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8A
PROGRESS REPORT

AEC RESEARCH AND DEVELOPMENT REPORT

CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT
FOR
PERIOD ENDING JUNE 30, 1949

J. A. SWARTOUT, DIRECTOR
G. E. BOYD, E. H. TAYLOR, ASSOCIATE DIRECTORS
M. T. KELLEY, ASSISTANT DIRECTOR

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CHEMISTRY DIVISION
QUARTERLY PROGRESS REPORT
for Period Ending June 30, 1949

J. A. Swartout, Director
G. E. Boyd, E. H. Taylor, Associate Directors
M. T. Kelley, Assistant Director

Date Issued: SEP 1 4 1949

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ORNL 286
Progress Report

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ABSTRACT

Introduction and Summary. The program of the Chemistry Division is divided into two efforts of approximately equal weight with respect to number of personnel, (1) chemical research and (2) analytical service for the Laboratory. The various research problems fall into the following classifications:

1. Chemical separations process, for
    a. Isolation and recovery of fissionable material,
    b. Production of radioisotopes,
    c. Military applications;
2. Reactor development;
3. Fundamental research.

Nuclear and Chemical Properties of the Heavy Elements. By the use of anion-exchangers, Th has been separated cleanly from Pa and U, and Pa has been separated from U, relying upon differential adsorption from, and elution by, HCl solutions of various concentrations. From the results of studies of the behavior of Cb, Ta and Pa in HCl-HF mixtures on anion-exchanger beds, it is evident that these elements can be separated by anion-exchange techniques. Likewise, separation of Zr from Cb and an appreciable separation of Hf from Zr have been achieved. Because of the potentialities of this method, particularly for the isolation of Pa^{233} and U^{233} from breeder reactors and for the preparation of pure Zr, emphasis of these studies will continue.

In the investigation of the system U(IV)-U(V)-U(VI) in aqueous solution, diffusion current constants of U(VI)-chloride solutions have been determined for various conditions of concentration, acidity and temperature, as part of an investigation of the applicability of the polarograph to the determination of U(VI). The equilibrium constant for the disproportionation of U(V) has been measured in chloride solutions of varying acidity and concentration. Measurements of the rate of the reaction of U(IV) with U(VI) are in fair agreement with values calculated from the previously measured rate for the reverse reaction and the equilibrium constant.

The program to clarify the phase relationships of potential fuel and breeder solutions for a homogeneous reactor was continued with emphasis on the UO_2SO_4-H_2O system. A higher concentration of fissionable material and a lower acidity with consequent lower corrosiveness result from dissolution of UO_3 in

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the UO_2SO_4 solution. Four points were determined along the solubility curve of UO_3 in the system, UO_3-UO_2SO_4-H_2O at 25° C.

Nuclear and Chemical Properties of Elements in the Fission Product Region. As a by-product of the preparation of large amounts of Xe^{135} for measurement of its cross section as a function of neutron energy, sufficient quantities of Cs^{135} have become available to permit measurement of the half-life, $3.0 \pm 0.3 \times 10^6$ y.

Preliminary characterization of I^{129} indicates a half-life of $2\text{-}4 \times 10^7$ y, radiations consisting of 100-130 kev electrons and a gamma or X ray of 28-32 kev, and a thermal neutron absorption cross section of about 15 barns.

Results of a search for 6.7 h Mo^{93} formed by neutron irradiation have indicated that if it exists, the cross section for its formation from Mo^{92} by neutron capture is less than 10 microbarns.

As a result of neutron bombardments of isotopically enriched Sn isotopes, the 30-33 m activity previously observed in Sn has been assigned to mass 113.

In the systematic investigation of hard gamma emitters among the fission products, I^{134} has been shown to have a half-life of 50.8 ± 1.4 m, a hard β-ray of 3.5-4.2 Mev and a softer β-ray of 1.5-1.75 Mev, in addition to the hard gamma (above 2.2 Mev) previously reported. On the basis of a comparison of the absorption coefficient of the hard gamma of I^{135} with absorption coefficients measured for gammas of known energy in the absorber rack placed over the heavy water, photoneutron fission chamber, the energy of the I^{135} gamma has been determined to be 2.4 Mev.

The intricate remotely-controlled apparatus installed in the hot-laboratory specifically for the Xe cross section problem has proved to have wide application. In addition to the original purpose it has served to prepare large amounts of fission iodine or decay products of the iodine for (1) the characterization of Cs^{135}, (2) the study of hard gamma emitters, (3) measurement of nuclear properties by microwave techniques, and (4) a recently initiated co-operative effort with the Y-12 Laboratory to measure the nuclear spins of the Xe isotopes by spectrographic methods.

The measurement of the absorption spectra of the chloride and nitrate of element 61 in aqueous solution has been completed. The absorption bands are in the same position and of the same magnitude for the two salts, resemble those of neodymium in intensity and number but are distinctly separable by at least 8 $m\mu$.

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General Nuclear Chemistry. In the program to clarify the nuclear chemistry of the rare earths, the beta ray spectra of Y^{90} and Y^{91}, the beta ray energy of Ho^{166}, the nature of the 12 m activity of Nd, and the origin of the Ho activity in irradiated Dy have been established.

The counting yields of a number of low energy beta emitters have been determined by comparison of the counting rates observed in a beta proportional counter with the absolute disintegration rates.

Radio-Organic Chemistry. New methods have been developed for the preparation of formaldehyde - C^{14} and acetic acid - 2 - C^{14}. The stockpiling of C^{14} labeled compounds for distribution, as well as for use in the research program, continued with addition of formaldehyde - C^{14}, carboxyl - C^{14} sodium acetate, sodium formate - C^{14}, and methanol - C^{14}. As a result of a recent move to new laboratories in a remodeled building in the Y-12 Area, space and facilities are available to permit initiation of production of compounds for which procedures were developed during the past year.

Chemistry of Separation Processes. In preparation for a study of the fundamental properties of the metallic fluorides of concern to separation problems, a laboratory is being equipped with apparatus essential for research with fluoride systems.

In connection with the proposed TTA-solvent extraction method for separating Hf from Zr, the extraction of Hf from HCl and HNO_3 solutions is being investigated. It has been found that, (1) the extractable species are not identical from the two media, (2) more than one species are extractable from HCl solution, (3) the acid dependence over the range, 0.5-3.5 M, is about 3 in both cases and (4) the TTA dependence is 3.0 in the case of HCl and 3.7 in the case of HNO_3 solutions.

The absorption process, utilizing silica gel, for the extraction of fission Zr and Cb from the waste raffinate of the first cycle of the Redox Process continues to appear promising. It is anticipated that testing of the process on a full Hanford activity level in apparatus now being installed in the hot-laboratory will be completed by September, 1949. In addition to research to clarify the effects of process variables, methods for concentrating the product after elution from the adsorbent and, also, alternative methods for extraction from both the Redox raffinate and original dissolver solutions are being developed.

In a co-operative program with the Technical and Operation Divisions, to improve the RaLa process, details of the Chemistry are being studied includ-

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ing (1) the distribution of fission products in the lead sulfate precipitation and carbonate metathesis steps, and (2) methods for purification of the electrolyzed product.

In connection with a study of the separation of anions by ion-exchange, Cl^-, Br^- and I^- have been separated by elution with Na_2CO_3 solution from a column of anion-exchanger.

Physical Chemistry and Chemical Physics. Work on low-temperature spectroscopy of crystals and solutions of heavy elements and rare earths has been concluded and the principal results will appear shortly. A summary of solvents fluid at -196° C appears in this report.

The first results of the co-operative program with Duke University have been the determination for I^{129} of the nuclear spin, nuclear magnetic moment and ratio of nuclear quadrupole moment to that of I^{127}. These are, respectively: 7/2, 2.74 ± 0.14 nuclear magnetons and 0.7353.

A calorimeter has been designed and built to operate isothermally at the temperature of liquid helium. It is intended for the measurement of easily absorbable nuclear radiations (beta particles).

Radiation Chemistry. The 2 Mev Van de Graaff generator has been assembled by members of the Physics, Instrument and Chemistry Divisions and will be in operation after drying out.

An apparatus has been built for measuring continuously the pressure (to 5000 lb/in^2) over solutions in the pile.

Instruments. Further study has been made of the beta proportional counter, directed toward establishment of optimum gas composition and improvement in the associated amplifier.

A coincidence circuit has been developed and built for use with beta proportional counters.

Analytical Chemistry. New analytical procedures which have been developed to meet the requirements of pilot-plant processes include (1) a micro-volumetric method for uranium using an automatic titrator, (2) a polarographic method for routine uranium analyses, and (3) a polarographic method for determination of micro amounts of iodine.

Research on radiochemical analytical procedures which are required for radioisotope production and for pilot-plant processes is necessarily broad in scope. Included during this period were investigations of (1) the decay scheme of Ba^{140}, (2) the decay and radiations of Cl^{38}, (3) the standardization of

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counting techniques entailing the accurate calibration of routinely used counters, measurement of gamma counting efficiency, and preparation of alpha counting standards, (4) measurement of activation cross sections, and the performance of activation analyses, and (5) development and improvement in analytical methods for radiozirconium, plutonium, the transuranic elements and rare gas activities.

Improvements have also been effected in the application of spectrochemical methods to the analysis of process solutions.

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NUCLEAR AND CHEMICAL PROPERTIES OF THE HEAVY ELEMENTS

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I. SOLUTION CHEMISTRY

BEHAVIOR OF NEGATIVELY CHARGED METAL COMPLEXES ON ANION EXCHANGE RESINS

K. A. Kraus and G. E. Moore

1. *Introduction.* In the previous quarterly report some initial anion exchange studies, pertaining to Pa(V), were described using the anion exchange resin Dowex A-1. These studies have been continued and extended to a number of other metal ions. In this report some results, partly preliminary, on the behavior of Cb, Ta, Pa, Zr, Hf, Th, and Fe in HCl and HCl-HF solutions will be given.

