-pressure Ion Chamber," private communication.

to disintegrations per second for Co^{60} have been prepared. Co^{60} has been assigned an efficiency ($E_{rel.}$) of 1.00, and a curve has been prepared from which $E_{rel.}$ is obtained as a function of gamma-ray energy (Fig. 9). Co^{60} emits two gamma rays, which must be taken into account when the curve is used in calculations. Radium standards have been provided for a daily performance check.

Past experience indicates that the gamma chamber is extremely stable. The sample volume should be kept as small as possible. However, on scales other than 10^8, physical distance of the sample from the bottom of the chamber within the lower 2 in. of the positioning tube is not important.

ASSAY OF VARIOUS RADIOISOTOPES

Quantitative Estimation of Carrier-free Tritium (R. A. Bolomey). The present design of the apparatus for monitoring tritium gas does not allow for the dilution of the sample during collection with a large volume of normal hydrogen gas. It is impossible, therefore, to reduce the contamination of the chamber walls due to adsorption of the active gas. The sample, once collected, was diluted with normal hydrogen except when, for comparative reasons, air was employed to bring the pressure of the chamber to atmospheric.

Tritium had been introduced into the apparatus used to make zirconium tritide targets and had been collected in the uranium pump. A small amount of tritium had undoubtedly been adsorbed on the glass walls of the apparatus and was presumably held there quite firmly. A 250-ml nickel-coated brass ionization chamber was connected to this apparatus, evacuated to 3×10^{-5} mm Hg, and kept at this pressure for an hour or so in order to evaluate the magnitude of the background that could be expected from such a system. The reading obtained on this chamber with a vibrating-reed electrometer was 3.3 mv on the 10^8-ohm scale at atmospheric pressure with air, which is a rather high value.

If the values for tritium given by Jenks, Ghormley, and Sweeton[17] are taken, $E_{avg.} = 5.69 \pm 0.06$ Kev and $t_{1/2} = 12.46 \pm 2$ years, by rough calculation the following result is obtained:

$$\text{Ion pairs produced per particle} = E_{avg.}/32.5 = 175$$

(17) Jenks, G. H., Ghormley, J. A., and Sweeton, F. H., "Measurement of the Half-life and Average Energy of Tritium Decay," *Phys. Rev.* 75, 701 (1949).

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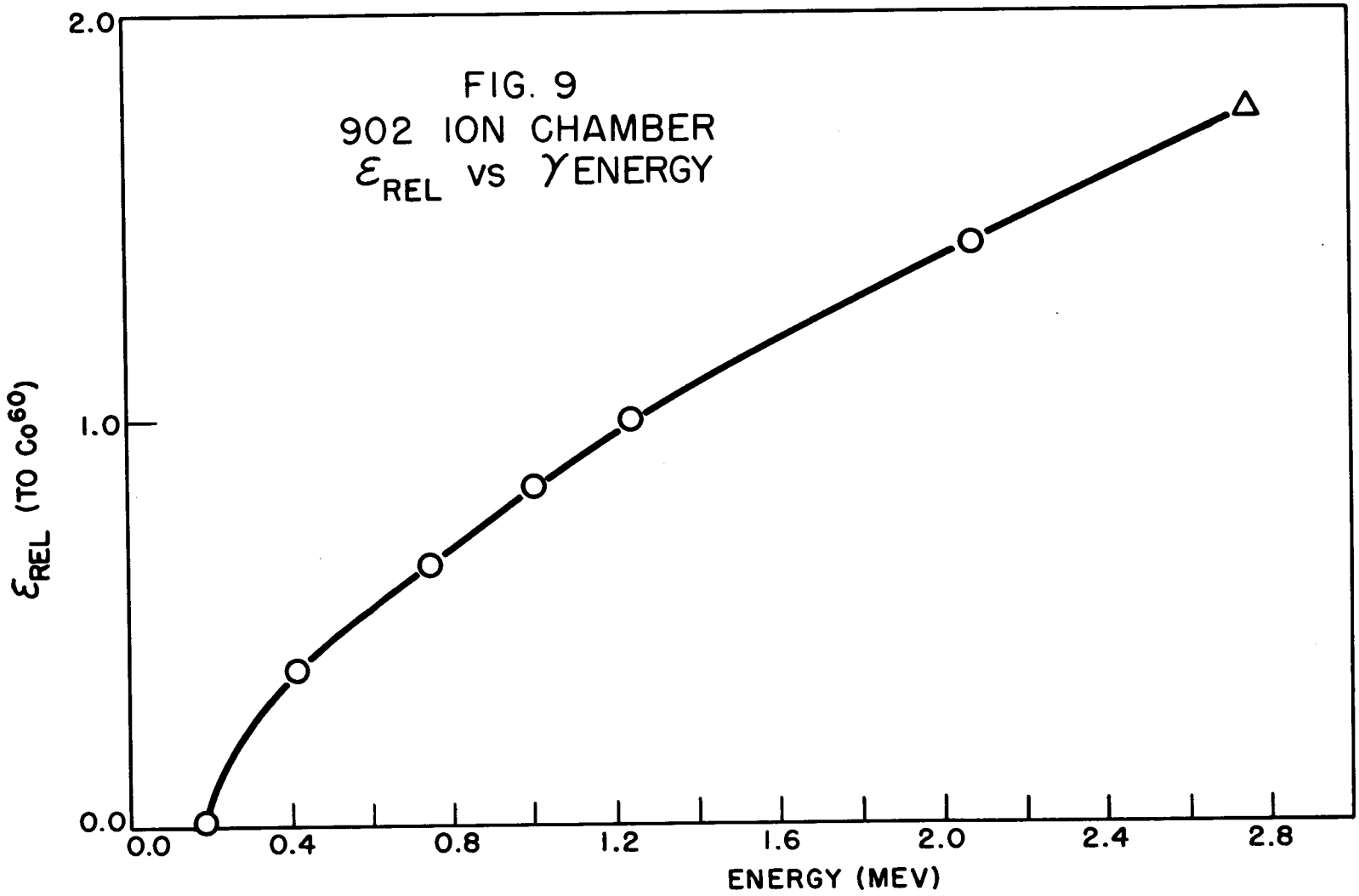

These calculations assume absolute efficiency for the equipment. Since no corrections are applied for the effects of self-absorption and adsorption of the tritium on the walls of the chamber, the observed values may be expected to be lower than those calculated in this manner.

Since the charge on each ion is 1.6×10^{-19} coulomb and half the ion pairs produced will create a measurable current in the ion chamber, the charge produced per particle will be

$$1.6 \times 10^{-19} \times 175 = 2.8 \times 10^{-17} \text{ amp}$$

From Ohm's law, $E = IR$, this value corresponds to 2.8×10^{-6} mv on the 10^8-ohm scale. The value of 3.3 mv on the 10^8-ohm scale therefore corresponds to a disintegration rate of

$$\frac{3.3}{2.8 \times 10^{-6}} = 1.18 \times 10^6 \text{ particles sec}^{-1}$$

and to

$$\frac{1.18 \times 10^6 \times 3.9 \times 10^8}{0.693} = 6.6 \times 10^{15} \text{ atoms of tritium}$$

and to a pressure of

$$\frac{6.6 \times 10^{15} \times 2.24 \times 10^4 \times 760}{2 \times 6.06 \times 10^{23} \times 250} = 3.7 \times 10^{-4} \text{ mm Hg}$$

while the pressure of the system, as measured by an ionization gauge, was 3×10^{-5} mm Hg.

The chamber was evacuated again and maintained under a vacuum of 2×10^{-5} mm Hg over the week end. After the chamber was brought to atmospheric pressure with air, the reading obtained on this sample was 100 mv on the 10^8-ohm scale, corresponding to a tritium pressure of 2.17×10^{-3} mm Hg.

After alternate evacuation to 2×10^{-5} mm Hg and filling to 1 atm with normal hydrogen a dozen or so times, the electrometer readings in air were reduced from 100 to 2.3 mv on the 10^8-ohm scale.

By employing a pumping system other than the one into which tritium had been introduced and flushing the chamber with hydrogen, low readings could be obtained when the chamber was brought to atmospheric pressure with hydrogen. The electrometer readings were somewhat higher in hydrogen than in air, and in both hydrogen and air they were higher at about 0.8 atm than at 1.0 atm, owing to the self-absorption factor. In all cases, the electrometer readings increased slowly with time, presumably because of the elution of tritium that had been adsorbed on the inner surfaces of the chamber.

I^{131} (W. S. Lyon). It is the policy of the Radioactivity Section of the National Bureau of Standards to submit to selected laboratories in the United States, Canada, and Great Britain check samples of radionuclides for interlaboratory assay and comparison. Approximately ten months ago a check sample of I^{131} was received at ORNL and its activity was determined in the Radioisotope Control Laboratory by routine methods. The activity of this sample was determined also by coincidence counting. Agreement between the results obtained by the two methods was excellent. However, when compared with the standard value set by the Bureau the results were found to be about 8% to 10% high. At that time the Bureau did not feel too confident of their own value, and no further checks were made.[18]

In June 1950 another check sample of I^{131} was received from the Bureau and was assayed in the Radioisotope Control Laboratory. Unfortunately, this was not submitted to the Analytical Chemistry Research and Development Group, and no coincidence-counting value is available for comparison. The activity value obtained at ORNL was found to be 9% higher than that obtained by the Bureau of Standards. Correspondence with H. H. Seliger of the Bureau reveals that their assay was made using a 4π counter. The values obtained at Chalk River and at Hammersmith Hospital in London using 4π counting and an "absolute ionization" method agree within 1.5% with the Bureau value. No further information concerning calibration of instrument, instrument losses, or sample preparation has been obtained. On the basis of the differences in activity determination, close scrutiny of the present method of I^{131} assay and comparison between coincidence counting and 4π counting methods seem advisable.

(18) Seliger, H. H., personal communication to J. A. Cox, Dec. 14, 1949.

The present method used for assay by the control laboratory involves diluting an aliquot of the I^{131} sample to a known volume with a basic medium containing, per milliliter, 0.76 mg of NaOH, 0.25 mg of KI, and 0.52 mg of $NaHSO_3$. A 200-λ aliquot of this dilution is treated with 1 drop of a 1 mg/ml solution of $AgNO_3$ on a thin glass disk, evaporated, and counted on a standard thin-end-window type G-M counter. A factor relating counts per minute to disintegrations per minute has been determined by coincidence counting of additional aliquots. This factor, originally determined by members of the Chemistry Division, has been in use for over two years. The procedure is quite reproducible, and experience indicates no detectable loss of I^{131} through volatilization. Thus it is apparent that the control method of assay should check the coincidence-counting method.

Coincidence Count of I^{131} Samples. An I^{131} sample that had previously been assayed by the Control Group was obtained, and two dilutions were made with the basic medium. Two samples were taken from each dilution, and after the $AgNO_3$ addition and evaporation all four were counted. One sample was then used to obtain coincidence absorption curves using two different coincidence counters. The counters consisted of a thin-window (1.7 mg/cm^2) beta proportional counter for the beta side and an anthracene crystal with photomultiplier tube for the gamma side. They were arranged facing each other in the horizontal plane, and sufficient beryllium absorber was placed before the crystal to absorb all the beta particles. The coincidence circuits used had resolving times of 0.65 and 0.61 μsec. Coincidence counting has been established as the most reliable method of determining absolute disintegration rates when the decay scheme is known, since the method is independent of the efficiency of the detecting devices for the various radiations. The observed disintegration rate may be calculated from the expression

$$d/m = \frac{\beta \text{ cts} \times \gamma \text{ cts}}{\beta, \gamma \text{ cts}}$$

In the case of I^{131} a coincidence absorption curve was determined by obtaining the apparent disintegration rate as a function of aluminum absorber placed before the beta tube (coincidence counts being made to 1% random error). These data were plotted and extrapolated to a negative absorber

thickness equivalent to the air, window thickness, and solid absorber, which is a standard method for determining absolute disintegration rates of nuclides decaying by more than one beta path. The extrapolated value was 5 mg/cm^2. In addition, the beta counting rate was plotted, together with the coincidence rate, and the extrapolated values were used to calculate a true d/m rate. The data obtained using two separate coincidence counters are listed in Table 8, together with the Control Laboratory value. As was expected, the coincidence values agree with the Control Laboratory value.

TABLE 8

Disintegration Rate of I^{131}

(Data Corrected to 8/2/50, 10:00)

INSTRUMENT	DISINTEGRATION RATE (d/m/ml)	
	CALCULATED	EXTRAPOLATED
12	3.22×10^9	3.27×10^9
81	3.32×10^9	3.30×10^9
Average	$(3.28 \pm 0.1) \times 10^9$	
Control	$(3.26 \pm 0.16) \times 10^9$	

4π Counting of I^{131}. T. H. Handley of this group has recently been studying the method of 4π counting using an instrument designed by C. J. Borkowski. He has observed that a nonquantitative counting yield is obtained when low-energy beta emitters are counted, a phenomenon presumably due to a slight absorption effect. Co^{60} ($E_{\beta(max)}$ 0.31 Mev) has been found to give values 18% to 20% lower than coincidence counting. (I^{131} is reported to decay 15% by a 0.315-Mev beta path, and the remainder by a 0.60-Mev beta path.) Therefore the most important problem here is to obtain a sample which is essentially solid-free and mounted on an essentially weightless backing. A method has been developed which will enable the preparation of a sample mount meeting the

above conditions; unfortunately, quantitative yield is questionable. Consequently, the comparison can be made only by coincidence counting of the identical sample which is counted in the 4π chamber. The method of sample preparation consists in extraction of active iodine into CCl_4 and evaporation of an aliquot of the organic phase on a Formvar film on which has previously been deposited, by evaporation, a thin layer of silver. No solid material could be observed on the plate so prepared, and the backing was sufficiently thin to be transparent. The samples, so prepared, were first desiccated under vacuum for 10 min, after which they were placed in the 4π counting chamber; the chamber was evacuated to 7 μ Hg and then filled to atmospheric pressure with argon-methane. On completion of the count the sample was coincidence-counted, using aluminum absorbers in the usual manner. The experimental results are given in Table 9.