2. *Experimental Procedure.* (a) **Resin:** The resin used was Dowex A-1, a quaternary amine polymer. Mesh size was 200-230 as obtained by wet screening. (b) **Columns and column operation:** The adsorption columns were constructed of "Transflex" tubing with cross-sectional area 0.0226 cm^2, as determined by weighing a column of water of known length. The eluent in most cases, particularly for HF solution, was contained in 50 ml "Bakelite" burettes, and the height of the liquid column occasionally adjusted to maintain approximately the desired flow rate. In general, it was not attempted to maintain exactly constant flow rates. Instead, the volume of eluent which had passed was determined from the burette readings at frequent intervals.

In most cases the ion (or ions) under investigation were added in a small volume to a column which had previously been equilibrated with the desired acid mixture. In general, it was attempted to have the added solution of approximately the same composition as the solution in the column and the eluent. In a few cases the additions were carried out with the column liquid at a composition to cause strong adsorption, and the material was then eluted by changing the composition of the eluent.

(c) **Tracers:** All experiments were carried out with radioisotopes of the various elements to permit the use of radiochemical techniques for analysis and to avoid complications in the analysis of the column data which might arise

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from non-linear adsorption isotherms which could be expected at high concentrations. In some experiments where the radioisotope was not carrier-free and of relatively low specific activity, such difficulties were encountered.

(1) **Columbium**: All experiments were carried out with Cb^{95} [β-emitter, $T_{\frac{1}{2}}$ = 35 d(1)] which was kindly furnished us by W. H. Baldwin and co-workers who isolated it from fission product mixtures.

(2) **Tantalum**: The experiments were carried out with pile-activated tantalum which contains Ta^{182} [β-emitter, $T_{\frac{1}{2}}$ = 117 d(1)]. The activation was carried out with tantalum metal of high purity. It was dissolved in an HNO_3-HF mixture (5 *M* HNO_3, 18 *M* HF).

(3) **Protactinium**: All experiments were carried out with Pa^{233} [β-emitter, $T_{\frac{1}{2}}$ = 27.4 d(1)] prepared by neutron activation of thorium metal. Isolation of the tracer was achieved in one case by solvent extraction from an HCl solution of the metal as described in ORNL 330, and in another case purification was achieved by anion-exchange as described in Section 3.

(4) **Zirconium**: The earlier experiments were carried out with Zr^{97} [β-emitter, $T_{\frac{1}{2}}$ = 17.0 h(1)] prepared by short neutron irradiation of Zr metal of high purity. The metal was dissolved in an HCl-HF mixture. In view of the short half-life of this isotope the later experiments were carried out with Zr^{95} [β-emitter, $T_{\frac{1}{2}}$ = 65 d(1)] which was kindly furnished us by W. H. Baldwin and co-workers who isolated it from fission product mixtures.

(5) **Hafnium**: All experiments were carried out with Hf^{181} [β-emitter, $T_{\frac{1}{2}}$ = 46 d(1)] prepared by neutron irradiation of spectrochemically pure $HfOCl_2$. We are indebted to Mr. J. P. McBride for a sample of this irradiated hafnium oxychloride. The material was dissolved in a mixture of 2 *M* HCl and 2 *M* HF.

(6) **Iron**: The experiments were carried out with (primarily) Fe^{59} [β-emitter, $T_{\frac{1}{2}}$ = 46 d]. We are indebted to the Operations Division for the sample of tracer.

(7) **Uranium**: The experiments were carried out with U^{233} [α-emitter, $T_{\frac{1}{2}}$ = 1.6×10^5 y. (1)] which was kindly furnished us by D. C. Overholt of the Technical Division.

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(1) Information from "Table of Isotopes", by G. T. Seaborg and I. Perlman, Rev. Modern Phys. 20, 585 (1948).

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(d) Analytical procedures: The data were collected using essentially two methods of analysis. Using a continuous recording system the activity of the effluent of the column was monitored. Positive characterization of the bands was effected through radiochemical assays. In addition, direct scanning of the column was used to locate the bands and determine the rate with which they moved down the column on elution.

(1) Continuous recording of activity of effluent: The activity of the effluent was recorded on a Brown Electronik strip-chart recorder by passing the solutions through a thin-window flow-cell which was placed near a G-M tube. The electronic circuit contained an integrating device and the recorder was of the logarithmic type.(2) The equipment was similar to that developed at ORNL and described by Ketelle and Boyd.(3)

(2) **Direct scanning of column:** In order to obtain more directly the elution rate of the element under a specified set of conditions, the position of the adsorption bands was obtained through scanning with a G-M tube. For this purpose a G-M tube was mounted on a cathetometer stand. Collimation was achieved with a $\frac{1}{4}$ inch lead shield containing a narrow slot, which was placed in front of the G-M tube. The tube was connected to a standard G-M scaler circuit. The shape and position of the bands were obtained from the counting rate as a function of column distance. Some typical results for Cb(V) can be seen in Fig. 1.

The determination of elution rates by this method offers a number of advantages over the method of continuous monitoring of the effluent. If a previously identified, pure activity is used, the elution rate can be determined rapidly and with relatively high precision, since the bands, in general, are quite sharp, particularly if they move slowly. In the latter case a precision of better than 10% appears to be obtainable with the band moving only through less than 2 cm of column. Thus, considerable savings in time can be achieved particularly for substances whose elution rates are unknown at the beginning of the experiment and for which it is therefore difficult to predict

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(2) The electrical circuit was prepared for us by F. W. Manning of the Instrument Division of ORNL.

(3) B. H. Ketelle and G. E. Boyd, J. Am. Chem. Soc. 69, 2800 (1947).

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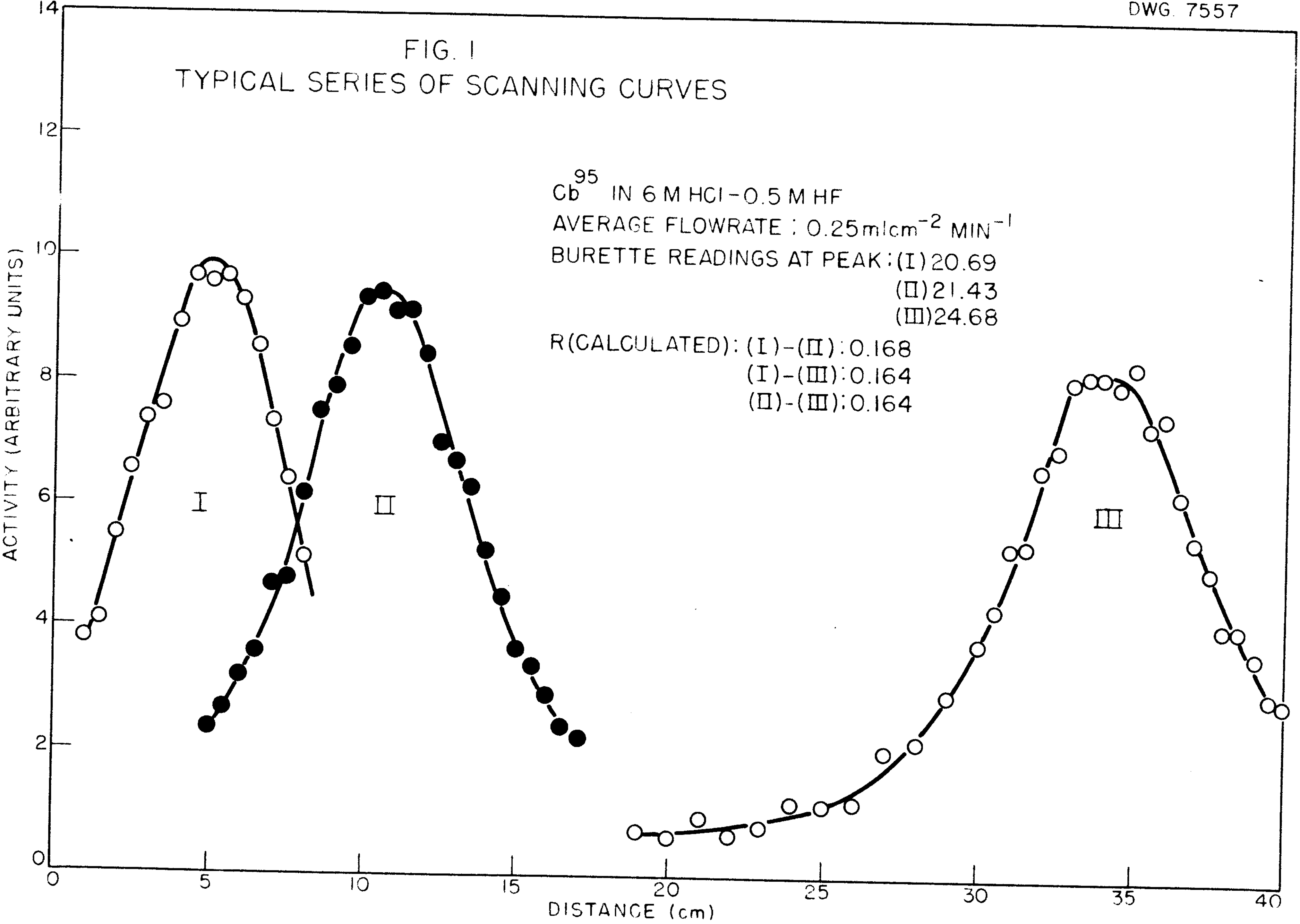

FIG. I
TYPICAL SERIES OF SCANNING CURVES

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what size column would give sufficient precision for the experiments. Using the scanning technique it is thus feasible to select a column of standard length, long enough to permit satisfactory measurements for rapidly moving bands and still complete experiments with slowly moving bands in a reasonable period of time. In addition, the method appears to furnish a promising check of adsorption theories, particularly in so far as changes of band characteristics with elution rate or distance are concerned. Unfortunately, however, the method is somewhat limited in its application since alpha-emitters cannot be used and since the wall-thickness of the column places serious restrictions on the use of weak beta emitters.

3. Separation of Th(IV), Pa(V) and U(VI). The results pertaining to this separation in HCl solutions have been reported in ORNL 330 (April, 1949). It may be repeated here that this separation can be carried out in strong HCl. The separation of Th from Pa and U is particularly effective since under conditions where Th rapidly breaks through the column, neither Pa nor U move appreciably. Separation of Pa and U was effected through selective elution with HCl.