TABLE 9

Comparison of Disintegration Rates Determined by Coincidence Counter and 4π Counter

METHOD	DISINTEGRATION RATE (d/m)	DIFFERENCE (%)
Coincidence counter	6.50×10^5	13.5
4π	5.62×10^5	
Coincidence counter	7.90×10^5	14.9
4π	6.72×10^5	

Attempts were also made to prepare a quantitative sample in a manner similar to that used in the Control Laboratory. Using a sample prepared by basic-medium evaporation, the 4π counter was found to give a value 17.4% low. The effect of the slight solid content is clearly seen here.

On the basis of data herein presented, the following facts seem evident:

1. The factor now used by the Control Laboratory gives satisfactory agreement with disintegration rates obtained from coincidence counting.

2. Inasmuch as the decay scheme of I^{131} is sufficiently well known to permit application of coincidence-counting methods, it seems that a great deal of reliance can be placed on coincidence data. Therefore, on an absolute basis, our coincidence data should be accepted as giving a true disintegration rate.

3. In our present state of uncertainty concerning 4π counting (uncertainty as to its applicability to low-energy beta particles and the effect of even minute amounts of solid on the recorded counting rate), it appears that no marked accuracy for I^{131} has been demonstrated with this instrument in this laboratory. Absolute accuracy would indicate that no change need be made in our factor.

Further information on the methods of sample preparation, purification, etc. used at the Bureau of Standards and elsewhere should be helpful in resolving this problem and would be most welcome. In addition, it would be interesting to ascertain what other methods of assay (if any) were used in determining the disintegration rate of the check sample of I^{131}.

Iodine process solutions, as received in the ORNL Radioisotope Control Laboratory, contain both I^{131} (8-day) and I^{133} (22-hr). Inasmuch as only I^{131} is of interest for shipping purposes, a method of analysis was desired which would distinguish between the amounts of I^{131} and I^{133} and which would not require allowing time for the I^{133} to decay. In the past, attempts at absorption-curve analysis have met with little success because of the complexity of the radiation and the time required to complete such a study. Decay measurements also are unsatisfactory because of the time involved. The following method, which utilizes a high-pressure ionization chamber, requires not more than 5 min and gives an accurate value for the amounts of I^{131} and I^{133} in the process solutions.

A known aliquot of the solution containing only iodine activity is placed in a glass tube, and a reading is taken on the high-pressure ionization chamber. Using the graphs relating ionization reading to disintegrations per second, the d/s value for the ionization chamber is obtained.

Utilizing data from fission yield and decay, the percent of the total activity due to I^{131} which remains at time t after bombardment is obtained. Using this value, the fraction of the ionization reading, f, due to I^{131} is read from a chart. The calculation is

$$d/s\ I^{131} = \frac{f \times (d/s \text{ from ionization chamber})}{0.186}$$

The value for the efficiency of I^{131} gamma rays was experimentally determined. Knowing the efficiency of the ionization chamber for I^{131} and I^{133} gamma rays, the chart relating percent of total I^{131} activity to fraction of ionization reading was prepared.

S^{35} (D. J. Coombe). S^{35} has been determined in tagged methylene blue samples. Aliquots of a solution prepared by dissolving a weighed sample in water were evaporated on polystyrene film. The mounted samples were counted on a proportional counter previously standardized with a Nb^{95} sample. (The disintegration rate of the Nb^{95} sample had been determined by coincidence counting.)

Niobium and Zirconium (R. H. Hahn). A method for the determination of radioniobium in the presence of soluble orthophosphates has been devised; it will be discussed in ORNL-831. This investigation led to the discovery of niobium phosphate, a compound not reported previously. Its preparation, properties, and composition will be reported in ORNL-840.

The fact that niobium forms a phosphate suggested that tantalum might form a corresponding compound. A tantalum phosphate compound was discovered, the preparation, properties, and composition of which will be discussed in ORNL-841.

The application of mandelic acid and its derivatives as precipitating agents for zirconium and hafnium is being investigated. The possibility of direct weighing of the zirconium mandelate without ignition to the oxide is also being considered for the analysis of radiozirconium.

Lewis' procedure[19] is being investigated to determine its possible use for the determination of radiozirconium.

(19) Lewis, M., *The Mandelic Acid Method for the Determination of Zr^{95} in Redox Solutions*, HW-17052 (Mar. 1, 1950).

Sn^{113} (D. J. Coombe). Radiochemical tin and antimony separations were made. The activity of the separated tin was read on the gamma-ray ionization chamber after allowing enough time for In^{113} to grow in and reach equilibrium. Calculations were based on the 0.39-Mev gamma-ray activity using a coefficient of internal conversion of 70% (estimated from Rose's tables with the aid of B. H. Ketelle of the Chemistry Division).

ANALYSIS FOR TRANSURANIUM ELEMENTS

F. L. Moore

An evaluation of the ZPA (zirconium phenylarsonate) method[20] for the determination of Pu(IV) both in the presence and in the absence of sulfamic acid was requested. This method is used frequently at Hanford.

Synthetic samples were prepared containing Pu(IV) tracer. A series of about twenty determinations was made using the ZPA method and the LaF_3 method. Although the conditions given in HW-10277 were duplicated as nearly as possible, it was found that ZPA did not carry Pu(IV) as efficiently as LaF_3. Assuming the LaF_3 values to be 100%, it was observed that the ZPA average carrying efficiency of Pu(IV) in the absence of sulfamic acid was 92%, and in the presence of the recommended amount of sulfamic acid was 80% to 83%. It seems reasonable to assume that the difference in the observed recovery of Pu(IV) is due to the reduction of the Pu(IV) by the sulfamic acid during the time that is required to perform the determination.

When samples containing Pu(III) tracer were analyzed by the ZPA method, it was found that about 2% of the Pu(III) was carried by the ZPA precipitate whether or not an addition of sulfamic acid was made.

Assistance has been given in training control-laboratory personnel for the determination of Np^{237} in process solutions.

IDENTIFICATION OF RADIOELEMENTS

W. A. Brooksbank
G. W. Leddicotte
T. H. Handley
S. A. Reynolds

A number of routine identifications have been made by methods outlined in previous quarterly reports.

(20) Ice, C. H., *Zirconium Phenylarsonate Tracer-scale Method for the Differentiation of Pu(III) and Pu(IV) in Redox Solutions*, HW-10277 (June 30, 1948).

The Naval Reactor Division of Argonne National Laboratory requested analyses of the cooling water of one of their experimental units in the ORNL pile. The chief activities present were I^{131} and I^{133}.

The decay of the long-lived gamma activity induced in ORNL TiO_2 by neutron bombardment has been followed for over a year (Fig. 10).

APPLICATION OF ION EXCHANGE TO RADIOCHEMICAL ANALYSIS

W. A. Brooksbank

Alkali Metals Separations. The use of ion exchange in analyzing Rb_2CO_3 for alkali impurities proved so successful at this Laboratory that work was extended to cover all four of the radioactive alkalies, *i.e.*, $Na^{22,24}$, K^{42}, Rb^{86}, and $Cs^{134,137}$.[21,22] The separation of the four alkalies had been attempted previously by Cohn and Kohn.[23] The elution curves from their experiments showed considerable overlapping of peaks between Na^{24} and K^{42} and poor resolution between the pairs K^{42} and Rb^{86} and Rb^{86} and Cs^{134}.

Since IR-1 resin had proved effective in the separation of Rb^{86} and Cs^{134} (Fig. 11), it was used for this investigation.

The column used in preliminary runs was identical to that used in the Rb^{86}-Cs^{134} separation. Results showed considerable overlapping between Na^{24} and K^{42} and no resolution between K^{42} and Rb^{86}.

The next column used was similar to the one used by Zaffarano *et al.*[24] for the separation of Cs^{134} in Rb_2CO_3. It was of glass, 11 by 150 cm with a sintered-glass disk 1.5 cm from the bottom. IR-1 resin, 100 to 120 mesh, in the acid form, was used in a bed 1 cm in diameter and 140 cm in length. HCl, 0.1 *N*, was the elutriant, and the flow rate was approximately 1 ml/min. All runs were made at room temperature. This method of separation, independently devised, is almost identical with that given by Kayas.[25]

(21) Brooksbank, W. A., and Leddicotte, G. W., "Radioisotope Target Material," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part II. Analytical Chemistry*, ORNL-686, p. 38 (May 18, 1950).

(22) Zaffarano, D. J., Kern, B. B., and Mitchell, A. C. G., "The Beta and Gamma Rays of Rb^{86}," *Phys. Rev.* 74, 682 (1948).

(23) Cohn, W. E., and Kohn, H. W., *Ion-exchange Separation of the Alkali Metals*, AECD-1810 (Mar. 16, 1948).

(24) *Op. cit.*

(25) Kayas, G., "Complete Separation of Alkali Metals by Ionic Exchange," *J. chim. phys.* 47, 408 (1950).

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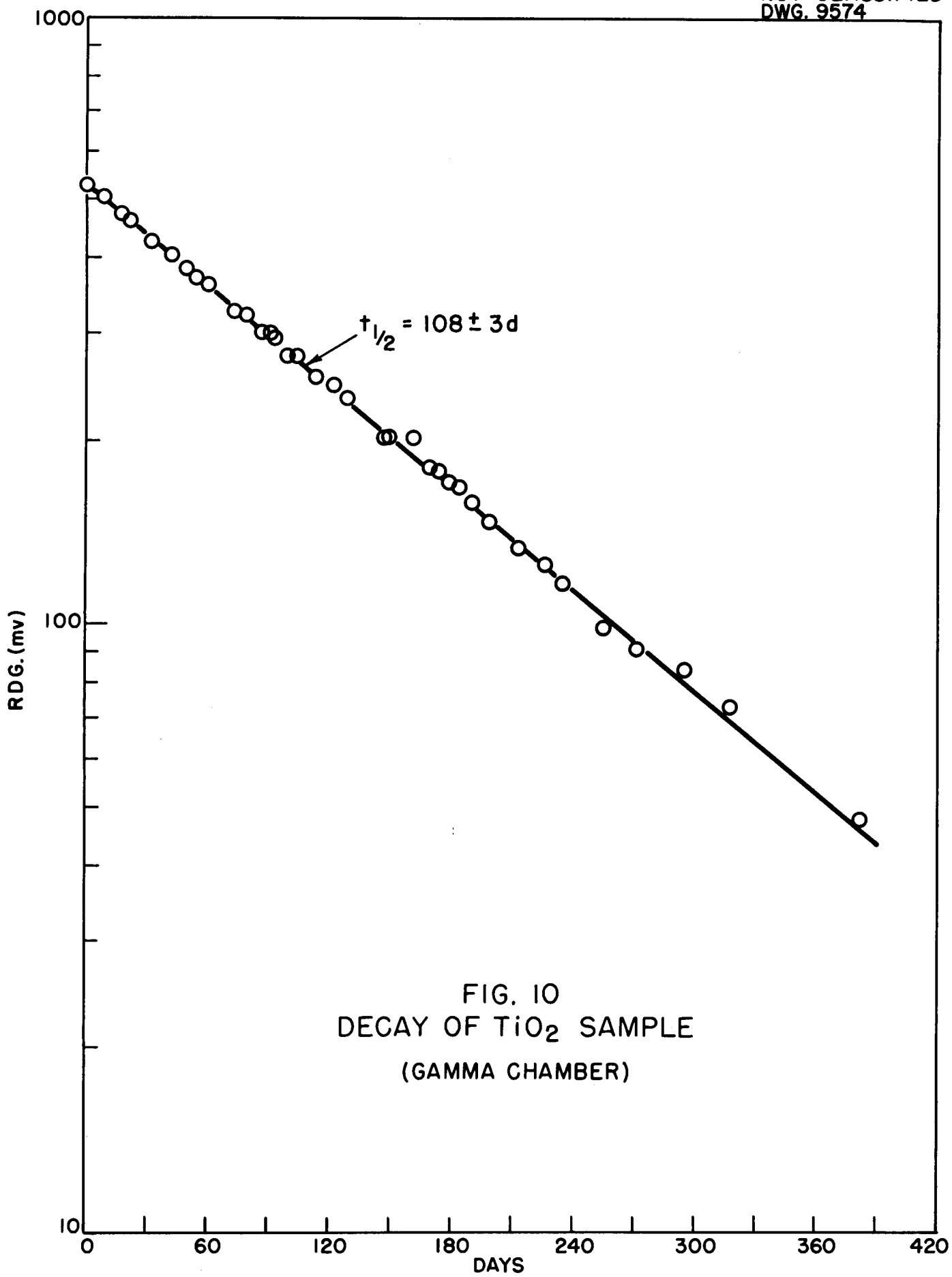

FIG. 10
DECAY OF TiO_2 SAMPLE
(GAMMA CHAMBER)