Since this report was issued, a sample of Pa^{233} tracer was completely separated from ca. 1 g of pile-bombarded thorium using a 6 cm column (0.031 cm^2 cross section) by adsorbing the Pa in 9 *M* HCl, washing with 9 *M* HCl and eluting with 3 *M* HCl. Since under these conditions and after prolonged washing the Pa was still in a narrow band, even shorter columns could have been used satisfactorily.

Using qualitative considerations the formulas $PaCl_8^{\equiv}$ (or a basic chloride complex of charge -3) and $UO_2Cl_5^{\equiv}$ (or $UO_2Cl_6^{-4}$) were tentatively suggested for the adsorbed negative complexes.

4. Separation of Pa(V) and Fe (III). This separation was found to be surprisingly difficult in HCl solutions, although only one set of conditions has been investigated at this time.

The separation was attempted in 3.8 *M* HCl, using a 14.5 cm column (0.031 cm^2 cross section), and the results are shown in Fig. 2.

It can be seen that Pa(V) is eluted first under these conditions. The elution band of Fe(III) in this experiment was highly unsymmetrical showing a very prolonged "tail". This distortion is believed to be, at least in part, due to the fact that the amount of Fe(III) used was very large for the small

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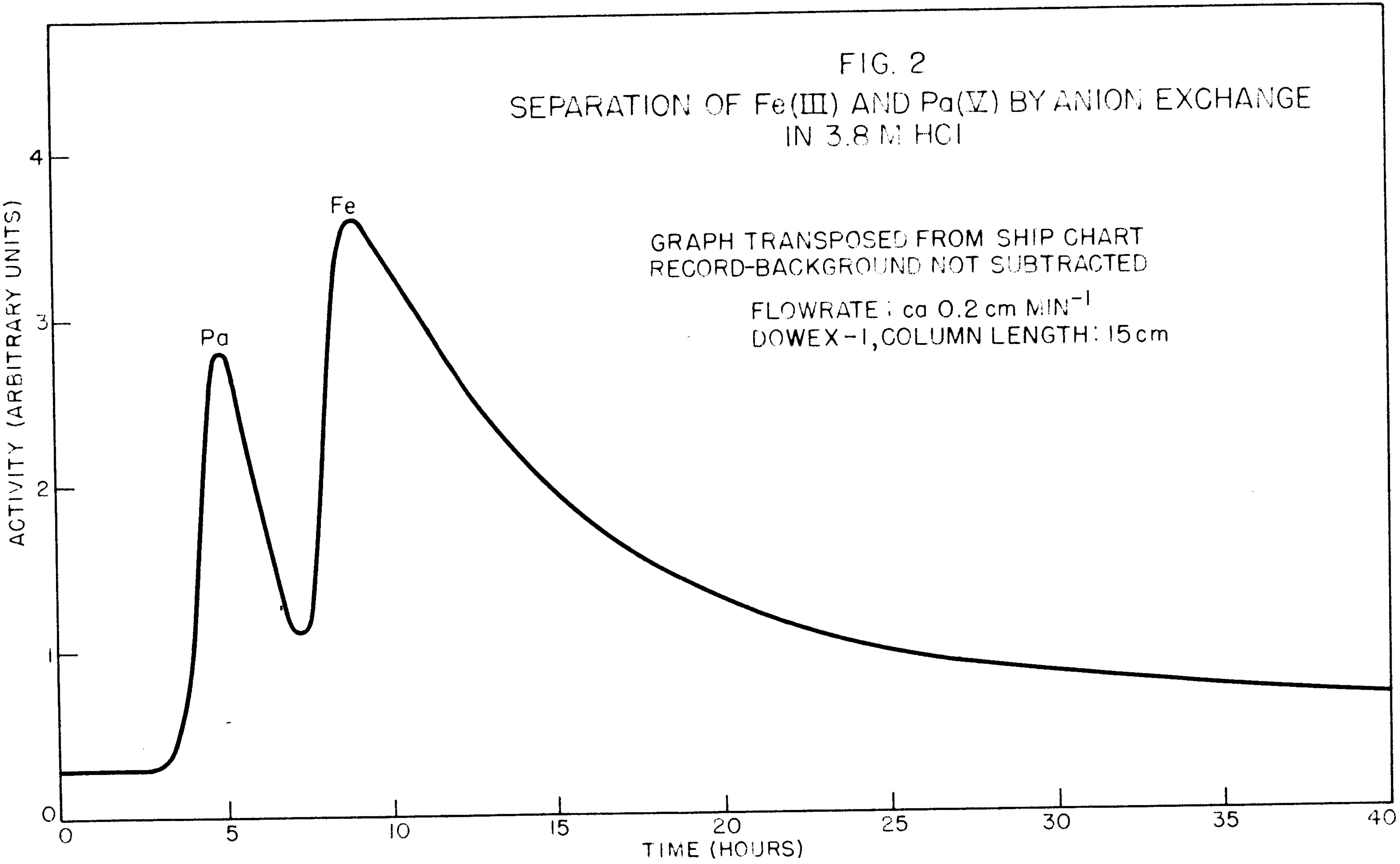

FIG. 2
SEPARATION OF Fe(III) AND Pa(V) BY ANION EXCHANGE IN 3.8 M HCl

GRAPH TRANSPOSED FROM SHIP CHART RECORD-BACKGROUND NOT SUBTRACTED

FLOWRATE: ca 0.2 cm MIN^{-1}
DOWEX-1, COLUMN LENGTH: 15 cm

[redacted]

diameter column used, so that the column was saturated with respect to **Fe** (III) over an appreciable fraction of its length. This saturation also probably caused undue acceleration of the front edge of the band. It is therefore believed that operation of the column under more ideal conditions would greatly improve the separation.

5. *Columbium in HF-HCl Media.* (1) **Definition of elution constant:** The experiments will be described in terms of a function which represents the rate of travel of the adsorption band along the column and which we shall call the elution constant R. R is defined by the equation.

$$R = \frac{d}{V/A}, \tag{1}$$

where d is the measured distance (in cm) which the maximum of a band has traveled after a throughput of V cm^3 of eluent in a column of cross-sectional area, A cm^2. Thus V/A represents the throughput normalized to unit cross-sectional area. R should be independent of column size, though it would not be expected to be independent of the mesh-size of the resin since the void space in the column would change with it.

The velocity with which an adsorption band moves through the adsorbent bed under equilibrium conditions has been given by Ketelle and Boyd(3) as

$$\frac{d}{t} = \frac{v}{1 + \delta/f} \tag{2}$$

where t is the time, v the linear flow-rate of the solution, δ the bed distribution coefficient and f the fractional void space.

Defining

$$K_d = \frac{C_s}{C_r} \tag{3}$$

where C_s and C_r are the concentrations of the material in question in the

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solution and resin respectively [e.g., in the units (moles/cc of solution) and (moles/g oven-dried resin)]. The bed distribution coefficient δ can be expressed as (3)

$$\delta = \frac{\rho}{K_d} \tag{4}$$

where ρ is the bed density (g oven-dried resin/cc bed).

It can readily be shown that d/tv is equal to Rf, since v = v'/fa (where v' is the volume of eluent entering the column per unit time) and since tv' = V. Thus

$$\frac{d}{tv} = \frac{dfA}{tv'} = \frac{dfA}{V} = Rf \tag{5}$$

Combining equations (2) and (5) it is found that

$$R = \frac{1}{f + \delta} \tag{6}$$

For values of $\delta >> f$ equation (6) reduces to

$$R = \frac{1}{\delta} = \frac{1}{\rho} K_d \tag{7}$$

(b) **Elution constant of Cb(V):** The elution constant R of Cb(V) was determined for two series of Hf-HCl solutions. In series (a) the concentration of HF was maintained at 0.5 *M* and the concentration of HCl varied (from 0.2 to 9.0 *M*) and in series (b) the concentration of HCl was maintained at 9.0 *M* and the concentration of HF varied (from 0.004 to 0.5 *M*).

The data are summarized in Tables I and II and Figs. 3 and 4.

It can be seen from Table I that the elution constant of Cb in 0.5 *M* HF first increases rapidly with HCl concentration, passes through a maximum near 3 *M* HCl and decreases sharply above 6 *M* HCl. In addition it can be seen from Fig. 3 that the increase in R below 3 *M* HCl is approximately linear and of approximately unit slope. Since according to equation (7) the elution constant is directly proportional to the distribution coefficient K_d, the data imply a

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TABLE I

Elution constant of Cb as a function of HCl concentration in 0.5 M HF

HCl MOLARITY	R	METHOD[a]	AVERAGE FLOW-RATE (ml min^{-1} cm^{-2})
0.2	0.013	S	0.15
0.5	0.050[b]	M	0.18
	0.042[c]	M	0.19
1.0	0.073	M	0.29
3.0	0.187	M	0.26
	0.174	S	
6.0	0.144	M	0.25
	0.159	S	
9.0	0.071	M	0.18
	0.076	S	
	0.074	S	0.18

(a) "S" and "M" indicate whether a scanning or monitoring method was used. The data obtained by monitoring are corrected for an estimated volume of connecting tubing. Because of uncertainties in this estimate they are considered to be somewhat less accurate than the values obtained through scanning.

(b) Calculated from a run of Hf-Cb mixture where only a single elution band was observed. Since no attempt was made to determine relative enrichment within the band, the value of R is only approximate.

(c) Zr-Cb-Hf band as in (b).

TABLE II

Elution constant of Cb as a function of HF concentration in 9.0 M HCl

HF MOLARITY	R	METHOD	AVERAGE FLOW-RATE (ml min^{-1} cm^{-2})
0.5	0.071	M	0.18
	0.076	S	
	0.074	S	0.18
0.1	0.26	S	0.19
0.02	0.019	S	0.19
0.004	0.0033	S	0.18

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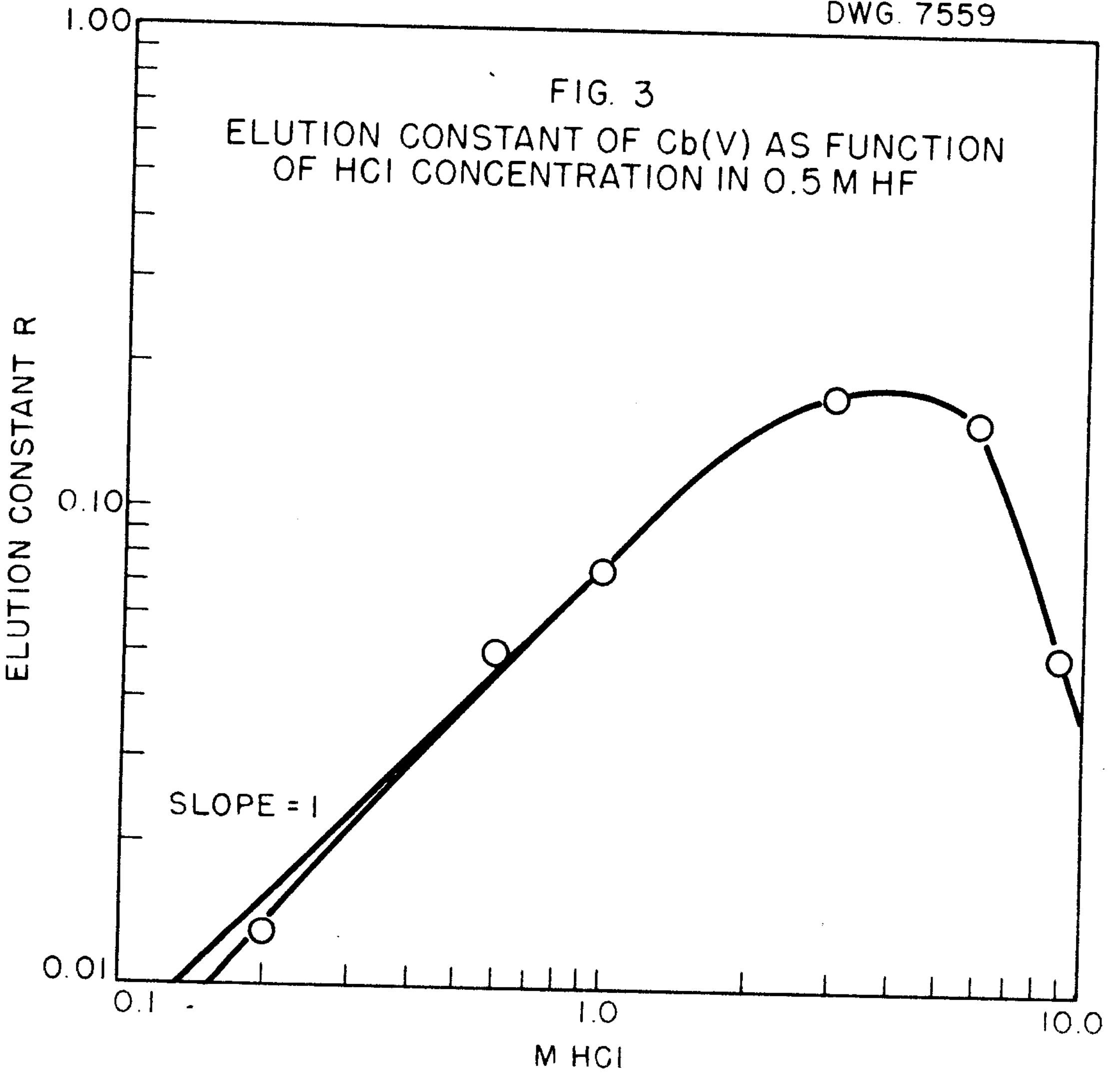

FIG. 3
ELUTION CONSTANT OF Cb(V) AS FUNCTION OF HCl CONCENTRATION IN 0.5 M HF

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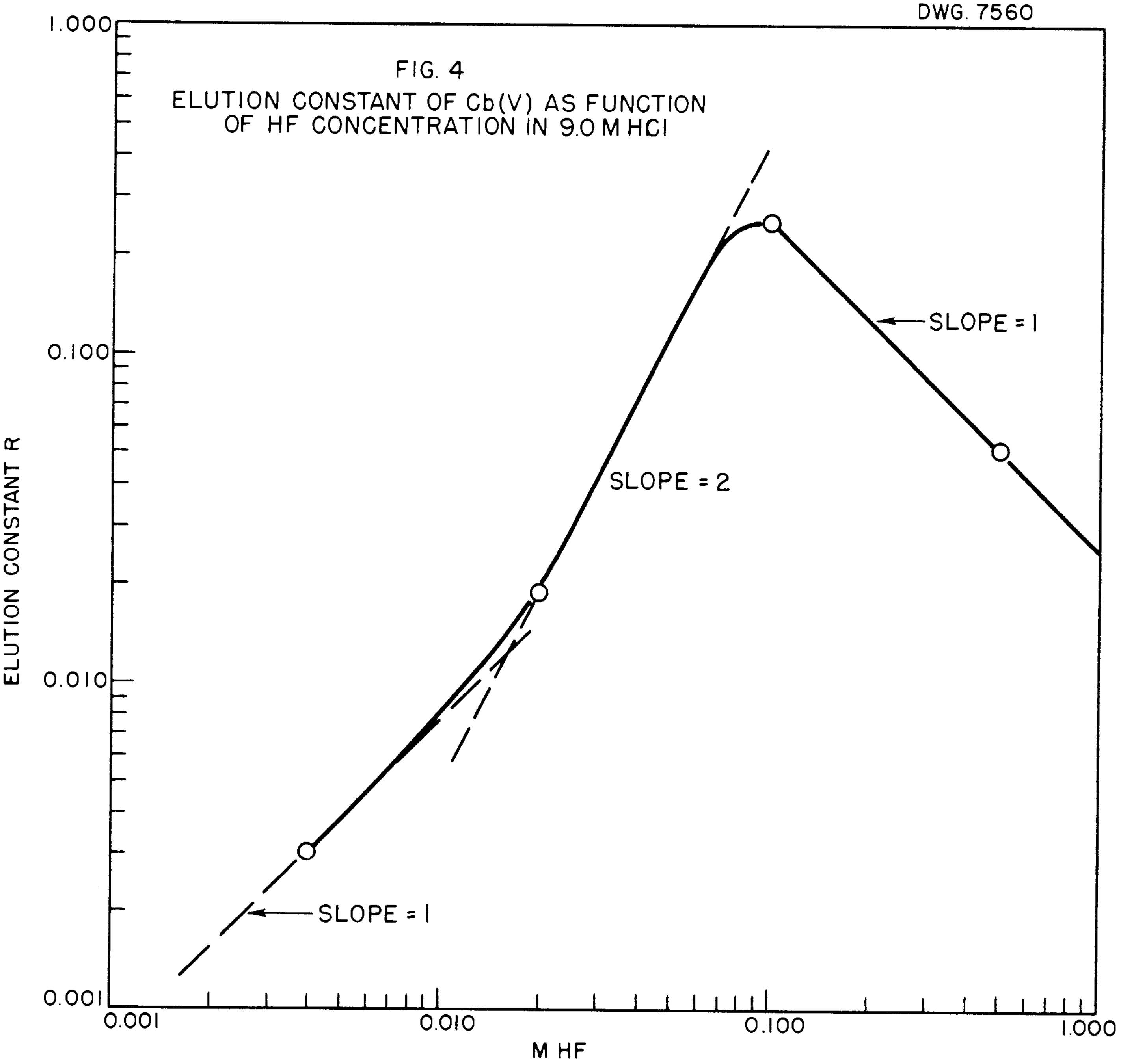

FIG. 4
ELUTION CONSTANT OF Cb(V) AS FUNCTION OF HF CONCENTRATION IN 9.0 M HCl

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linear decrease of K_d with increasing HCl concentration. This rate of change of K_d with HCl concentration is surprisingly small since it represents the combined effect of the increasing elution power of the solvent with increasing Cl^- concentration and of the change in concentration of the adsorbable species due to the concomitant decrease in fluoride (F^-) concentration (through the equilibrium $HF + H_2O \rightleftarrows H_3O^+ + F^-$).

To illustrate the solvent effect alone, one can consider the simple case where the metal complex (A^{-n}) is completely formed and is distributed between the solvent and resin according to the equilibrium

$$n\ RCl + A^{-n} \rightleftarrows R_nA + n\ Cl^- \tag{8}$$

for which the mass action expression

$$\frac{(R_nA)\,(Cl^-)^n}{(RCl)^n\,(A^{-n})} = K_d' \tag{9}$$

applies. For tracer solutions the simplification $K_d'\ (RCl)^n = K_d^*$ can be made and hence

$$K_d \ = \ \alpha[Cl^-]^n, \tag{10}$$

where $\alpha = 1/K_d^*$ is a proportionality constant. Thus, barring an increase in average negative charge of the complexes with increasing HCl concentration the observed unit slope of the plot of log K_d *vs* log [HCl] implies that the adsorbed ion has and maintains a charge of minus one. This suggests that the sum of F^- and Cl^- ions coordinated to the Cb(V) is six (i.e., CbX_6^-) or that the adsorbed species is an acid with one or more protons (e.g., $HCbX_7^-$, $H_2CbX_8^-$, where X represents either F^- or Cl^-). Unfortunately, however, an increase in charge with increasing HCl concentration cannot be entirely eliminated (though it is improbable as discussed below) in spite of the fact that a decomposition of the fluoride complex with increasing HCl concentration would be expected. For each fluoride ion lost from the complex, more than one chloride ion could become attached or the replacement of a coordinated fluoride ion by a chloride ion might be accompanied by the loss of a proton from an acid complex of the type described or through a hydrolytic reaction.

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In this connection it is of interest that on going to very high HCl concentrations, R decreases, and in this range a minimum increase of two in negative charge on the complex seems to be occurring.

The results for HF solutions of varying strength (and constant 9.0 *M* HCl), as shown in Fig. 4, are equally surprising. Here the elution power of the solvent remains constant and the concentration of the complexing agents (HF) changes. Following the curve to lower HF concentrations it appears to be composed of a linear branch (A) of unit slope where R increases with decreasing HF concentration. The curve then passes through a maximum (near 0.1 *M* HF). The maximum is followed by a branch (B) where R rapidly decreases with decreasing HF concentration. The curve does not have a constant slope, but it might be composed (in the limits) of two lines of slope one and two as indicated in Fig. 4.