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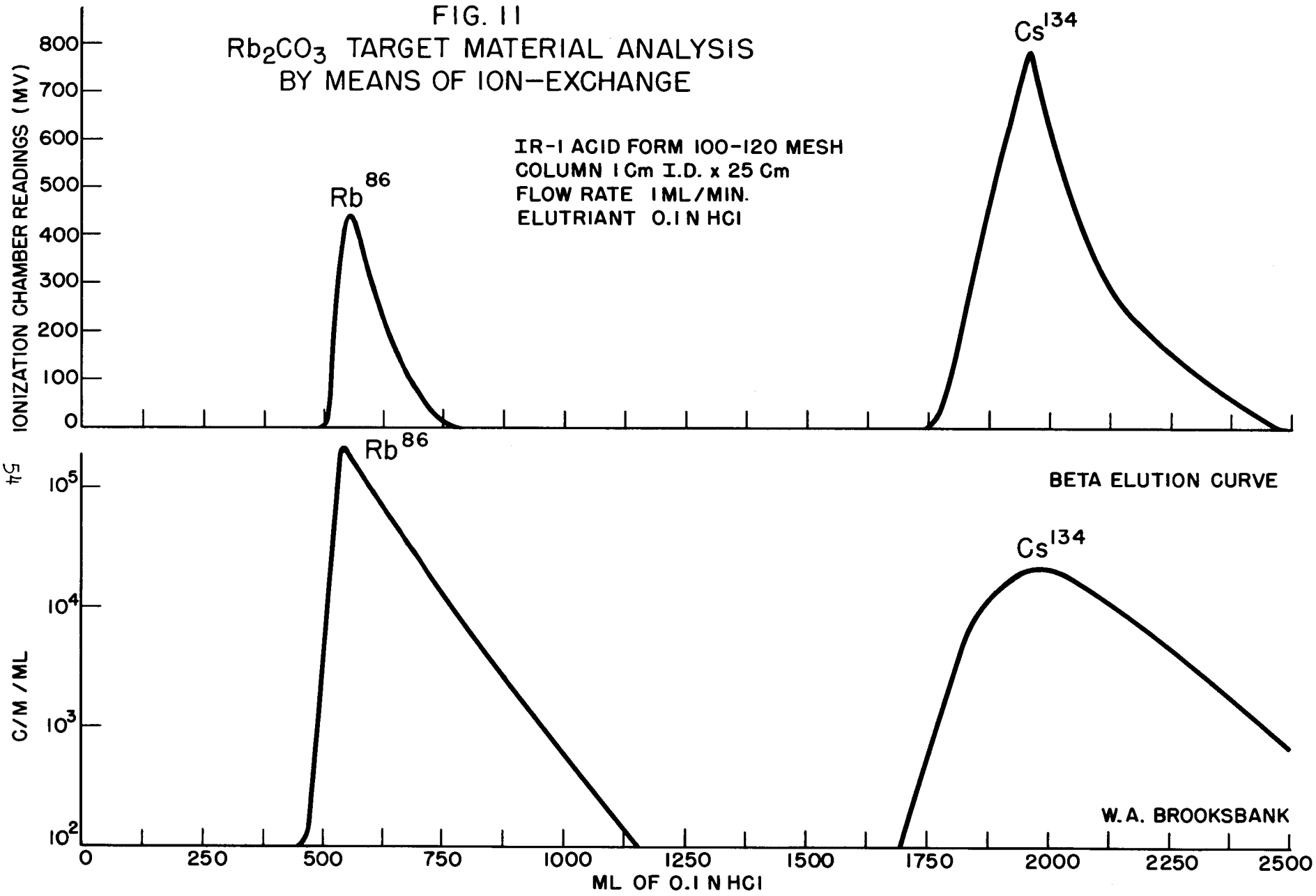
FIG. 11
Rb_2CO_3 TARGET MATERIAL ANALYSIS
BY MEANS OF ION-EXCHANGE



The eluate went from the bottom of the column through a standard ORNL pipet counter and was collected on an automatic sampling table. The pulses from the pipet counter were counted by a "64 scaler" and permanently recorded by a five-pen E-A recorder (Fig. 12). Although elution curves of c/m vs. time were plotted automatically by the E-A recorder, gross beta counts were run on each fraction for confirmation.

Very good results were obtained with this column. The curve shown in Fig. 13 was obtained from a mixture of Na^{22} tracer, 7.5 mg of K_2CO_3 and 45 mg of Rb_2CO_3 irradiated in the pneumatic tube in the pile for 16 hr, and tracer Cs^{137}. No overlapping of peaks was observed, and a peak-to-valley ratio of approximately 10^4 was obtained in all cases.

The column was used in the analysis of a sample of K_2CO_3 containing approximately 0.001% Na. Fifty milligrams of K_2CO_3 was irradiated for 16 hr, dissolved in dilute HCl, and transferred quantitatively to the column. Na^{24} was eluted in 350 ml of 0.1 *N* HCl. The volume was reduced by evaporation, and the solution was assayed for sodium. The Na^{24} activity corresponded to $2.19 \times 10^{-6} \pm 20\%$ of the sodium present in the K_2CO_3, or 0.005%.

Two samples of Rb_2CO_3 which have been analyzed spectrographically will be analyzed for potassium. Potassium concentrations as low as 0.1% might be detected by this method.

A Na_2CO_3 target material for J. A. Cox is being analyzed for Na^{22} and Cs^{134} by means of this column.

Rare Earth Separations. Samples of irradiated rare earth samples have been submitted for analysis. The Ketelle and Boyd[26] method of ion exchange and complex elution with citric acid buffer was used. The chief differences between our setup and that of Ketelle and Boyd are the changed counting cells and the permanent record of the elution curve on a five-pen E-A recorder.

Preliminary runs are in progress, but there are no data to report at this time.

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

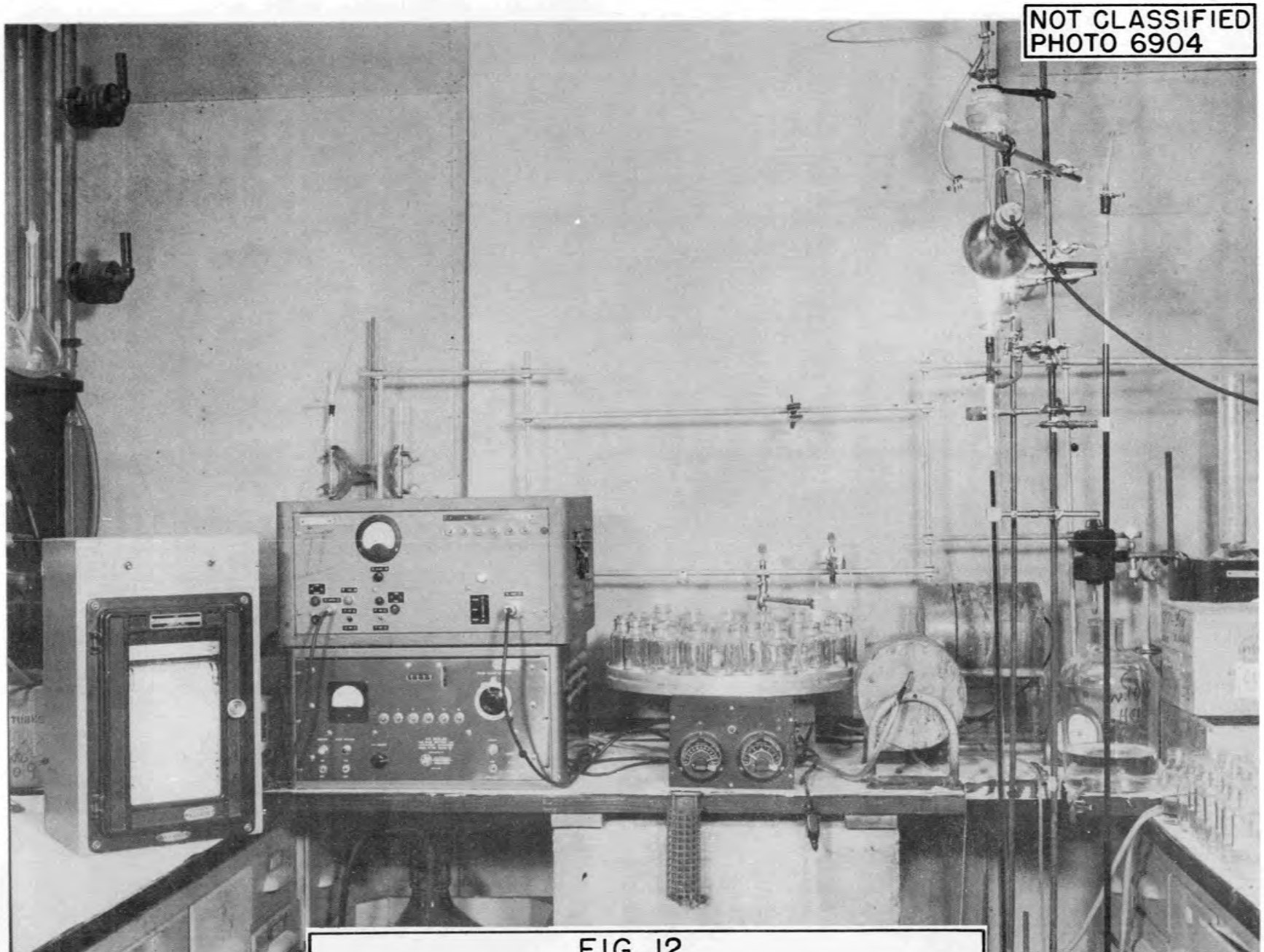


FIG. 12
ANALYTICAL ION-EXCHANGE APPARATUS

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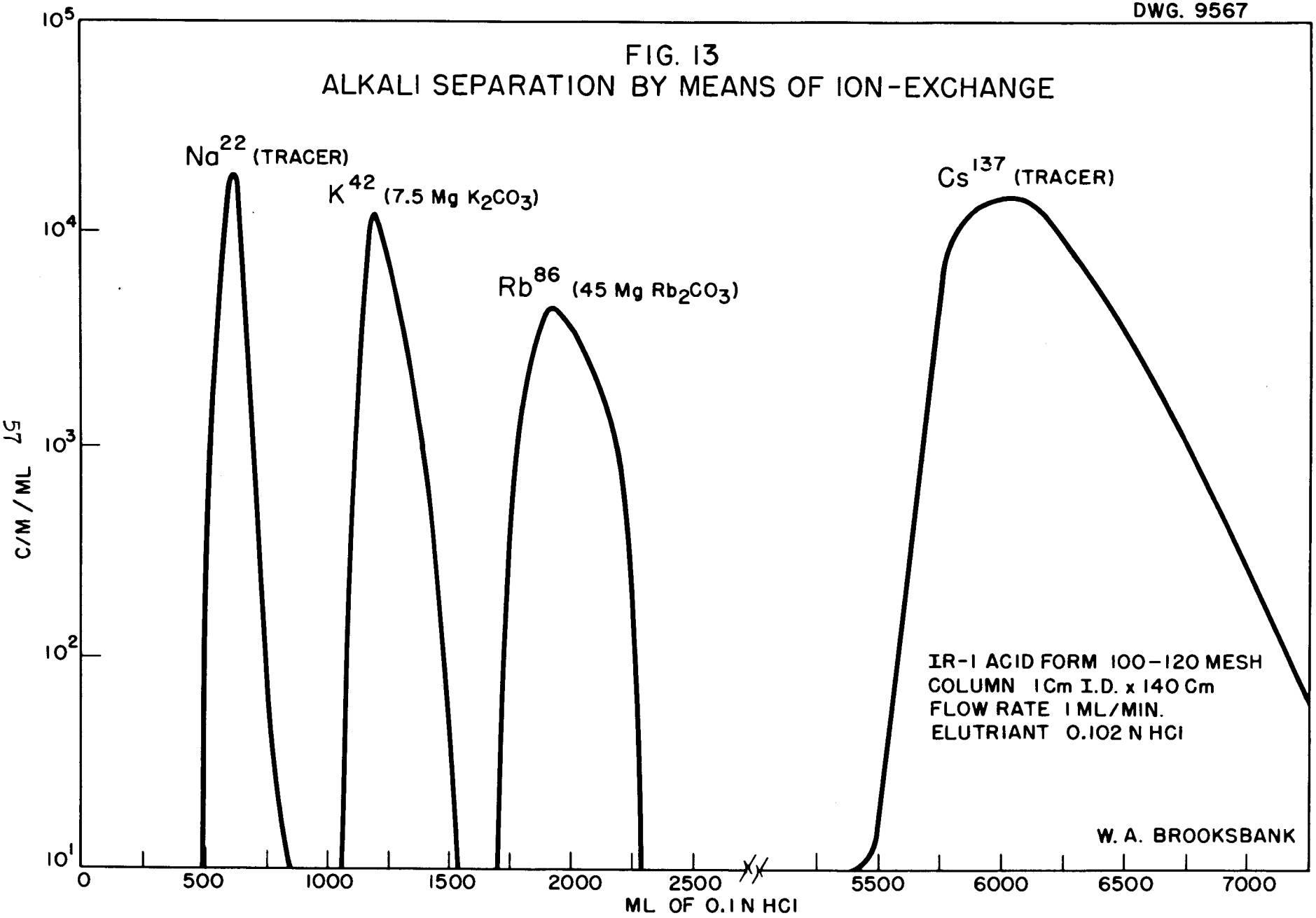
FIG. 13
ALKALI SEPARATION BY MEANS OF ION-EXCHANGE



MISCELLANEOUS ACTIVITIES

Sorption of Radionuclides by Arco Soil (E. K. Wilson). A cursory inspection of soil submitted from the Arco site was made for the purpose of determining the behavior of this material toward solutions containing radioactive elements.