Branch "A" appears to be "normal", i.e., the average negative change of the complexes decreases with decreasing concentration of the complexing agent. However, the behavior in branch "B" is surprising since here the average negative change of the complexes increases with decreasing concentration of the complexing agent. This implies either that fluoride ions are replaced by more than an equal number of chloride ions or that some of the fluoride ions which are replaced by chloride ions also carry protons away with them. Again, as above, this could occur because the complexes are complex acids or because complicating hydrolytic effects occur. The latter are hard to imagine however, in view of the already rather high negative change of the complexes which leaves little coordination space for waters of hydration which could undergo hydrolysis.

6. *Tantalum in HF-HCl Mixtures.* This study of tantalum has only recently been started and data are available only for a 4×10^{-3} *M* HF-9.0 *M* HCl solution. It was found that under these conditions tantalum moves extremely slowly, the elution constant R being less than 0.0001. This value is approximately a factor of 30 smaller than the corresponding value of R for columbium (R = 0.0033) and approximately 900 times smaller than the corresponding value for protactinium (R = 0.09).

A study of R under other conditions is under way. However, it appears quite obvious that the separation of the triad, columbium, tantalum and protactinium, is quite feasible with anion-exchange resins.

7. *Protactinium in HF-HCl Mixtures.* For 0.5 *M* HF solutions the elution constant for Pa was found to increase rapidly with increasing HCl concentration

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as shown in Table III. The slope of the log R - log [HCl] curve appears to be between 2 and 3 at low HCl concentrations. In the mixture 0.5 *M* HF-9.0 *M* HCl, R is very large, and approaches the theoretical limit. In contrast to this, Pa was found to elute only very slowly in 9 *M* HCl (not containing HF).(4)

The correspondingly small value of R for 9.0 *M* HCl has now also been confirmed by the scanning method where $R \leqslant 0.0004$ was found.

At constant 9.0 *M* HCl, R decreases only slowly with decreasing HF concentration down to ca. 0.01 *M* HF. Below this HF concentration, R appears to decrease rapidly, possibly with the square of the HF concentration although the data are too limited to establish the slope conclusively. At the rather low HF concentration of 0.004 *M* in 9 *M* HCl (where the concentration of F^- is probably considerably less than 10^{-6} *M*) R is still at least 200 times larger than in pure HCl.

This very large influence of a small amount of HF on the elution behavior of Pa in 9.0 *M* HCl is very perplexing, particularly since the HF causes an *increase* in the elution constant (i.e., a decrease in average charge). As discussed earlier the reverse might be expected since HF is the stronger complexing agent. Since a similar effect was found for Cb and Zr, however, it appears that this is a reasonably general phenomenon.

In order to investigate if this effect is due to a non-reversibility phenomenon, Pa was put onto a column which had previously been equilibrated with 9.0 *M* HCl. After sufficient column volumes had been passed through to prove that adsorption was very strong and $r \leq 0.0004$, elution with a mixture of 9.0 *M* HCl-0.004 *M* HF was started. The Pa under these conditions showed $R = 0.087$, in close agreement with the value $R = 0.095$, which was found when the Pa was both adsorbed from and eluted with the HCl-HF mixture. This experiment thus gave no indication of irreversible complex formation.

It is also unlikely that the phenomenon is due to hydrolytic colloid formation in the HCl solutions since it had previously been shown(4) that Pa elutes readily if it is adsorbed from 9 *M* HCl and eluted with HCl of lower concentration, where colloid formation would be expected to be more important.

8. Zirconium in HF-HCl Mixtures. The elution constant of Zr(IV) as a function of HCl concentration (at 0.5 *M* HF) are shown in Table IV and Fig. 5.

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(4) K. A. Kraus, G. E. Moore, ORNL 329, April 1949.

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TABLE III

Elution constant of Pa in HF-HCl mixtures

(Average flow rate 0.2-0.3 ml min^{-1} cm^{-2})

HF MOLARITY	HCl MOLARITY	R	METHOD
0.5	0.2	0.042	S
0.5	0.5	0.37	M
0.5	9.0	1.5	S
0.1	9.0	0.9	S
0.02	9.0	0.8	S
0.004	9.0	0.085(a) 0.093(b)	S S
0.0	9.0	≤ 0.0004	S

(a) Adsorbed from 9 *M* HCl-eluted in the HCl-HF mixture.

(b) Adsorbed from and eluted with HCl-HF mixture.

TABLE IV

Elution constant of zirconium as a function of HCl concentration in 0.5 M HF

(Average flow rate 0.2-0.3 ml min^{-1} cm^{-2})

HCl MOLARITY	R	METHOD
0.5	0.047 0.042	M M
1.0	0.17	M
3.0	0.96	M
6.0	0.6	M
9.0	2-2.8	M

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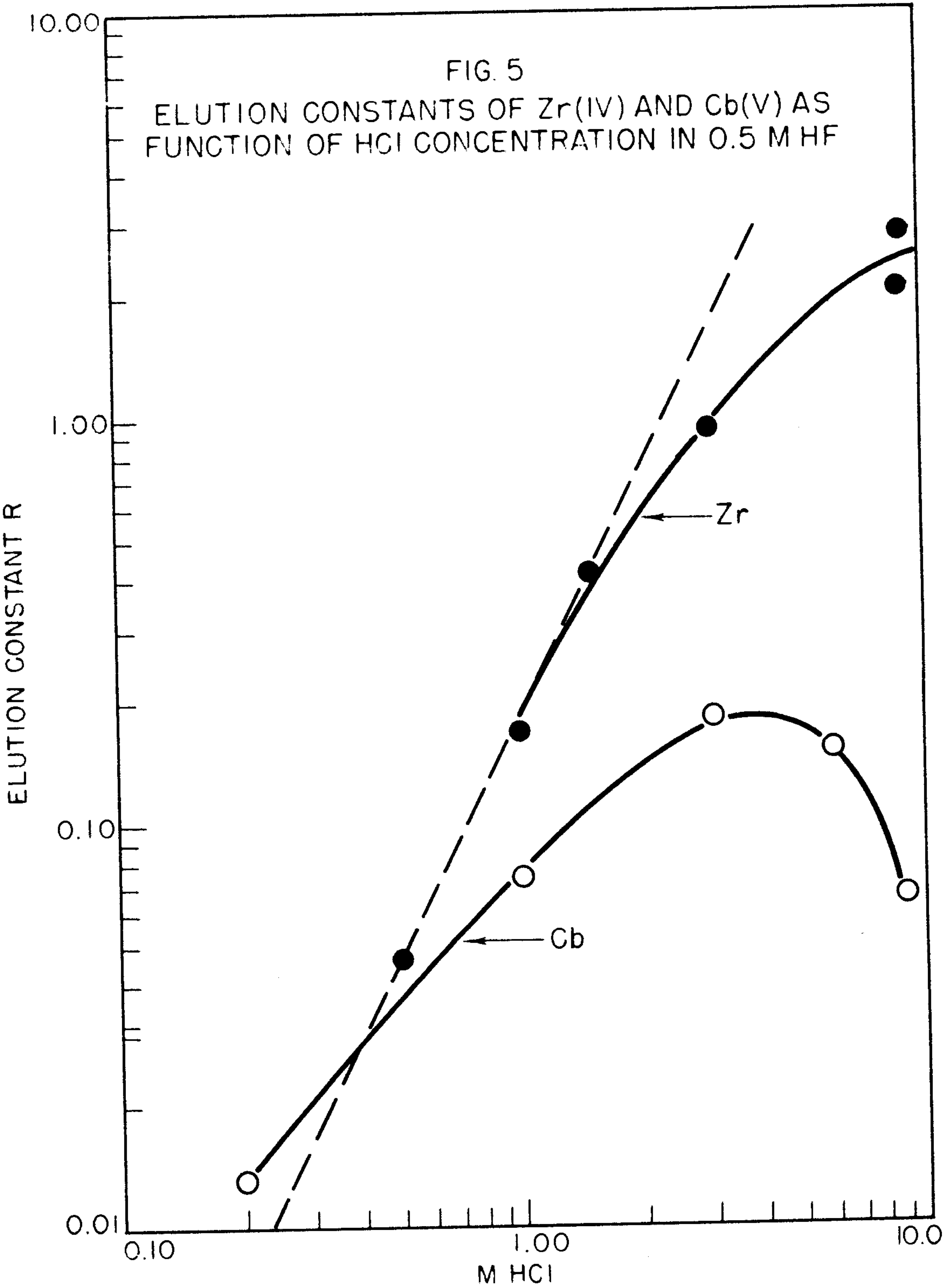

FIG. 5
ELUTION CONSTANTS OF Zr(IV) AND Cb(V) AS FUNCTION OF HCl CONCENTRATION IN 0.5 M HF

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It may be noticed that the elution constant increases rapidly with increasing HCl concentration except for the point at 6.0 *M* HCl, which may be in error. It should be pointed out that the errors in estimating R become very large when R is of the order of unity and thus approaches its theoretical limit, which is probably of the order of 3 if the fractional void space is 0.3.

When R is large, errors result from the following causes: (1) the distances travelled by the band per minute is so large, as to almost preclude its measurement by scanning. (2) If the tracer is added from a solution which is not exactly of the same composition as the eluent, the measurement will be with respect to the solvent of the tracer rather than the eluent, since there is not sufficient time for replacement of the solvent by the eluent. (3) errors in the estimation of the volume of the connecting tubings can become serious if the monitoring method is used.

The plot of the data in Fig. 5 indicates that at low HCl concentration R varies with the square of the HCl concentration (slope = ca. 2).

9. Separation of Zirconium and Columbium. The essential features of this separation in HF-HCl mixtures can be deduced from the data given in Parts 5 and 8 and from Fig. 5. It may be noticed from this figure that the change in the specific elution constant of zirconium is different from that for columbium; the former changing with a second power HCl dependence and the latter with a first power dependence. The two curves cross at ca. 0.5 *M* HCl, and in this region separation is difficult if not impossible. It may be pointed out that by operating on either side of this cross-over point separations should be possible. At the high acid side Zr should elute first, and at the low acid side Cb should elute first.