Samples were taken from the basement excavation at 1, 6, 11, and 16 ft. Four samples, 25 lb each, were shipped to this Laboratory and passed through ¼-in. hardware cloth. This procedure served to separate out the very coarse fraction; the fine-particle portion was used for the experimental investigation. Table 10 gives the percentage of fine-particle portion separated from the submitted samples.

TABLE 10

Particle-size Separation of Arco Soil

LEVEL (ft)	FINE SOIL (%)
1	23
6	25
11	50
16	63

The absorption of each activity was studied separately to eliminate the radiochemical determination of each constituent. Stock solutions of the following activities were prepared using radioactive tracers: Ru^{106}, Ce^{144} (trivalent), Sr^{89}, Ba^{140}, Zr^{95}-Nb^{95}, and Cs^{137}. The *p*H of each stock solution was adjusted to 2 with 6 *N* HNO_3.

Six series of determinations were made, each series consisting of eight samples and a blank. The blank contained a 10-ml aliquot of the stock solution. One-gram samples of the soil were placed in 15-ml glass-stoppered centrifuge cones. Ten-milliliter aliquots of the stock solution were added to each cone, and the cones were placed in a rotary shaker and shaken for 17 hr.

It seemed reasonable to assume that an equilibrium of exchange had been reached in this time. Following the absorption period the cones were centrifuged until no visible soil particles were seen in the supernatant.

In the case of beta emitters an aliquot of the supernatant was examined for activity. Gross beta counts were made on an end-window G-M counter. In the case of gamma emitters the supernatant was decanted, and readings were made of the soil in the gamma ionization chamber.

It was found that the absorption properties of soil samples taken from various levels did not vary appreciably. The results shown in Table 11 are average absorption values.

TABLE 11

Sorption of Radionuclides by Arco Soil

ACTIVITY STUDIED	% ABSORPTION PER GRAM PER 10 ml OF ACTIVE STOCK SOLUTION
Ru^{106}	93
Ce^{144} (trivalent)	100
Sr^{89}	38
Ba^{140}	68
Zr^{95}-Nb^{95}	100
Cs^{137}	85

SPECTROCHEMICAL ANALYSES—RESEARCH AND DEVELOPMENT

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

The following sections for the publication of suggested practices in photographic photometry being prepared by the American Society for Testing Materials have been completed:

(a) Properties of photographic emulsions: sections on blackening functions, speed, grain size, scanning area, and macro and micro errors are included.

(b) Plate calibration with the stepped sector: preliminary optical alignment, light source, suppression of scattered light, illumination, and synchronism are discussed.

(c) Measurement of intensity ratios: A description of the preparation of rulers for direct measurement of relative intensity on photometer tracings is given. The detection of and the correction for hidden background are discussed. The preparation of working curves and sample calculations are included.

Operating conditions were worked out and working curves were prepared for the following analyses by the porous-cup method:

(a) 0.7 to 10 ppm of Mn in 1% Be solution (70 to 1000 ppm of Mn in Be)

(b) 1.6 to 25 ppm of Zr in 0.2% Th solution (0.08 to 1.25% Zr in Th)

(c) 12.5 to 100 ppm of Nb in 0.5% Zr solution (0.25 to 2.0% Nb in Zr)

(d) 250 to 2000 ppm of K in 1.0% Rb solution (2.5 to 20% K in Rb)

(e) 7.5 to 75 ppm of Co in 0.2% Ni solution (0.38 to 3.8% Co in Ni)

(f) 2.3 to 75 ppm of Ni in 0.1% Co solution (0.3 to 7.5% Ni in Co)

Preliminary tests made on a Blank-Sventitskii solution excitation apparatus, constructed in the ORNL shops, indicated that this device will make it possible to excite solutions with power levels higher than those used with the porous-cup electrode.

SERVICE ANALYSES

RADIOCHEMICAL ANALYSES—DEVELOPMENT GROUP

S. A. Reynolds

Activation cross sections have been determined for the Physics Division. Samples received from the Chemistry Division were chiefly for the identification of activities. Radiomolybdenum (fission product) analysis was requested by the Chemical Technology Division. Activation analyses on beryllium were run for the Metallurgy Division. Radioisotope product samples were assayed for the Operations Department.

IONIC ANALYSES—DEVELOPMENT GROUP

P. F. Thomason

Service analyses for the past quarter were performed principally for the Chemistry Division and the Radioisotope Production Department. Work for the Chemistry Division included determination of water and acid in different organic solvents for F. S. Chance, who is making a study of ion exchange in nonaqueous media, bromide analyses for J. W. Cobble in connection with his studies of the Szilard-Chalmers process with $KBrO_3$, and miscellaneous analyses. The analyses for the Radioisotope Production Department were for miscellaneous ions, including Na, Ca, Mg, Sb, P, Hg, Cd, Zn, and Fe.

WATER ANALYSIS LABORATORY

J. H. Edgerton

Complete analyses were made on filtered water, demineralized water, distilled water, and water from evaporators.

The total hardness of water, due to both calcium and magnesium, was determined by titrating the water sample with a solution of the tetrasodium salt of ethylenediaminetetraacetic acid, using erichromeschwartz T (F241) as an indicator. This method requires less time than the soap titration method and is more accurate.

The colorimetric determination of magnesium in the presence of calcium was accomplished by the use of titan yellow (an azo dye). Calcium interference was reduced by the addition of sucrose.

Polarographic analyses for lead in the presence of Versene were run for the Chemical Technology Division.

Hexone concentrations were determined polarographically.

Considerable difficulty was encountered in finding a suitable method for the colorimetric determination of iron in the presence of Versene. It was found, however, that when the ferric iron was reacted with potassium thiocyanate, identical curves were obtained in the presence and in the absence of Versene. This determination is based on the formation of a red soluble compound of ferric thiocyanate. Nickel and chromium in the presence of Versene were determined colorimetrically.

The determination of copper colorimetrically in aqueous solutions without extraction with carbon tetrachloride was carried out by adding an aqueous solution of sodium diethyldithiocarbamate to the ammoniacal sample solution containing cupric ions. The depth of the yellow color produced in dilute solutions is proportional to the concentration of copper.

Corrosion-test solutions from the Homogeneous Reactor and the Materials Testing Reactor were submitted by the Reactor Technology Division for uranium, chromium, aluminum, zirconium, zinc, chloride, nitrogen, carbon, and hydrogen peroxide analyses.

Hydrogen peroxide was determined colorimetrically by adding a titanium sulfate solution to the acid sample solution and measuring the yellow color produced. Titanium in the presence of thorium was determined by adding a constant amount of hydrogen peroxide and measuring with a spectrophotometer the yellow color formed by the reaction between titanium sulfate and hydrogen peroxide.

Zirconium was quantitatively determined in the presence of thorium, iron, and titanium by precipitating the zirconium as zirconium mandelate from a hydrochloric acid solution.

Samples containing thorium, uranium, phosphorus, and fluoride were submitted by the Chemistry Division for phosphorus and fluoride assays. The

fluoride was separated by steam-distilling, as hydrofluosilic acid, from a solution of sulfuric acid, and titrating the hydrofluosilic acid with standard thorium nitrate solution, using sodium alizarin sulfonate as an indicator. The phosphorus was determined as the orthophosphate by extracting the ammonium phosphomolybdate complex with butyl alcohol, reducing this complex with stannous chloride, and measuring the molybdenum blue color spectrophotometrically.

Beryllium was determined in the presence of thorium by extracting the thorium with 1% TTA in carbon tetrachloride. The beryllium in the aqueous phase is then precipitated with ammonium hydroxide, filtered, ignited, and weighed as beryllium oxide.

Numerous physicochemical determinations, such as refractive indices, conductivity, and surface and interfacial tensions, were performed for the Chemical Technology Division. Viscosities were run on solutions with viscosities lower than the viscosity of water by using a special viscosimeter with a very small orifice.

Miscellaneous samples were analyzed also for the Chemistry, Chemical Technology, Reactor Technology, Physics, and Metallurgy Divisions, Argonne National Laboratory, and the ORNL Power House.

LABORATORY AND SEMIWORKS CONTROL UNIT

L. T. Corbin G. R. Wilson
C. E. Lamb

This quarter the Chemical Technology Division submitted 93.25% of the total number of samples analyzed by this laboratory. Uranium, plutonium, gross beta, aluminum, thorium, and acid analyses were requested. The following methods were used:

1. Uranium: (a) Spectrophotometric, using ammonium thiocyanate, and (b) Fluorimetric
2. Plutonium: (a) LaF_3 and (b) Direct counting
3. Aluminum: (a) Specific gravity and (b) Volumetric
4. Thorium: Spectrophotometric, using thoron reagent
5. Nitric acid: (a) Oxalate and (b) $K_4Fe(CN)_6$

The Chemistry Division submitted 4.15% of the total samples analyzed; the procedures used were the same as those above except that some of the uranium samples were analyzed volumetrically using ceric sulfate as the titrant.

Measurement of small surface areas by ethane adsorption at 90°K and under extremely low pressures have been made on a series of UF_4 and ThF_4 samples submitted by the Chemistry Division. The apparatus was constructed as described by R. R. Williams.[1]

Five measurements were made on a standard ThF_4 sample whose surface area had been predetermined by microscopic measurement[2] and N_2 adsorption as 0.59 m^2/g. By using 25 A^2 as the surface area of an ethane molecule, calculations of the five measurements gave 0.59 m^2/g.

The standard deviation using results calculated on the basis of 27 A^2 was 0.641 ± 0.024. Results reproducible within 5% were obtained.

In previous work[3] good agreement with the N_2 adsorption method was obtained when 27 A^2 was used as the area of an ethane molecule. It was later found that better agreement was obtained if 23 A^2 was used.

The Metallurgy Division submitted uranium-aluminum alloy samples which made up 2.6% of the total number of samples analyzed. Uranium was determined potentiometrically with ferric sulfate.

RADIOISOTOPE ANALYTICAL GROUP

E. I. Wyatt

The routine ionic chromium procedure was modified to allow for the determination of microgram quantities of Cr(III) in the presence of milligram quantities of Cr(VI) in redox waste solutions. The submitted samples were 1 *M*

(1) Williams, R. R., "Construction of an Apparatus for Measurement of Small Surface Areas," *K-25 Secret Notebook* DP-44.

(2) Schneider, S. D., *K-25 Secret Notebook* BR-917.

(3) Brosi, A. R., *Studies in the Physical Chemistry of Precipitate Formation: $BiPO_4$*, Part I, CN-S-2037 (June 1, 1945).

in $Al(NO_3)_3$ and contained no free acid. Cr(VI) was precipitated as $BaCrO_4$, and the supernatant was analyzed colorimetrically with diphenylcarbazide before and after oxidation. The Cr(III) content was obtained by difference.

The redox waste solutions were also assayed for Np^{237} using a procedure developed by Moore.[4] It was found that a preliminary TTA extraction from 0.5 to 1.0 *M* nitric acid was necessary in order to reduce the Zr level sufficiently for pulse analysis of the alpha activity.

For work with resin columns a method has been developed to approximate the total cation strength of a solution in the presence or absence of free acid. An aliquot of the sample solution is shaken thoroughly with acidified resin, and the supernatant is decanted and titrated. If the sample contains free acid, the initial acidity of another aliquot is determined by titration, and the total cation strength is obtained by difference.

P^{32} product samples are now being analyzed polarographically for copper, lead, and zinc.

The gamma ionization chamber in Building 902 has been calibrated and is now being used. Work is in progress on a method for the determination of I^{131} in the presence of other fission iodines by direct reading of the samples on the gamma ionization chamber.

PILOT PLANT LABORATORY

E. J. Frederick

During the early part of this quarter analytical services were supplied for the Chalk River and the Hot Pilot Plant Decontamination Programs. Following the Hot Pilot Plant shutdown, the analytical personnel were dispersed on loan to various groups at X-10 and Y-12 in order that the laboratory space could be made available for reconstruction under Program H.

An investigation of the routine analytical procedures for possible use at Arco is near completion, and a detailed report is to be issued soon. A brief discussion of each procedure is given below.

(4) Moore, F. L., "Analysis for Transuranium Elements—Np^{237}," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-788, p. 35 (Oct. 4, 1950).

Colorimetric Estimation of Uranium. The Coleman model 14 spectrophotometer has been replaced with the Beckman model B as a routine instrument. Tests showed the optical system of the Coleman to be inferior, causing erroneous results in certain concentration ranges. Excellent reproducibility has been obtained with the Beckman, and the desired accuracy of ±3% seems possible.

Polarographic Determination of Uranium. This method is in need of no refinement since an accuracy of ±5% has been repeatedly obtained using the standard addition technique.

Fluorimetric Estimation of Uranium. TBP (tributyl phosphate) extraction followed by fluorescence measurement of the uranium concentration shows that reproducible results can be obtained consistently.

Specific Gravity Determination. Refinements of this method show that an accuracy of ±0.001 g/cc is possible. The apparatus is being redesigned to fit in with the barricade design of the new building.

Nitric Acid Determination. This method is satisfactory.

GENERAL RADIOCHEMICAL ANALYSES

C. L. Burros

The RCA laboratory has been operating at about 60% maximum efficiency owing to the reconstruction of the building. The new laboratory facilities are about 90% complete.

During the past quarter the greater number of the analyses were requested by the Chemical Technology Division. Active-constituent assays were made on samples obtained in (1) the decontamination studies of the Purex process (including first and second cycles) and (2) the recovery of active constituents from the waste stream. About half these samples were in an organic medium (Varsol-TBP), and some difficulty was encountered in the analyses. Analyses were also made on samples obtained in the decontamination studies of the homogeneous pile fuel program. Uranium from plutonium separations (in the presence of high concentrations of copper and nickel) were made on samples submitted from the fluorination studies program. Valence-state analyses were performed on several samples submitted by the Plutonium Recovery Group.

Miscellaneous samples were analyzed for the Army clothing-decontamination studies, Radiation Hazards (K-25), and the Chemistry and Health Physics Divisions.

The service work completed in the period July through September is summarized in Table 12.

TABLE 12

Summary of Service Analytical Work for Period
July 1 Through September 30, 1950

GROUP MAKING ANALYSES	NO. OF PERSONNEL		NO. OF ANALYSES MADE FOR									
	TECH.	NONTECH.	BIOLOGY	PHYSICS	CHEMISTRY	CHEMICAL TECHNOLOGY	METALLURGY	REACTOR TECHNOLOGY	OPERATIONS	HEALTH PHYSICS	MISC.	TOTAL
Radiochemical Development	10	2		30	28	18	50		288		99	513
Ionic Development	5	1			171	61		8			35	275
Spectrochemical	4	0		12	197	26	80	96	236	16	10	673
General Radio-chemical	4	7			28	4,577	4			325	292	5,226
General Ionic	4	1		8	59	4	10	11			1	93
Water Analysis	1	4		25	74	539	32	4,839			82	5,591
Laboratory and Semiworks Control	2	12		1	499	11,173	312			1		11,986
Pilot Plant	5	19			25	3,746						3,771
Production Control	7	19			800	1,590			9,406			11,796
Total	42	65		76	1,881	21,734	488	4,954	9,930	342	519	39,924

INORGANIC PREPARATIONS

PREPARATION OF THE ANHYDROUS CHLORIDES OF Fe^{++}, Co^{++}, Ni^{++}, AND Mn^{++}

D. E. LaValle

The anhydrous chlorides of Fe^{++}, Co^{++}, Ni^{++}, and Mn^{++} were prepared using a modification of the method reported by Domange.[1] The method consists in passing a stream of dry HCl gas over the salts heated to 300°C. It was found desirable to pretreat the tetra- and hexahydrated salts by first passing HCl gas through the saturated solutions to precipitate the mono- or dihydrate. The precipitate was filtered off, dried under vacuum, and used as the starting material for further dehydration with HCl.

In the case of $FeCl_2$, the starting material was prepared by the action of HCl on iron powder in a CO_2 atmosphere. Iron was added to concentrated hydrochloric acid until it was in excess. While some reaction was still going on, thus assuring the reduced state, the supernatant was filtered through a suction disk of fritted glass.

PREPARATION OF ANHYDROUS FLUORIDES OF Fe^{++}, Co^{++}, Ni^{++}, and Mn^{++}

D. E. LaValle

The fluorides were prepared by passing anhydrous HF over the anhydrous chlorides at 500°C for about 1½ hr.

PREPARATION OF LITHIUM COMPOUNDS

R. H. Sampley

The following series of compounds were prepared for the Physics Division:

Silicate series: $Li_2Si_2O_5$, Li_2CaSiO_4, and Li_2SiO_3
Titanate series: Li_2TiO_3, $Li_2Ti_2O_5$, and Li_2TiSiO_4
Zirconate series: Li_2ZrO_3, $Li_2Zr_2O_5$, Li_2ZrSiO_5, and Li_2CaZrO_4

(1) Domange, L., "Réaction d'equilibre de la vapeur d'eau, à haute temperature, avec quelques fluorures métalliques," *Ann. Chim.*, Series 11, 7, 225 (1937).

Procedure. Silicon dioxide, titanium dioxide, and calcium carbonate were used as the starting materials. A stoichiometric amount of the compound was combined with lithium carbonate and heated for 12 hr at 750°C. The reacted mass was ground and heated for 3 hr at 1000°C.

One-tenth mole of each compound was prepared without the addition of an activator. Then 0.1 *M* quantities of each compound were prepared with each of the following activators: copper, lead, bismuth, nickel, tin, zirconium, tantalum, silver, vanadium, titanium, thallium, manganese, rhenium, ruthenium, and cerium. The compounds activated with ruthenium and cerium were prepared in an inert atmosphere.

PURIFICATION OF CRUDE ZIRCONIUM OXIDE

R. H. Sampley

Approximately 1200 g of crude zirconium oxide was purified for use in the preparation of the zirconate series of lithium compounds.

ANALYTICAL CHEMICAL CONTROL OF HOMOGENEOUS REACTOR SOLUTION

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

An investigation of methods for the analytical chemical control of the reactor solution has been reported previously.[1] The two most feasible methods appeared to be (1) the determination of density by an electromagnetic densitometer and (2) the determination of the concentration of uranium by its effect upon the Q of a suitable high-frequency coil (20-megacycle range). Accordingly, work has been concentrated on the development of these methods.

ELECTROMAGNETIC DENSITOMETER

The complete unit must be capable of withstanding the conditions of temperature, pressure, and radiation of the solution to be used in the experimental homogeneous reactor, and all parts will be tested under conditions that approach as nearly as possible those to be found in the reactor solution. The unit will have an intake and outlet pipe so that it can be incorporated into the reactor system after first being tested and calibrated in the laboratory. While in operation, the fluid will be static and the unit will be protected against sudden pressure changes which would result from dumping of the "soup." Present plans do not include the introduction of insulated electrical leads into the high-pressure system.

As a starting point, certain materials and specifications have been decided upon. All parts exposed to the soup will be constructed of stainless steel and, if necessary, will be passivated. The temperature effect on density measurements is important. It is expected that changes in temperature greater than 0.2°C cannot be tolerated unless proper corrections are applied. The control or measurement of temperature with this degree of accuracy would be difficult owing to the continuous internal heating of the solution by radiation and to the problem of obtaining a suitable thermometer.

It is thought that the problem of temperature control may be circumvented by using two densitometers, both pressurized to the condition of the reactor.

(1) Davenport, W. H., Jr., and Powell, R. H., "Experimental Homogeneous Reactor Chemical Control," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-788 p. 51 (Oct. 4, 1950).

One of these will contain a solution of U^{238} of known concentration, and the other will contain the unknown soup solution. Both solutions will be thermostated by the soup solution itself. The densitometer containing the known U^{238} will then become in effect a thermometer since changes in the temperature will be reflected in the coil readings. The magnetic flux required in the coil of the unknown densitometer will be governed by changes in the temperature and concentration of the soup solution. When calibrated, the difference in the two coil readings should be independent of temperature. Even though the solutions are thermostated in this way, there may still be problems of temperature gradients.

The principle of the densitometer may be applied to either a sinker, in which case the coil strength required to raise or hold the sinker is observed, or to a float, in which case the coil strength required to overcome the bouyancy force and pull or hold the float down is determined. A sinker must have a density slightly greater than the highest density to be studied; the density of a float must be less than the lowest density to be studied. A sinker was designed for the preliminary densitometer because this best fitted the plan of using a magnetic switch as a position-detecting device. Since the sensitivity increases as the density difference between the float or sinker and the solution decreases, it may be necessary to employ a float to measure densities in the lower density range. A cylindrical float constructed of No. 309 stainless steel by the research shops and hydraulically pressure-tested, using Y-12 Plant facilities, was found to withstand a pressure of 500 psi, but it collapsed at 750 psi. The float was 4 cm long and 1.6 cm in outside diameter and had a wall thickness of 0.005 in. throughout, except at the ends where threaded nubs were provided for the addition of a soft iron core and/or an alnico magnet. The attachments can be made leakproof. The desired shape was obtained by the heliarc welding of two dome-shaped cylinders. The general collapse of this float under a pressure of 750 psi indicated that greater wall thickness rather than improved construction would be necessary to achieve pressure stability in a 1000-psi medium.

Two floats of similar external dimensions but with 0.010 in. wall thickness were constructed of No. 309 stainless steel (Fig. 14). Both floats were tested at increments of 200 psi every 2 min from a 500-psi base. One of these floats was sacrificed to determine maximum collapsing pressure with a uniform collapse, which was found to be 1700 psi. This collapsing pressure was determined accurately. The other float was tested to 1000 psi and was assumed to

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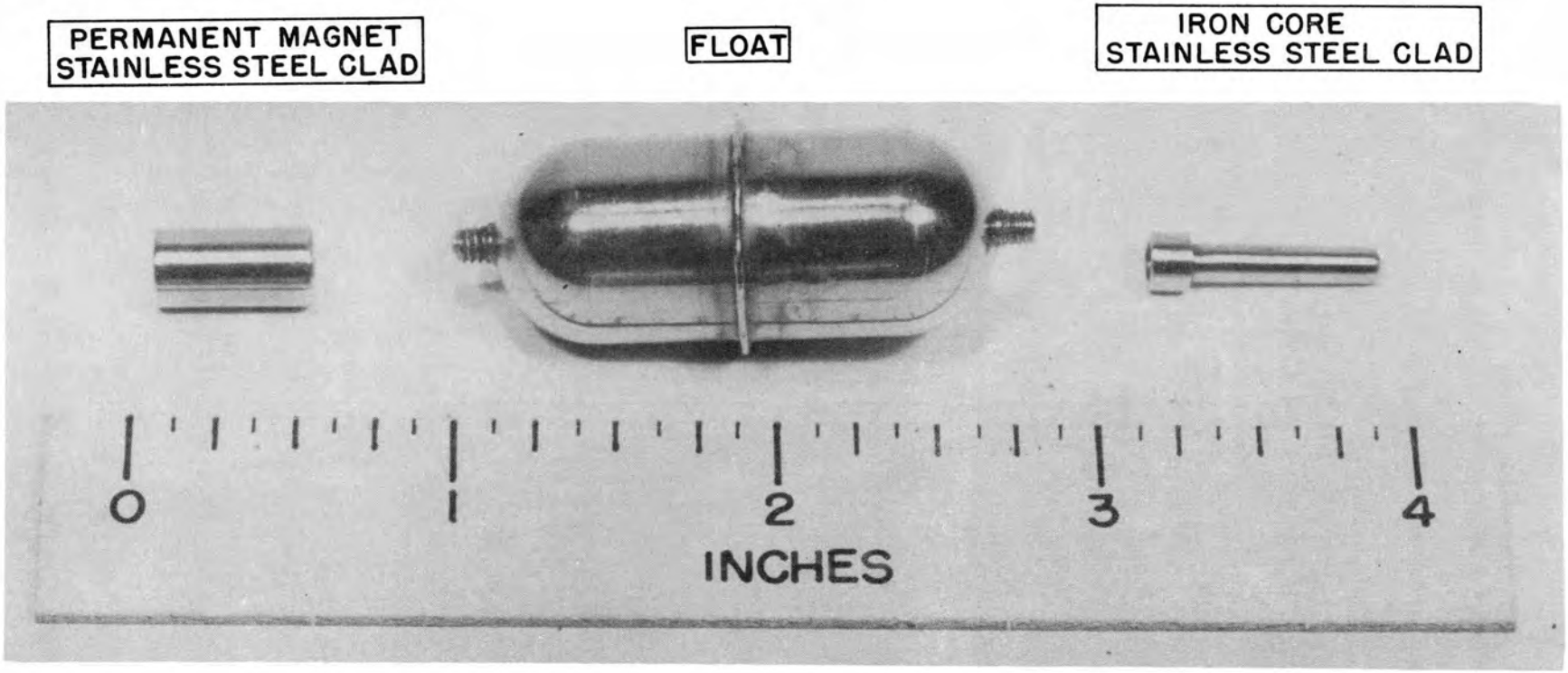

FIG. 14
SINKER

be able to withstand pressures up to 1700 psi. Ultimately, it is planned to test such a stainless-steel shell, passivated, if necessary, for temperature and radiation stability.

When the float was equipped with a soft-iron core and an alnico magnet (Fig. 15), it became a sinker for the reactor solution with a density of 1.113 at 20°C. By changing the weights of soft-iron core and alnico magnet, the density of the float or sinker may be varied to cover the anticipated density range of the soup.

The problem of radiation or temperature stability of the permanent alnico magnet has been partially investigated. A preliminary pile experiment for radiation damage showed no loss in magnetic strength when an alnico magnet was exposed to 75% of the maximum flux of the ORNL pile at 152°C for three weeks. The material has been returned to the pile for an additional four months' irradiation, and further data will be available after Dec. 21, 1950.

Since the operating temperature of the Homogeneous Reactor Experiment will be 250°C and the highest ORNL pile temperature is 152°C,[2] an out-of-pile test was also made at 300°C in a controlled furnace for one week. No loss in magnetic strength was detected. The test is being continued for an additional period of six weeks.

The magnetic strength before and after the above tests was measured by placing an aluminum slug containing a positioned magnet in a movable boat on a track and observing the effect of the magnetic field on a dip needle at various points (Fig. 15). The track was calibrated with an identically mounted control magnet, and hence the testing mechanism may be recalibrated with the control magnet for any future test. Results indicate that it will be feasible to use a permanent magnet in the float or sinker and in the magnetic switch.

Two methods for detecting the position of the sinker are under consideration. For one a magnetic switch responding to a given position of the permament magnet inside the sinker has been developed. The second method, which has not yet been investigated, involves the detection of the position of the sinker by using a lead-shielded slit window to the ionization chamber and observing a change in the radiation level produced by displacement of the soup by sinker movement. This method probably would employ the same sinker as that used in the magnetic switch. The radiation device has the advantage of having

(2) Stanley, W. M., private communication.