Considering only the region on the high acid side of the cross-over point, it can be seen that, as both elution constants increase, their ratio becomes increasingly different from unity. Thus the separation of zirconium from columbium becomes increasingly effective as the time necessary for elution of the slowest component decreases.

Typical elution curves which illustrate the separation of Zr and Cb by this method and which were obtained through continuous monitoring of the effluent are shown in Fig. 6.

10. Attempted Separation of Zirconium and Hafnium. Only two experiments have been carried out at this time. In both experiments only a singly elution band was observed, although enrichment of Zr in the earlier fractions and Hf

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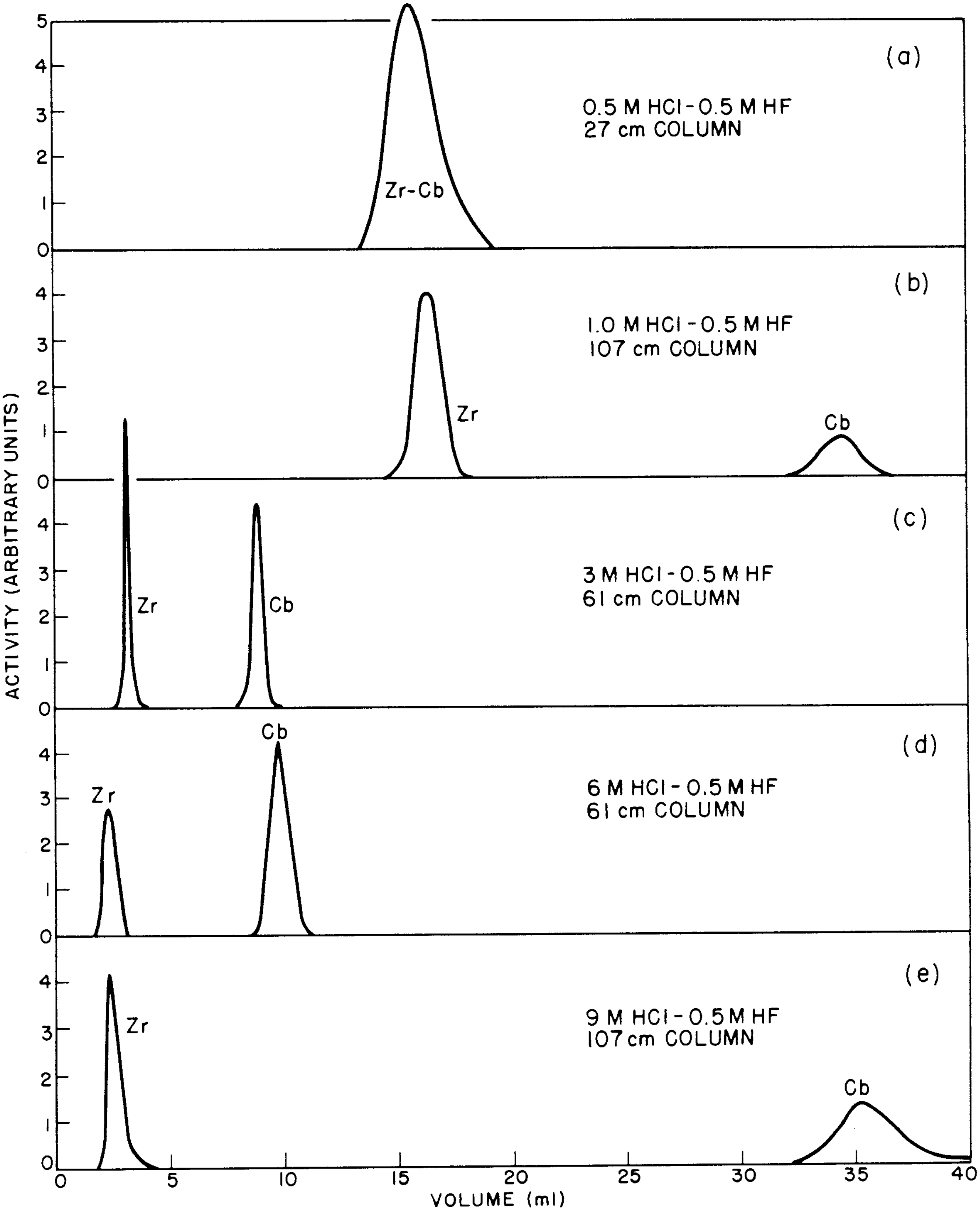
FIG. 6
SEPARATION OF Zr AND Cb WITH DOWEX-I ANION EXCHANGE COLUMNS

AVERAGE FLOWRATE: ca 0.3 ml/cm^2
CROSS-SECTION OF COLUMN: 0.0226 cm^2



[redacted]

in the later fractions was demonstrated for an experiment where the eluent was a mixture of 0.5 *M* HF and 1.0 *M* HCl and where the column length was 107 cm. In the second experiment, with 0.5 *M* HF-9.0 *M* HCl as eluent and a 107 cm column, the fractions were not analyzed for relative enrichment of the two components.

The fractions in the first experiment were analyzed for Hf through delayed coincidence counting, taking advantage of the fact that the daughter of Hf^{181} is the metastable Ta^{181} with 20 μ-sec half-life. We are indebted to Mr. F. K. McGowan of the Physics Division for the use of his delayed coincidence circuit and for his assistance in using the instrument.

The results of the experiment are summarized in Table V, where the specific coincidence rate is given for each fraction. Percent enrichment was not calculated for these fractions since in the cases of high specific coincidence rate the reproducibility appears to be sufficiently low to leave the specific coincidence rate of pure Hf^{181} in doubt. However, it is believed that fractions 10 through 13 were practically pure Hf^{181}. Similarly, of course, fractions 4 through 6 were better than 90% Zr^{95}.

The enrichment, which was demonstrated in this experiment was sufficiently high to suggest that Zr and Hf can be separated practically completely with a somewhat longer column (e.g., 3-5 m). Even with such very long columns the time necessary for a separation still would not be excessive in view of the large value of R of Zr and Hf which pertains under these conditions (R = ca. 0.17). However, it is believed that the separation can be improved by the use of different eluents, and corresponding experiments are now under way.

11. Separation of Pa from Cb, Ta and Zr. (a) **Erratum:** In the previous quarterly report a separation of Cb and Zr from Pa at high HCl concentration was erroneously reported. The tracer used at that time was not Zr^{95} and Cb^{95} as stated, but primarily a mixture of Ce^{144} and Pr^{144}. The separation of Pa reported is thus with reference to these elements.

(b) The separation of Pa from Ta was discussed briefly in Section 6. It is expected to be relatively simple in view of the large ratio of the elution constants of Pa and Ta.

(c) Since the elution constant for Pa is considerably larger than that for Cb under all conditions studied, their separation in HF-HCl mixtures should be quite effective. Unfortunately no cross-over point has been found as yet and thus separations at this time can only be achieved by eluting Pa first and retaining Cb.

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TABLE V

Separation of zirconium and hafnium in 1.0 M HCl-0.5 M HF

Column length-107 cm
Average flowrate-0.29 ml cm^{-2} min^{-1}

FRACTION	VOLUME ml	SPECIFIC ACTIVITY ($c/min/\lambda$)	COINCIDENCE RATE per 1000 counts/min.
4	2.20	16.8	0.08
5	0.40	290	0.7
6	0.32	580	1.9
7	0.27	616	6.6
8	0.31	609	12
9	0.29	510	17
10	0.31	321	22(a)
11	0.31	147	21
12	0.43	30.7	24
13	0.45	3.3	19(a)

(a) Radiochemical analyses by S. A. Reynolds did not show presence of Zr^{95}. Estimated purity of the Hf fractions according to S. A. Reynolds is better than 90%.

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In view of the differences in slope of the log R - log [HCl] curves (at 0.5 *M* HF), the separation of Pa and Cb is expected to go more rapidly and with greater efficiency with increasing HCl concentration. A number of separations have been carried out and Fig. 7 illustrates a typical one.

(d) As can be seen from Sections 7 and 8, the separation of Pa and Zr should be satisfactory in 0.5 *M* HF at most HCl concentrations. Under these conditions Pa would elute first. In Fig. 7 a typical separation is illustrated.

THE URANIUM (IV)-(V)-(VI) SYSTEM

F. Nelson and K. A. Kraus

1. *Introduction.* During the last quarter the investigation of the kinetics and of the equilibria in the U(IV)-(V)-(VI) system has been continued. Emphasis has been placed (a) on the determination of the diffusion constants of U(VI) under a variety of conditions which were of interest to the study in general, (b) on the equilibrium constants of the U(IV)-(V)-(VI) system in chloride and perchlorate solutions as a function of ionic strength and (c) on the rate constants, particularly the rate of reaction of

$$2U(V) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} U(IV) + U(VI) \quad . \qquad (1)$$

At the same time the problem of the hydrolysis of U(IV) has been re-opened since the acid constants at high ionic strength are still needed for the complete description of the system.

In general, the data are still fragmentary and will be reported here only in their general outline.

2. *Diffusion Current Constants of U(VI) Solutions.* To investigate the applicability of the polarographic analytical procedure for U(VI), the diffusion current constants of this ion in chloride solutions between 0.1 and 2 *M* ionic strength have been determined and some of the data are summarized in Table VI. Investigations of this type have previously been carried out by Kolthoff and Harris(5), and the results obtained here were in general agreement with theirs.

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(5) I. M. Kolthoff and W. E. Harris, J. Am. Chem. Soc, 68, 1175 (1946).