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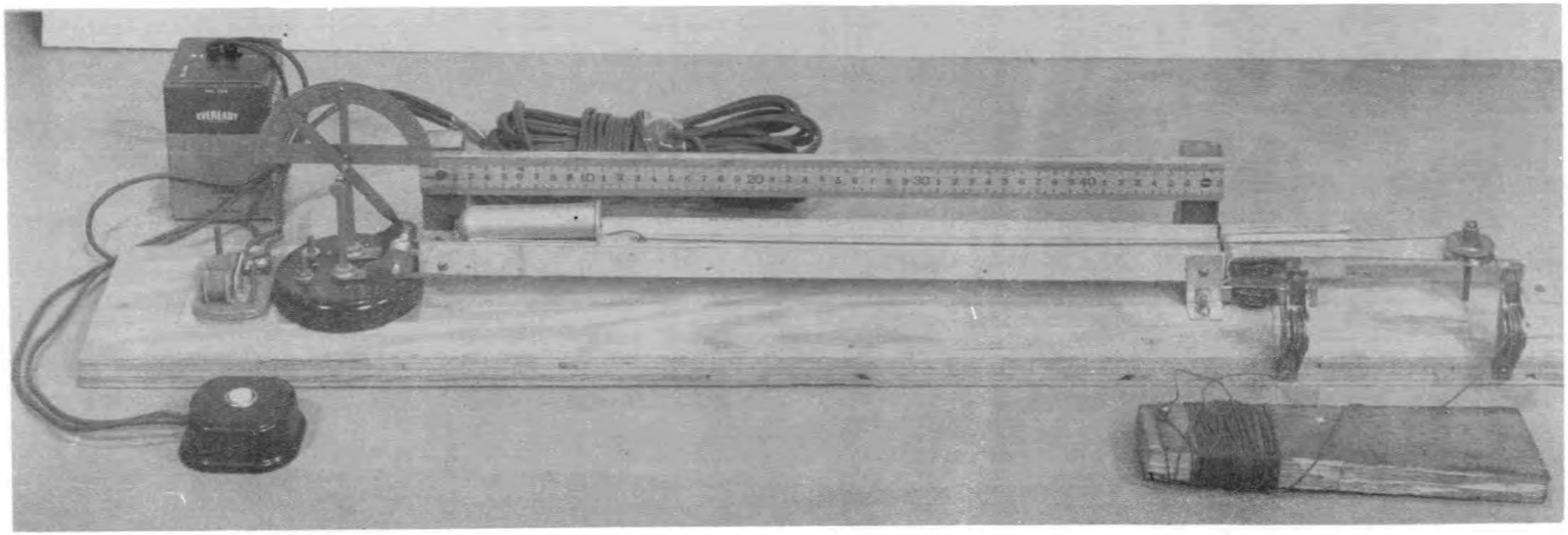

FIG. 15
MAGNETOMETER

no moving parts, but it might become inoperative at the low radiation level of startup or in the densitometer containing the U^{238} standard.

A magnetic switch designed and constructed by H. L. Hemphill and the research shops is shown in Fig. 16. The switch is designed to be placed on the outside of a stainless-steel pipe ¼ in. in wall thickness; the mechanical response of the switch may be adjusted remotely. A movable arm *A* is supported by a stainless-steel wire *B*, which in turn is held taut by a stainless-steel spring *C*. A permanent magnet *D* is attached to one end of the arm and is delicately counterbalanced by a lock-nut arrangement *E* at the other end. Platinum wire contacts *F* are placed to contact the swinging arm and to signal the switch position, which in turn activates a new measurement cycle.

The Instrument Group under R. E. Toucey is starting work on the winding of a d-c coil and the wiring of an electrical circuit which will record the coil strength and also coordinate the action of the sinker, magnetic switch, and coil. The choice of a suitable insulation for the coil is being studied. Copper wire clad with fiberglas insulation will be tried first for the coil.

In order to achieve greater sensitivity, the coil strength will be measured by balancing the voltage drop across a standard resistor with a 0- to 1-mv Brown recorder, an external source of constant voltage, and a calibrated potentiometer. Mr. Toucey believes that this circuit may be used to record voltage with an accuracy of 1 part in 10,000. If possible, the circuit will be made completely automatic.

Q MEASUREMENT

One of the very important problems in the measurement of the *Q* of a high-frequency coil, as affected by changes in uranium concentration, is the introduction of an electrically insulated coil directly into the high-pressure high-temperature soup solution. The insulating material must combine ruggedness, to withstand the conditions of the reactor, with low power loss. Increasing the wall thickness of the insulator, in order to strengthen the unit, results in a greater power loss. The reactor temperature of 250°C approaches, and in some cases is higher than, the softening temperatures of many of the common plastics such as bakelite and polythene. The higher melting plastic teflon, as well as these low-melting ones, has been reported to

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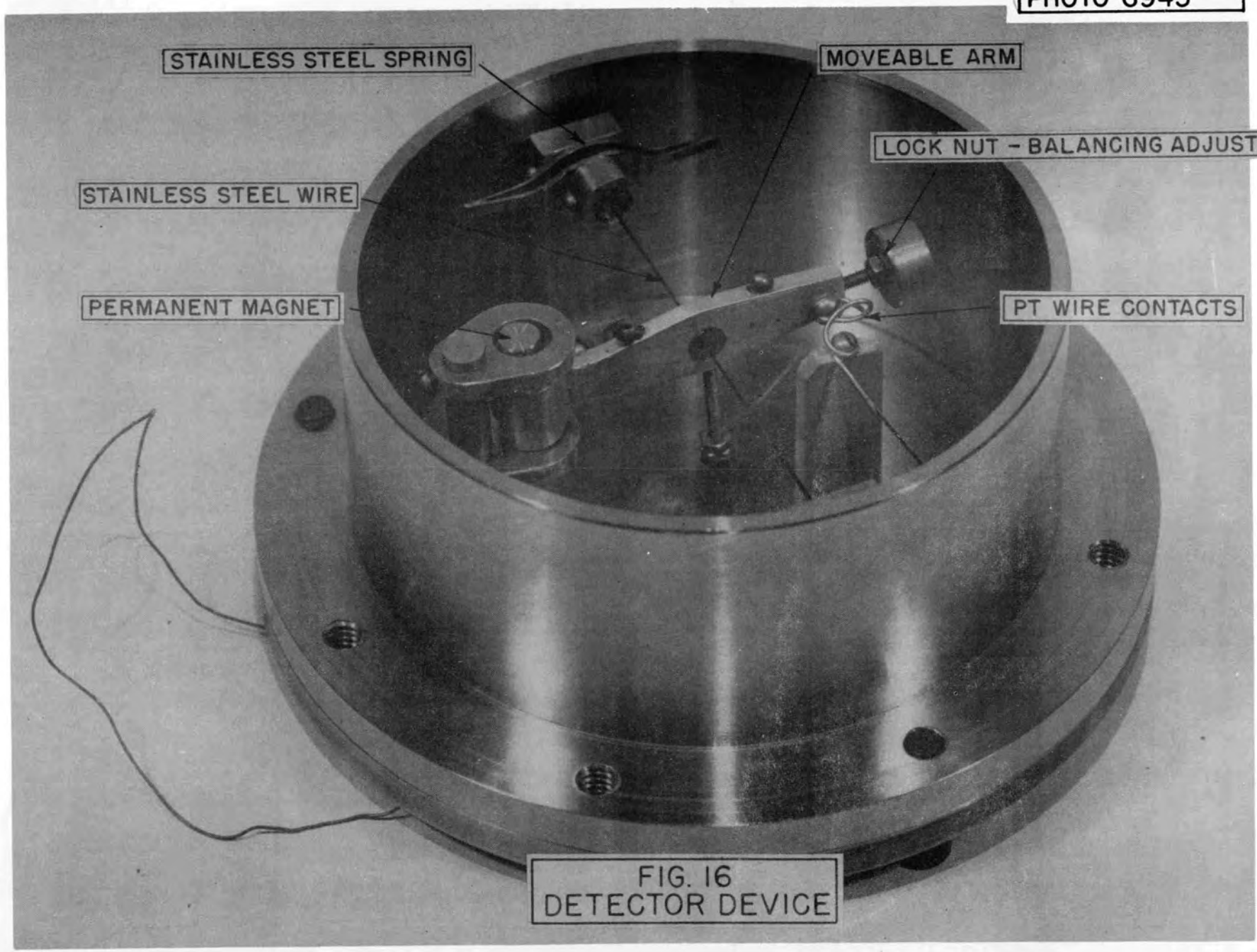

FIG. 16
DETECTOR DEVICE

deteriorate badly under the maximum flux radiation of the Chalk River pile.[3]

Several ceramics are being investigated. Commerical lava and AlSiMag have low power loss and high mechanical strength. Favorable radiation stability is reported. They are both porous, however, and a method for impregnating the pores or glazing the surface would have to be developed before these insulators would be considered further.

There is a possibility that quartz could be used, but its mechanical strength in the presence of high radiation has not been satisfactorily investigated. It should be noted that fused quartz and crystalline quartz are being examined at Chalk River for changes in electrical insulating properties and dimensional stability as part of the general radiation-damage studies. Plastics are also being examined.[4]

The results of these tests should be obtained as speedily as possible, since the Chalk River reactor has, at present, the nearest approximation to the highest rate of the proposed homogeneous experimental reactor, and the rate of flux, as well as total irradiation, is a factor to be considered in radiation damage.

A semiquantitative laboratory experiment gave indication that the change of Q with concentration should increase with increasing temperature. The test was not conclusive since the temperature was varied only from room temperature to 85°C.

(3) Averbach, B. L., Billington, D. S., Irvine, J. W., Jr., Johnson, W. E., Kaufman, A. R., Lawson, A. W., Jr., Low, J. R., Untermyer, S., and Slater, J. C., *Survey of Effects of Radiation on Materials*, AEC-500, p. 127 (no date).

(4) *Ibid.*

OPTICAL AND ELECTRON MICROSCOPY

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

In cooperation with the Reactor Technology Division, further microscopic studies have been made of Bureau of Mines zirconium.

A sample of Bureau of Mines zirconium (1-in. disk, hot-forged at 750°C, hot-swaged at 750°C, cold-swaged to shape) was metallographically polished and given a very light etch, with an etchant composed of 10 parts of glycerin, 2 parts of HF (48% C.P. grade), and 1 part of concentrated HNO_3, to ensure the preservation and good definition of any included carbides but without causing attack on the surrounding zirconium structure. Three areas on the polished face were marked off by scribing circles 2 mm in diameter; each area was photographed at approximately 50×, and enlargements were made to 150×. In Fig. 17*A* is shown a portion of one selected area (note the carbide stringers). At this magnification individual carbide grains are not very well resolved.

The polished sample was returned to the Corrosion Section of the Reactor Technology Division, where it was immersed in 0.17 *M* UO_2SO_4 containing 0.1 *M* HNO_3 for 168 hr at 250°C. At the completion of this test the sample was again examined microscopically to observe any changes that had taken place in the previously mapped areas.

It was found that the polished surface was encrusted with a heavy deposit of the grayish-white material earlier identified as the monoclinic variation of zirconium oxide. Carbide inclusions, if any remained at the photographed plane, were hidden beneath this mass. To determine if the carbides or the adjacent areas had been attacked, and, if so, the extent of corrosion damage, the layer of corrosion product was carefully removed by polishing very lightly with alumina 1000. To ensure against overpolishing, frequent microscopic observations were made until the plane of carbide inclusions could be seen again. Photomicrographs of the areas were made. Figure 17*B* shows the same area as that in Fig. 17*A*. A composite print of these two areas, Fig. 17*C*, was made to show more readily that the areas of heaviest corrosion appear to follow the pattern of the included carbides. Photomicrographs of the carbide grains (Fig. 18*A*) indicate that they underwent little or no attack, whereas the adjacent zirconium structure (Fig. 18*B*) was severely damaged. The lines

[redacted]

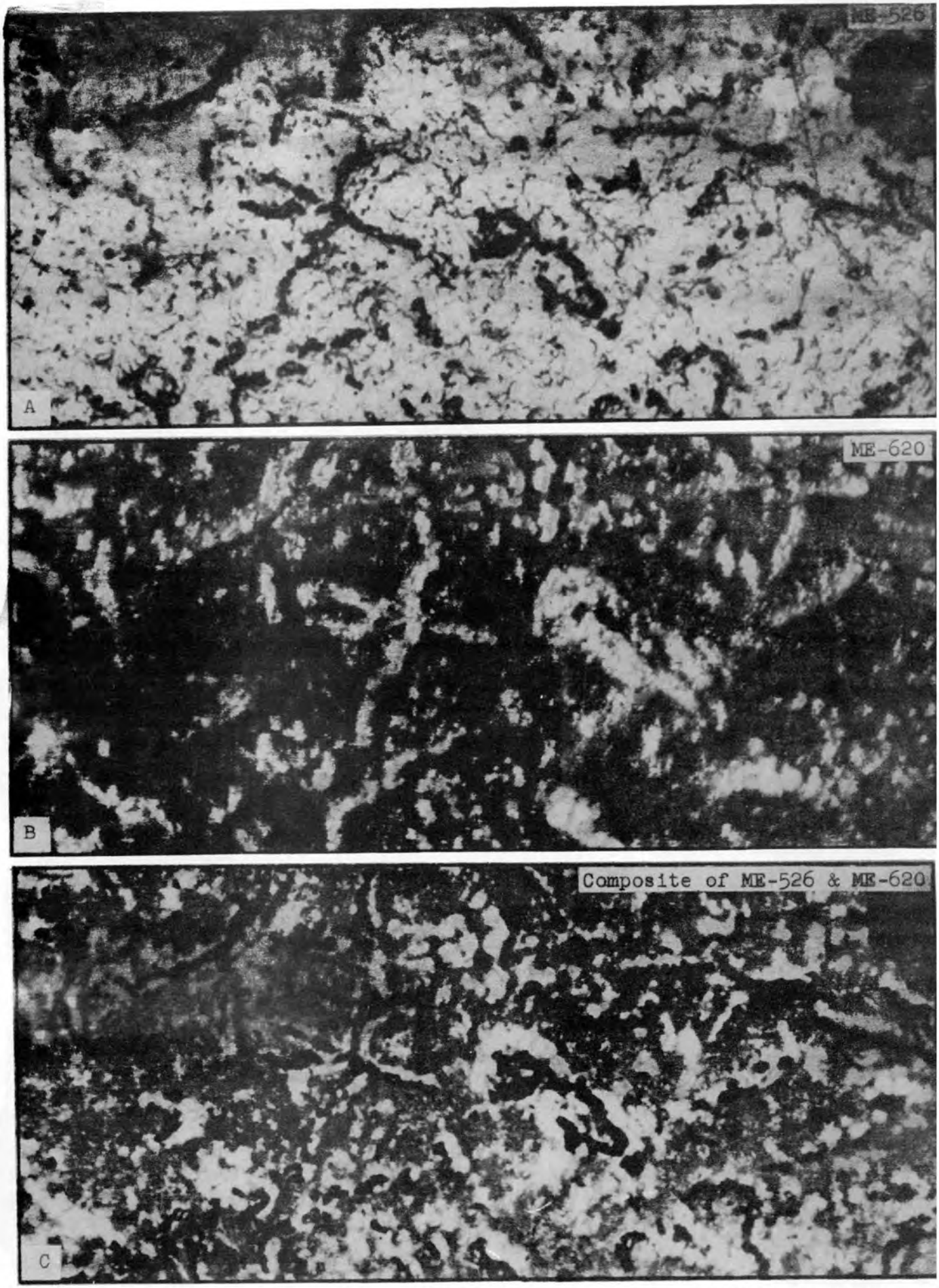

FIG. 17 CORROSION STUDY

[redacted]

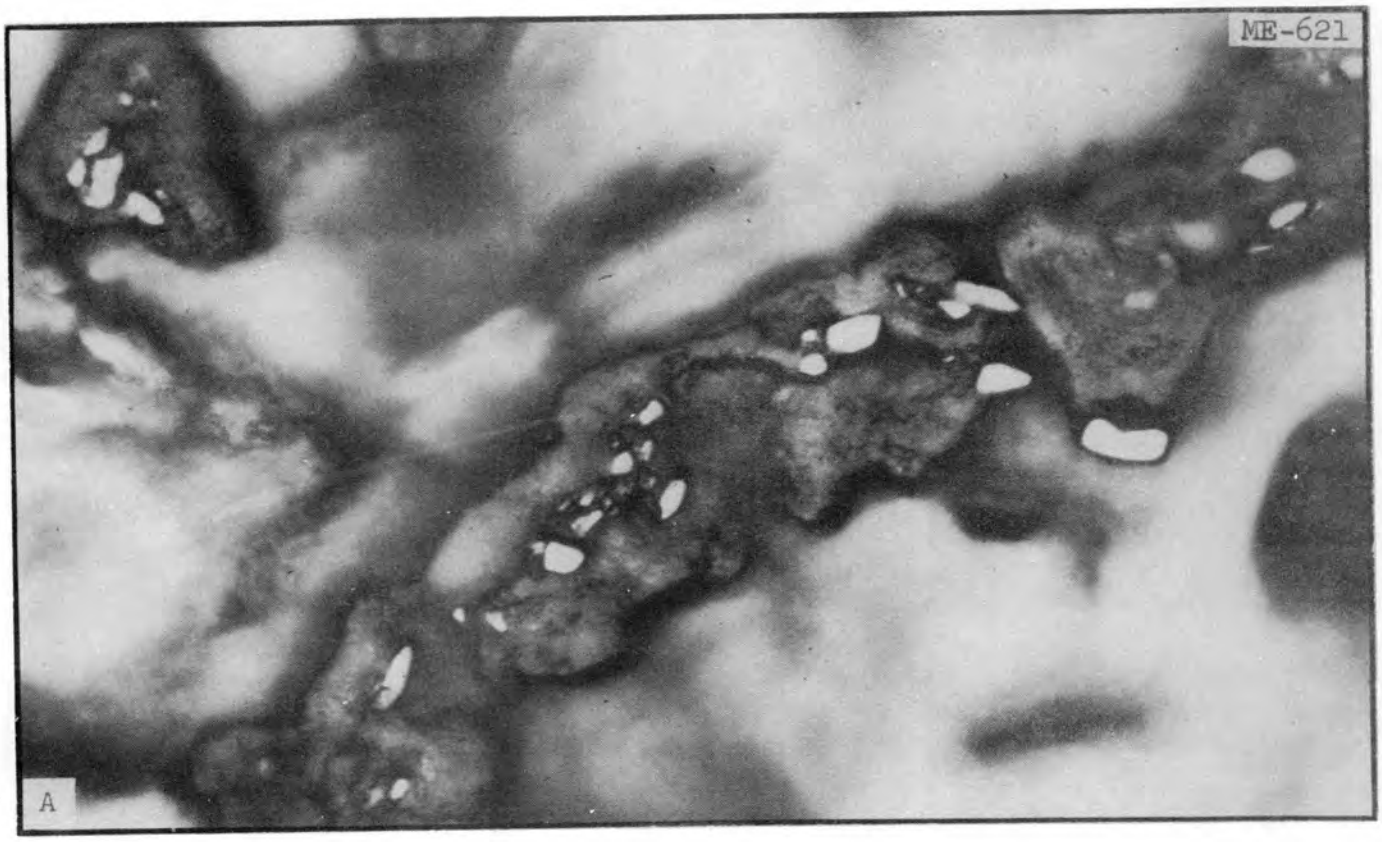

FIG. 18
CORROSION STUDY

of attack not only followed grain boundaries but also cut across the face of the grains.

Recent electron-microscope and polarized-light studies of Bureau of Mines zirconium having the same initial structure as the above-described material indicate the presence of microcrystalline material (particle size less than 1 μ) residing at grain boundaries, within the zirconium grains, and bordering the carbide inclusions in small clumps and chains. It has been impossible to identify this material positively at this date because of its dispersion and minute size. Its location, together with observations made on corrosion-attacked metal, indicates that a relation exists between it and the place at which the metal is attacked.

BUTT-WELDED TANTALUM TUBING

Of possible interest is a study of the cross section of a length of tantalum tubing welded in an argon atmosphere by a method using tungsten electrodes which do not contact the tantalum tubing. A panoramic cross section of the tube is shown in Fig. 19*A*. This includes the microstructure of the weld, the affected zone, and the parent metal. The very large grains in the fusion zone are oriented at an approximately 90° angle with the original structure. Figure 19*B* shows the structure of the weld as observed at the exterior surface of the tube.

SUMMARY OF WORK DONE IN THE OPTICAL AND ELECTRON MICROSCOPY SECTION

During the period from June 20 to Sept. 20, 1950, eighty samples were received. The following work was done:

Electron micrographs and diffraction patterns (107 plates of 5 frames each)	535
Metallographs	24
Photomicrographs	40
Lantern slides	14
Copy negatives	2
Radioautographs	4
Total	619

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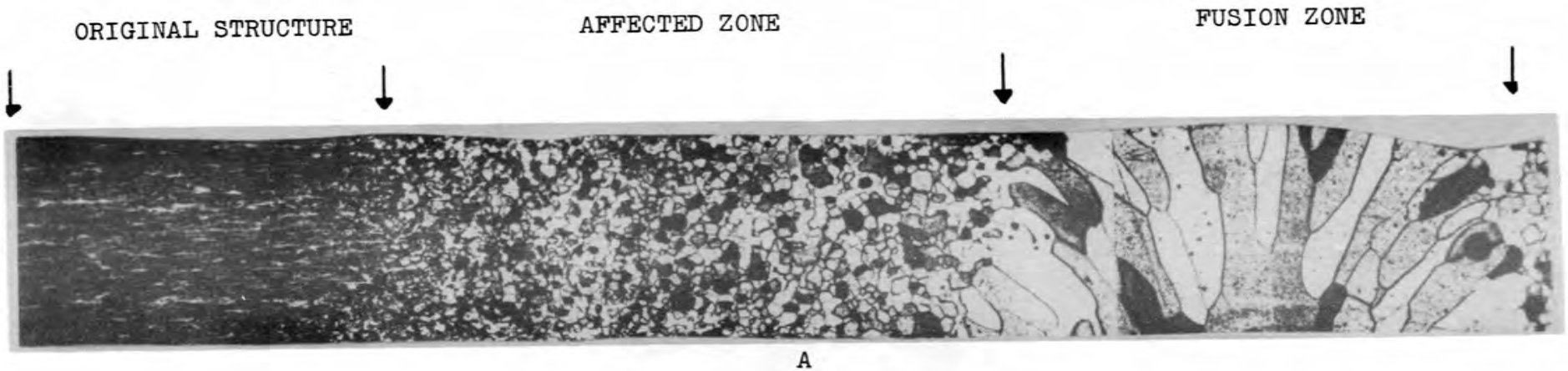

A

B

FIG. 19

MICROSTRUCTURE OF BUTT
WELDED TANTALUM TUBING

The bulk of the time in this section has been spent on work of a service nature on problems best reported by the persons instituting them. The major part of the electron microscopy work was devoted to particle-size determinations and metal replica studies. Other service work covered a wide range of subject matter, including studies of metal cross sections, films, and exchange resins.

During this period the metal evaporator was overhauled and several changes were made which reduced the pumping-down time between samples from 1½ hr to 40 min. A focusing ocular for the electron microscope was designed and built. Changes were made in the darkroom setup to increase efficiency.

Future work is contemplated on finding a suitable etch for the electron microscopy of zirconium. An attempt will be made to find a reproducible method of producing conducting metal films with a resistivity within an established limit, and a study will be made of the temperature range in the evaporator and the effect of temperatures within the evaporator on particle size and dispersion of metallic films produced therein.

ANALYTICAL CHEMISTRY DIVISION

Y-12 SITE

IONIC ANALYSES—RESEARCH AND DEVELOPMENT

DETERMINATION OF ZIRCONIUM IN ZIRCONIUM TETRAFLUORIDE

Roberta McCutchen and A. F. Roemer, Jr.

Statistical analysis of results of the determination of zirconium tetrafluoride by precipitation of the zirconium with phenylarsonic acid[1] and ignition and weighing of the oxide revealed that the precision was less than anticipated and that the results, in general, tended to be low. Considerable work has been done toward improving this determination. A method of dissolution of the sample with aqua regia and sulfuric acid has been successfully substituted for $HF-H_2SO_4$ treatment, thus reducing the amount of fluoride that must be removed before precipitation of the zirconium phenylarsonate.

The comparative merits of mandelic acid,[2] cupferron,[3] and phenylarsonic acid as precipitating agents for zirconium in fluoride-free solutions and in the presence of varying concentrations of fluoride ion have also been studied. A report summarizing this work is to be published.

In general, the results indicate that (1) satisfactory results may be obtained by all three methods of precipitation, (2) the difference in reliability of the three methods is not outstanding but the phenylarsonic acid method gives a slightly better precision than the other two, (3) no significant difference is to be noted in the precision attained by two different analysts, and (4) fluoride interference is most serious with mandelic acid as the precipitant, less so with phenylarsonic acid, and negligible with cupferron, at least with F/Zr atomic ratios of 4. When the fluoride concentration is negligible, the mandelic acid or the phenylarsonic acid method, either of which gives more selective precipitations than the cupferron, is recommended. When fluoride contamination is a factor and the zirconium is essentially free of other metals yielding precipitates with cupferron, the cupferron precipitation will be found preferable.

(1) United States Steel Corporation, *Sampling and Analysis of Carbon and Alloy Steels*, Reinhold, New York, 1938.

(2) Kumins, C. A., "Zirconium Determination in Presence of Interfering Elements," *Anal. Chem.* 19, 376 (1947).

(3) Furman, N. H., *Scott's Standard Methods of Chemical Analysis*, Van Nostrand, New York, 1944.

DETERMINATION OF IMPURITIES IN LITHIUM BY MEANS OF THE FLAME PHOTOMETER

S. Blumkin

During this quarter a study was made of the flame emission of potassium, calcium, and magnesium solutions in concentrations up to 50 γ/ml with 0 to 10,000 γ of lithium per milliliter added. Lithium was found to have a complex effect upon the emission of these elements, differing in detail but similar in each case. A net enhancement or depression resulted; which of these occurred depended upon the concentration of the particular element as well as that of the lithium.

Obviously, the presence of these elements as impurities in the lithium standard contributes in whole or in part to the enhancement phase of the total effect. The "spiking technique," usually employed to evaluate the concentration of an unknown, yielded unreliable results for the impurity content of the lithium standard. The failure of this method, it is believed, stemmed from the variable interference effect and the responsibility of the lithium itself for some of the emission increase noted.

However, to establish calibration curves for flame emission as a function of the concentration of these elements in the presence of lithium, it is essential that the exact content of these elements in the lithium standard be known. The aid of spectrographic and activation analytical techniques has been enlisted to this end. Also, some initial steps have been taken looking toward the possible reduction of the impurities in the standard to amounts insignificant with respect to the concentration range of 1 to 1000 parts of contaminant per million of lithium. Extraction with water of sodium and potassium salts from lithium carbonate in a Soxhlet apparatus has shown some promise in this direction.