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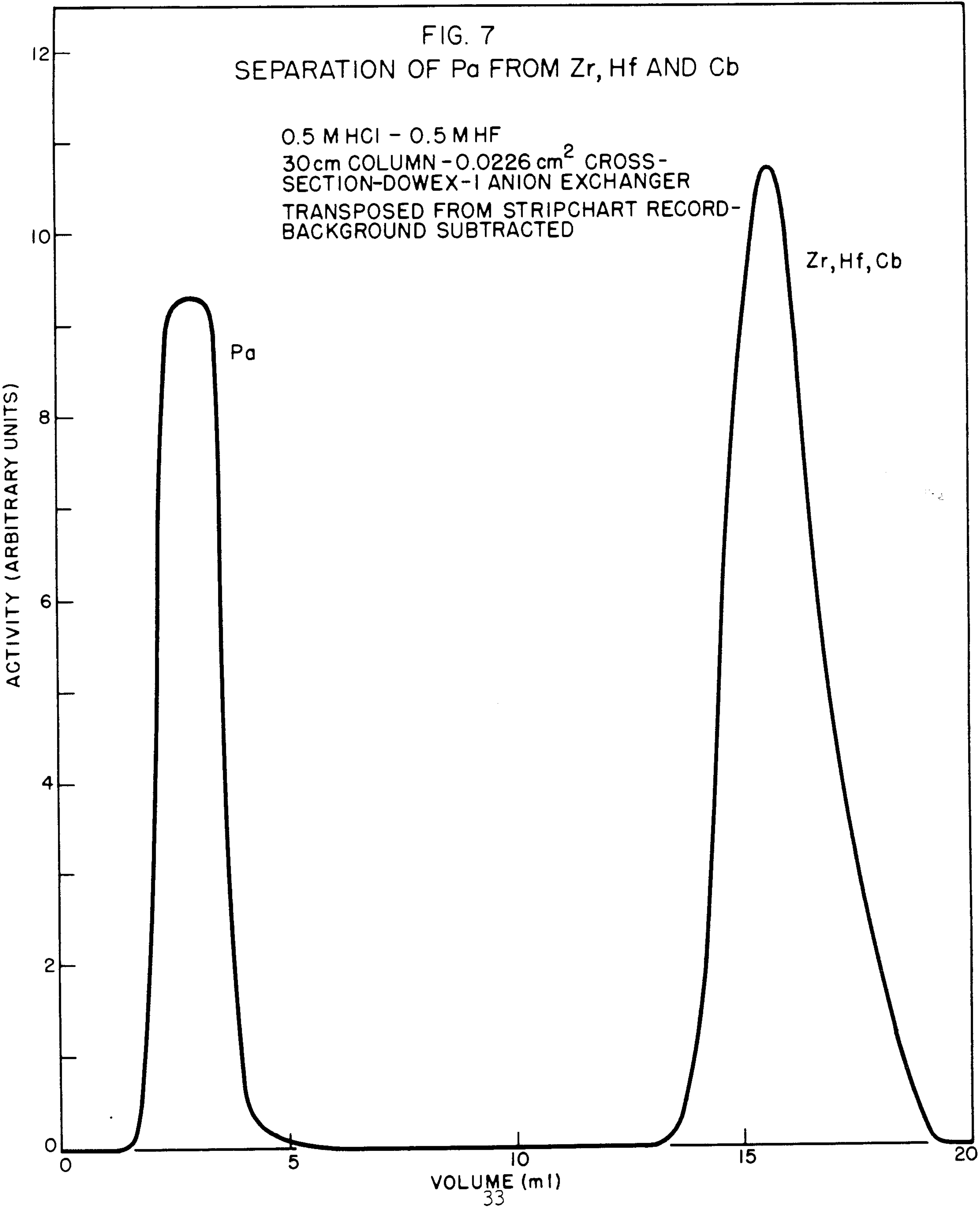

FIG. 7

SEPARATION OF Pa FROM Zr, Hf AND Cb

0.5 M HCl - 0.5 M HF
30 cm COLUMN - 0.0226 cm^2 CROSS-SECTION-DOWEX-1 ANION EXCHANGER
TRANSPOSED FROM STRIPCHART RECORD-BACKGROUND SUBTRACTED

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TABLE VI

Diffusion current constants of UO_2^{++} in KCl-HCl solutions at 25.0 ± 0.1° C

Molarity of UO_2Cl_2: $8 \times 10^{-4} — 4.5 \times 10^{-3}$

$m^{2/3}\ t^{1/6}$: $2.465\ mg^{2/3}\ t^{-1/2}$ at 0.5 V (vs
Ag/Ag Cl in 0.1 *M* KCl

KCl	HCl	$I_d \frac{\mu\ amp}{m\ mole}$	K[(a)]	D $cm^2\ sec^{-1}$
0.10	0.001	3.74	1.516	0.629×10^{-5}
0.10	0.003	3.73	1.514	0.626
0.09	0.01	3.74	1.519	0.630
0.09	0.011	3.79	1.538	0.646
0.09	0.34	3.90	1.582	0.685
0.09	0.53	4.22	1.713	0.802
0.49	0.003	3.78	1.534	0.643
0.49	0.01	3.79	1.611	0.710
0.49	0.01	3.78(S)	1.533	0.643
1.00	0.003	4.03	1.635	0.731
1.00	0.003	3.82(S)	1.548	0.654
0.99	0.01	3.83	1.555	0.660
0.99	0.01	3.83(S)	1.555	0.660
1.97	0.003	3.89	1.578	0.681
1.97	0.003	3.88	1.574	0.676

(a) K = diffusion current constant = $I_d / [UO_2^{++}]\ m^{2/3}\ t^{1/6}$

(S) Suppressor added (2×10^{-4} % thymol)

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[redacted]

Thus our data confirm that at high acidities the diffusion current constant of U(VI) increases very rapidly. This effect has been attributed to the disproportionation of U(V) at the dropping mercury electrode.

At low acidity (e.g., *p*H 2-3) and at low concentrations of U(VI) (of the order of 10^{-3} *M*) the polarographic waves are usually very smooth and do not show any troublesome maxima (using 0.1 to 0.5 *M* KCl as supporting electrolyte). The addition of thymol (2×10^{-4} %) as a maximum suppressor does not markedly change the diffusion current constant.

Under other conditions [particularly at higher acidity or higher concentration of U(VI)] two types of maxima can be found. Some maxima show extremely pronounced current increases near the half-wave region and others show only a slight maximum or no maximum at all at the half-way region, but show abnormal limiting current slopes. Examples of these two types of maxima can be found in Fig. 8. Maxima of the second type are generally observed at the higher ionic strengths. Addition of 4×10^{-4} % thymol as suppressor tends to lower the limiting current but does not always remove the small maxima or abnormal slope in the limiting current region. Maxima of the first type when occurring at low ionic strength are readily removed by the addition of thymol (2×10^{-4} %) and then yield normal appearing polarographic waves with diffusion constants comparable to those occurring under conditions where maxima are not generally observed.

As can be seen from Table VI the diffusion current constants are reasonably constant at low chloride concentrations but rise slowly (after the maximum has been suppressed) with increasing chloride concentration. It appears reasonable to assume that this rise in the diffusion current constant of U(VI) with increasing chloride concentration is due to chloride complexing of U(VI). However, although it is known that such complexing occurs with U(VI), this explanation is not necessarily correct, and the increase in the diffusion current constant at high chloride concentration may be due to change in the medium.

No attempts have been made to obtain the change in the diffusion current constants of U(V) with ionic strength or with chloride concentration. It has previously been found(6) that at ionic strength 0.1 the diffusion current constants of U(V) and U(VI) are approximately equal and it appears reasonable

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(6) K. A. Kraus, G. L. Johnson and F. Nelson, ORNL 188, (December 1948).

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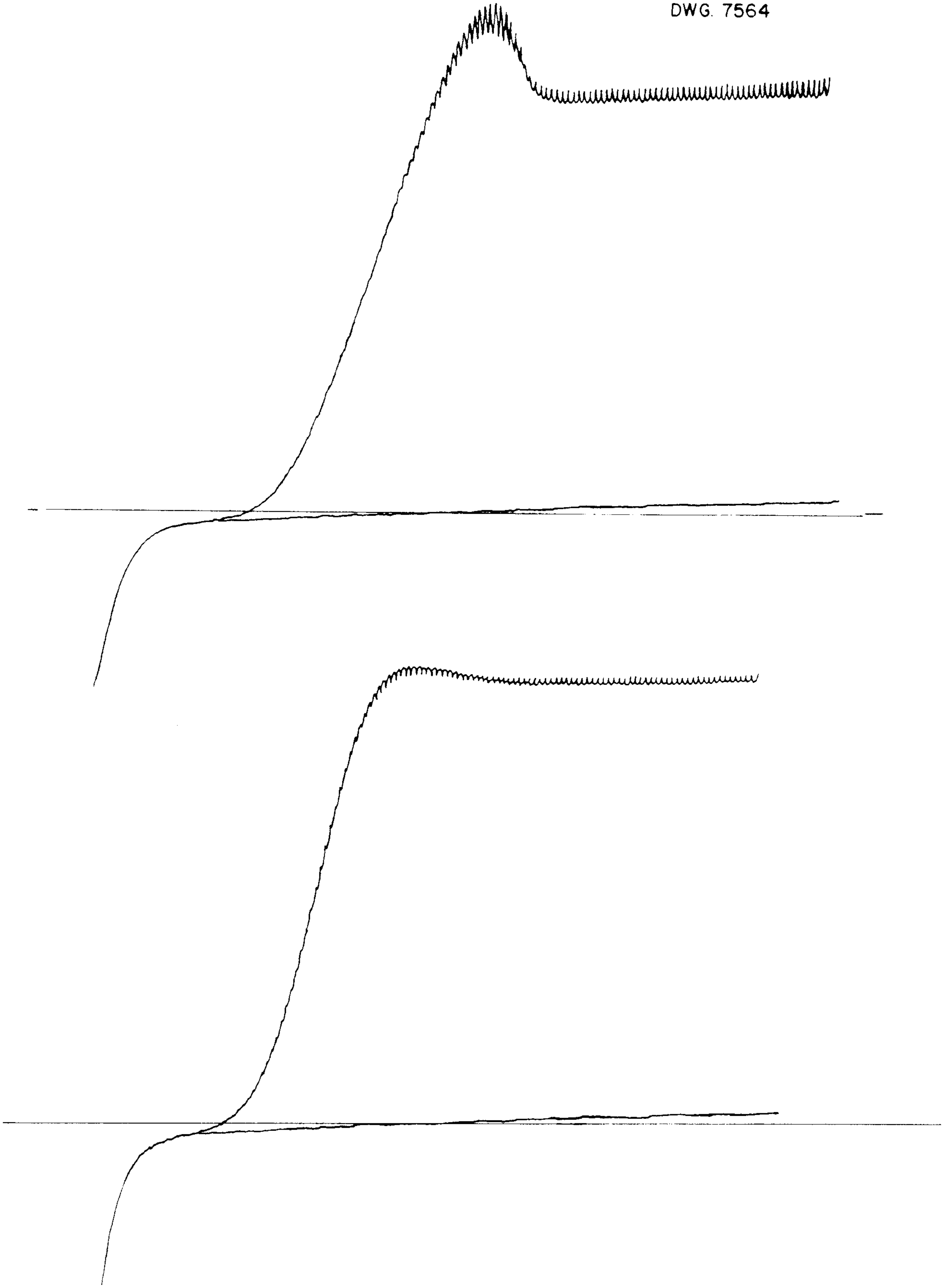