MICROCHEMICAL ANALYSES

Mary Barnes and J. W. Robinson

Microchemical methods for analysis of very small samples of methylene blue and its derivatives for carbon, hydrogen,[4] nitrogen,[5] sulfur,[6,7]

(4) Niederl, J. B., and Niederl, V., *Organic Quantitative Microanalysis*, Chap. 5, Wiley, New York, 1946.

(5) *Ibid.*, Chap. 3.

(6) Parr Instrument Company Manual No. 116.

(7) Grant, J., *Pregl's Quantitative Organic Microanalysis*, p. 85, Blakiston, Philadelphia, 1946.

and chlorine[8] are being tested. Some difficulty was encountered in obtaining precision in the sulfur and chloride determinations. Efforts toward correction of this difficulty are now being made.

(8) Grant, J., *op., cit.*, p. 101.

SERVICE ANALYSES

ANALYTICAL WORK FOR THE NEPA PLANT

L. J. Brady

The spectrographic work for the NEPA plant this quarter has consisted mainly in the analysis of sodium samples for trace impurities. The method of analysis of these samples consists briefly in dissolving the sodium in alcohol and water, filtering off the insoluble residue, and recovering the metal impurities by precipitation and filtration methods. The precipitate and the insoluble residues are dissolved in acid, a known amount of standard platinum solution is added, and the sample is diluted to a known volume. The solution is then analyzed spectrographically by the porous-cup technique of Feldman.[1]

Titration of a known aliquot of the alcohol-water solution of the sodium with standard acid permits the calculation of the weight of sodium in the sample. The concentration of impurities is reported in micrograms per gram of sodium.

Since in the method just described the sodium is separated from the impurities and is not present in the solutions analyzed spectrographically, standard solutions containing known concentrations of the various components of stainless steel and a definite amount of platinum standard but without sodium were prepared for use as standards in the spectrographic analysis of these samples.

The stainless-steel capsules in which the sodium samples are submitted are cleaned, dried, and returned to NEPA for further investigation of the degree of corrosion.

Apparatus for use in the determination of sodium monoxide in sodium by the method of Pepkowitz and Judd[2] has been built and assembled. This apparatus will be used in determining the oxygen content of sodium samples prepared in connection with the corrosion tests being performed at NEPA.

(1) Feldman, C., "Direct Spectrochemical Analysis of Solutions," *Anal. Chem.* 21, 1041 (1949).

(2) Pepkowitz, L. P., and Judd, W. C., "The Determination of Sodium Monoxide in Sodium," KAPL-127 March 9, 1949 (declassified July 14, 1949, AECD-2660).

Bismuth and bismuth-lead samples have also been submitted for spectrographic analysis. Chemical analyses have been made of a wide variety of miscellaneous samples, comprizing approximately 50% of the total samples received during the period. Included in this group are the following types of samples: ferrous and nonferrous alloys, uranium compounds, carbon and graphite, lead, nickel, and boron and boron-containing compounds. The analysis of these materials required the adaptation of a variety of standard methods.

The analytical work carried out for the NEPA plant during the period June 26 through September 15, 1950, may be summarized as follows:

	NO. OF SAMPLES
Backlog, June 26	46
Received, June 26 through September 15	129
Total	175
Reported, June 25 through September 15	125
Backlog, September 16	50

ANALYTICAL SERVICES FOR ORNL

J. W. Robinson

Samples obtained during the investigation of the uranium-carbonate-fluoride system continued to account for a large portion of the analytical work completed during the quarter. These materials were analyzed for sodium, uranium, and carbonate ions which oocurred in micro or macro concentrations, and for fluoride, chloride, sulfate, ammonium, and potassium ions.

The determination of the water and the nitrogen content of ion-exchange resins also constituted a part of this program. The Kjeldahl method currently employed for the determination of the nitrogen in such resins is time-consuming, and replacement of it with the Dumas method is being considered.

By far the greatest number of uranium determinations were made on residues and solutions obtained in the studies on the recovery of uranium from phosphate rock. The head samples of this material have a uranium content of the order of 150 ppm. The uranium is extracted with TBP (tributyl phosphate) and determined fluorimetrically.

It was found that the "free lime" content of samples of calcium fluoride could be determined according to the procedure given for "free lime" content of cement, ASTM, C-114-47.

Approximately forty metal samples, together with a few miscellaneous materials, were analyzed for the X-10 plant during this period.

A summary of the analytical work done for ORNL during this quarter is given in Table 13.

TABLE 13

Summary of Analytical Work for ORNL for Period June 16 Through September 15, 1950

TYPE OF MATERIAL	NO. OF SAMPLES
Sodium-uranium-carbonate solutions and solids	310
Residues and solutions of phosphate rock	250
Calcium metal	110
Transformer oils	80
Zirconium compounds	70
Sodium-uranium-arsonic solutions and solids	60
Resins	40
Calcium fluoride	40
Zirconium metal	30
Lithium metal	30
Aluminum and iron phosphate solutions	30
Silver alloys	20
Preparation of standard solutions (outside)	20
Hafnium compounds	20
Corrosion products	20
Stainless steel	20
Calcium chloride solutions	20
Propane gas and combustion products	10
Uranium metal and uranium compounds	10
Air samples	10
Barytes	10
Miscellaneous	50
Total	1260

Total number of determinations = 3350

QUALITY CONTROL

Standard samples for the most commonly occurring types of analyses are analyzed regularly, and a statistical analysis is made of the test results. In this way limits of error of any method or determination may be fixed, and the source of trouble recognized.

Quality-control-data for the current period are given in Tables 14 and 15.

DISCUSSION OF FINDINGS

Roberta McCutchen

Chemical Analyses. The limits of error for determination of sodium by the flame-photometer method and of carbonate by the gas-evolution method in carbonate solutions which also contained varying amounts of uranium and sulfate were found to be higher than had been anticipated. The uranium had little or no effect on the sodium determination, but the presence of small amounts of sulfate did decrease the sodium emission. Precipitation of the sulfate by barium in both the unknown and the standard effectively eliminated this sulfate interference.

As was noted in ORNL-788, the determination of Zr in ZrF_4 is neither as precise nor as accurate as would be expected for such a gravimetric determination. This observation has led to a study of factors affecting the reliability of the determination, using modified procedures and three different precipitating agents. The summary of this study is given on p. 86.

In general, results of tests made on control samples during this period indicate that the modifications which have been made in various methods of analysis and in the selection and preparation of standard samples have increased the quality of work being done in the chemical laboratories.

Spectrographic Analyses. Quality-control data indicate that the spectrographic methods of analysis of Bi and Bi-Pb alloys for impurities (Fe, Ni, Cu, Mn, and others) and of sodium for Fe, Ni, Cu, and Mn are satisfactory, both in regard to sample preparation and the actual spectrographic determination.

TABLE 14

Chemical Analyses, June 16 Through September 15, 1950

TYPE SAMPLE	SUBSTANCE DETERMINED	METHOD OF ANALYSIS	STANDARD NO.	NO. OF SAMPLES ANALYZED (N)	ACCEPTED VALUE (Y)	AVG. VALUE ($\overline{X}$)	STANDARD ERROR OF AVG.	STANDARD DEVIATION ($\pm S$)	% BIAS OF ONE DETERMINATION	% LIMIT OF ERROR OF ONE DETERMINATION ($L.E.$)
Na_2CO_3	Na (mg/ml)	Flame photometer	E-100	5	0.482	0.484	0.001	0.003	+0.4	1
			G-100	4	0.491	0.484	0.007	0.007	-1.0	3
			E-200	6	1.21	1.21	0.02	0.03	0	5
			G-200	4	1.23	1.25	0.02	0.02	+1.0	3
			E-300	6	2.41	2.43	0.03	0.04	+0.7	3
			G-300	3	2.46	2.45	0.03	0.04	-0.5	1
Na_2CO_3	CO_3 (mg/ml)	Gas evolution	E-100	4	0.63	0.66	0.01	0.01	+5	3
			G-100	3	0.64	0.66	0.01	0.01	+3	3
			E-200	4	1.57	1.58	0.01	0.01	+0.8	2
			G-200	3	1.60	1.60	0.01	0.01	0	1
			E-300	5	3.15	3.14	0.01	0.01	-0.4	1
			G-300	4	3.20	3.20	0.01	0.01	0	0.5
ZrF_4	Zr (%)	Phenylarsonic acid precipitation	1	86	54.5	54.9	0.1	0.3	*	1
	H_2O (%)	Karl Fischer	1	22		0.2	0.2	0.09	*	100
NaCl	Na (mg/ml)	Flame photometer	J-100	5	0.273	0.295	0.005	0.005	+7	4
	Cl (mg/ml)	Mercuric nitrate titration	J-100	3	0.427	0.426	0.001	0.0007	-0.3	0.3
Calcium metal	Mn (ppm)	Periodate colorimetric	2	6		10.5	0.04	0.5		10

* The accepted values for zirconium and water have not been determined; consequently the bias cannot be computed.

Standard error of average = $\pm 2S/\sqrt{N}$

Percent limit of error of one determination = $L.E. = 2S \times 100/\overline{X}$

Percent bias of one determination = $100(\overline{X} - Y)/NY$

TABLE 15

Spectrographic Analyses, June 16 Through September 15, 1950

TYPE SAMPLE	ELEMENT DETERMINED (γ/ml)	STANDARD NO.	NO. OF SAMPLES (N)	ACCEPTED VALUE (Y)	AVERAGE VALUE ($\bar{X}$)	STANDARD ERROR OF AVG.	STANDARD DEVIATION ($\pm S$)	% BIAS OF ONE DETERMINATION	% LIMIT OF ERROR OF ONE DETERMINATION ($L.E.$)
Bi	Fe	1	4	150	164	20	20	+9	25
		2	5	180	192	44	22	+7	25
Bi	Ni	1	5	110	123	14	16	+12	25
		2	2	216	*	*	*	*	*
Bi	Cr	1	4	40	45	12	12	+6	50
		2	4	30	25	2	1.5	-7	10
Bi	Mn	1	4	45	50	12	12	+10	50
		2	4	<10	<10	0		0	0
Bi-Pb alloy	Fe	1	6	150	145	13	15	-6	20
Bi-Pb alloy	Ni	1	4	110	130	7	13	+18	20
		2	3	<10	<10				
Bi-Pb alloy	Cr	1	5	40	41	7	8	+13	40
Bi-Pb alloy	Mn	1	3	50	54	16	14	0	50
		2	3	85	92	36	31	0	50
Na	Fe	16&17	33	185	185	16	26	0	30
		18&19	15	225**	160	13	14	-30	20
Na	Ni	17&18	18	55	70	5	6	+30	15
		16&19	30	135	135	9	15	0	20
Na	Cr	18&19	15	35**	30	2	4	-20	25
		16&17	33	50	45	6	11	0	50
Na	Mn	17&18	18	25	25	2	2	0	10
		16&19	30	60	55	7	11	-15	40

* Insufficient data available to establish average, bias, and limit of error.
** Controls of this type were not analyzed last quarter.

Standard error of average $= \pm 2S/\sqrt{N}$

Percent limit or error of one determination = $L.E. = 2S \times 100/\bar{X}$

Percent bias of one determination = $100(X - Y)/NY$

INORGANIC PREPARATIONS

PURIFICATION OF ZIRCONIUM OXIDE

S. R. Buxton H. P. House
J. W. Robinson

The purification of ZrO_2 for use as spectrographic standard material was completed during this period. About 7 lb of $ZrO_2 \cdot xH_2O$ was processed through five recrystallizations as $ZrOCl_2$ in 8.7 *N* HCl. The purity of the product approached that obtained in laboratory-scale purifications with the exception of iron contamination (100 ppm), which probably was introduced from the reaction kettle.

The ZrO_2 obtained from ignition of the $ZrOCl_2$ was dissolved in dilute HCl, filtered, and reprecipitated as the salicylate in a solution adjusted to *p*H of 0.7 with respect to HCl, somewhat less than the theroretical amount of salicylic acid being used. The precipitate was ignited to ZrO_2. This separation reduced the iron content to 10 ppm and gave a product in which all impurities except hafnium, which was less then 250 ppm, were reduced to 10 ppm or less. Approximately 2 lb of highly purified material suitable for spectrographic standards was thus made available.

PREPARATION OF URANIUM CHLORIDE SOLUTION FOR NUCLEAR INDUCTION STUDIES

Roberta McCutchen and H. P. House

A quantity of U^{235} in the form of an aqueous solution of uranyl sulfate is being converted to UCl_5 for use in nuclear induction experimental work. Difficulties in this preparation are magnified by the requirements that the UCl_5 be delivered in a small sealed glass tube (16 mm O.D. and 250 mm long) and that the salt be preferably in solution in a solvent which contains little, if any, oxygen.

The sulfate has been converted to U_3O_8 by evaporation and ignition at 1000°C, and equipment, including a tubular shield, has been assembled for reacting this oxide in a closed tube with a suitable chlorinating agent.

[redacted]

Chlorination by means of hexachloropropene would be favored because of the low temperature and relatively low pressures required. However, with this chlorinating agent the final product would be insoluble UCl_4, and the liquid phase would contain a product of the reaction, trichloroacrylyl chloride, which contains oxygen.

Carbon tetrachloride will chlorinate U_3O_8 to form UCl_5, which is soluble in excess CCl_4 while the oxygen goes to form gaseous $COCl_2$. Chlorination by this method would, however, present the difficulty that excessively high pressures may be anticipated if the required amount of uranium is chlorinated in a sealed tube of the specified dimensions. To circumvent this difficulty, it is planned to seal a length of tube of larger diameter to the smaller tube, carry out the reaction in the larger-volume apparatus, bleed off the gases, and seal off the smaller tube containing the solution of UCl_5.

[redacted]