FIG. 8
MAXIMA IN U(V)/(VI) POLAROGRAPHIC WAVES

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that the diffusion current constant of U(V) is actually independent of chloride concentration. This would be particularly true if the observed increase in the diffusion current constant of U(VI) is actually due to chloride complexing of U(VI) since such complexing would not be expected with U(V). Since the effect is small for U(VI), such an assumption could probably only cause an error of less than 3%.

To summarize, the following diffusion current constants for U(V) and U(VI) in chloride solutions have been assumed:

$$\mathrm{U(V)}:\quad 1.52\ (\mu = 0.1 - 2.0)$$

$$\mathrm{U(VI)}:\ 1.52\ (\mu = 0.1),\ 1.52\ (\mu = 0.5),\ 1.55\ (\mu = 1.0),\ 1.58\ (\mu = 2.0).$$

3. *Effect of Temperature on the Diffusion Current Constant of U(VI) in Chloride Solutions.* The change in diffusion current constants of U(VI) with temperature was measured for 0.5 *M* KCl-HCl mixtures from 10° C to 47° C for calibration purposes. The experimental results are given in Table VII. The dropping mercury electrode had a value of $m^{2/3}t^{1/6} = 2.465\ \mathrm{mg}^{2/3}\ \mathrm{sec}^{-1/2}$ at 0.5 volts (***vs*** silver/silver chloride in 0.1 *M* KCl) at 25° C. The temperature coefficient near 25° was found to be approximately 1.3% per °C with slightly lower values at lower temperatures and somewhat higher values at higher temperatures.

No determination of the change in diffusion current constant of U(V) has been carried out, and in all calculations it was assumed that its temperature coefficient is equal to that of U(VI).

4. ***Equilibrium Constants*** *in the U(IV)-(V)-(VI) System in Chloride Solutions.* As described in ORNL 189, under suitable conditions the U(IV)-(V)-(VI) system can be in equilibrium or steady state with respect to the monomeric species of U(IV), U(V) and U(VI). Further studies of this equilibrium have been carried out and the equilibrium constants for reaction (1) have been determined under a variety of conditions. The equilibrium mixtures were prepared by dissolution of UCL_5 in KCl solutions, by addition of U(IV) solutions to U(VI) solutions and by dissolution of UCl_4 in solutions of U(VI). The results of the experiments are summarized in Table VIII. It may be seen that the equilibrium constant K_{eq}, calculated according to equation 1, varies appreciably with acidity, as would be expected, and in addition changes markedly with the chloride concentration of the solutions. If it is assumed that the

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TABLE VII

Effect of temperature on the diffusion current constant of U(VI) in HCl-KCl solutions

Molarity of UO_2Cl_2 : 1×10^{-3}-4.5×10^{-3}

$m^{2/3}\ t^{1/6}$: 2.465 $mg^{2/3}\ sec^{-1/2}$ at -0.5 V
(vs Ag/AgCl in 0.1 *M* KCl) calibrated at
25.0° C.

(No maximum suppressor added)

TEMPERATURE (°C)	KCl	HCl	$\bar{I}_d$ (μamp/m mole)
10.0	0.49	0.005	3.17
25.0	0.49	0.003	3.78
45.0	0.49	0.005	5.02
47.0	0.49	0.003	5.09

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TABLE VIII

Equilibrium constants for the U(IV)-U(VI) system in KCl-HCl solutions

$$K_{eq} = \frac{[U(IV)][U(VI)]}{[U(V)]^2} \qquad K'_{eq} = \frac{K_{eq}}{[H_3O^+]^3\,[H_3O^+ + K(IV)_1]} \quad (a)$$

	$[H_3O^+]\times10^3$	M U × 10^3	M U(V)×10^4	K_{eq} (obs.)	K'_{eq} × 10^{-8}	PREPARATION
Ionic Strength 0.10-0.11 KCl-HCl	7.2	2.48	7.25	1.475	0.51	UCl_5 in KCl solution.
	9.9	3.57	7.56	3.460	0.44	UCl_5 in KCl solution.
	10.4	5.64	7.98	4.43	0.48	UCl_4 solution to U(VI)-KCl solution.
	11.2	5.67	7.90	4.72	0.37	UCl_4 solution to U(VI)-KCl solution.
				(Ave = 0.45)		
Ionic Strength 0.49-0.51 KCl-HCl	4.65	5.16	4.42	0.94	2.8	UCl_5 salt in U(VI)-KCl solution.
	5.2	1.499	4.29	1.56	3.3	UCl_5 salt in KCl solution.
	5.6	1.23	5.10	1.61	2.7	Disprop. of electrolytically prepared U(V) solution.
	5.65	5.89	8.01	2.05	3.4	UCl_5 salt in U(VI)-KCl solution.
	5.84	6.01	8.45	2.12	3.1	UCl_5 salt in U(VI)-KCl solution.
	7.10	6.36	11.85	3.18	2.5	UCl_4 salt in U(VI)-KCl solution.
	7.30	5.08	5.30	4.19	3.0	U(IV) solution to U(VI)-KCl solution.
	7.80	5.91	6.01	5.24	3.1	UCl_5 salt in U(VI)-KCl solution.
	8.38	6.12	9.15	5.40	2.5	UCl_4 solution to U(VI)-KCl solution.
	10.2	5.64	7.98	12.1	3.0	UCl_4 solution to U(VI)-KCl solution.
	12.8	2.50	2.38	22.4	2.6	UCl_5 salt in KCl solution.
	13.5	1.50	1.40	23.4	2.3	UCl_5 salt in KCl solution.
				(Ave = 2.9)		
Ionic Strengths 0.99 KCl-HCl	5.45	5.78	6.42	3.55	(b)	UCl_5 in KCl solution.
1.97-2.00 KCl-HCl	3.87	4.70	3.82	3.25	(b)	UCl_5 in KCl solution.
	6.00	4.62	4.25	13.0	(b)	UCl_5 in KCl solution.
1.97-NaClO$_4$-HClO$_4$	4.95	3.31	5.36	3.02	(b)	UCl_5 in $NaClO_4$ solution.

(a) Calculated assuming $pK(IV)_1 = 1.55$ (1.15) at $\mu = 0.5$ (0.1) for the reaction $U^{+4} + 2H_2O \longrightarrow U(OH)_3^{+3} + H_3O^+$.

(b) $pK(IV)_1$ under these conditions not yet determined.

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equilibrium involves the species U^{+4}, UOH^{+3}, UO_2^+, and UO_2^{++}, the (acid independent) equilibrium constant K'_{eq} for the reaction

$$4H_3O^+ + 2UO_2^+ \rightleftharpoons UO_2^{++} + U^{+4} + 6H_2O \qquad (2)$$

becomes

$$K'_{eq} = \frac{K_{eq}}{[H_3O^+]^3 \{[H_3O^+] + K(IV)_1\}} \qquad (3)$$

It may be noticed that equation (3) contains the acid constant $K(IV)_1$ of U^{+4} for the reaction

$$U^{+4} \rightleftharpoons UOH^{+3} + H_3O^+ \qquad (4)$$

This acid constant has been determined by spectrophotometric methods[7] for 0.1 and 0.5 *M* chloride solutions [$pK(IV)_1 = 1.55$ and 1.15 for $\mu = 0.5$ and 0.1, respectively]. No determinations of this acid constant at higher chloride concentrations have been carried out and the acid independent constant K'_{eq} can therefore not yet be calculated for these solutions. Experiments are now underway to determine $K(IV)_1$ under these conditions.

The acid independent equilibrium constant K'_{eq} is approximately 2.9×10^6 in the acid range studied (ca. 5×10^{-3} to 1×10^{-2} *M*). The data do not show any significant trend with acidity and it can therefore be assumed that equations (2) and (3) apply and that the value of the acid constant of $K(IV)_1$ is correct. At ionic strength ca. 0.1, the equilibrium constant K'_{eq} was found to be ca. 0.45×10^6, again also apparently acid independent. Experiments are now under way to study the equilibrium constants in perchlorate solutions to help estimate the influence of chloride complexing of U(IV) and U(VI) on the equilibrium.

5. *The Reaction of U(IV) with U(VI).* Previously, and particularly in the last quarterly report, a number of data have been presented on the rate of disproportionation of U(V). The studies have now been extended to the rate of reaction of U(IV) with U(VI). Conditions of equal concentrations of U(IV) and U(VI), as well as excess of either U(IV) and U(VI) have been studied. In

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[7] K. A. Kraus, F. Nelson, AECD-1888 (April 1948).

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general it was found that the directly determined rate constants were in good agreement with those calculated from the equilibrium constants (K_{eq}) and the disproportionation rate constant.

In general, the experimental procedure was to add either solid UCl_4 or a reasonably concentrated solution of UCl_4 in 0.5 *M* HCl to oxygen-free U(VI) solutions of the desired initial *p*H and to follow the rate of formation of U(V) polographically. Some experiments have also been repeated on the dissolution of UCl_5 in either acid or U(VI) solution, since UCl_5 can serve as a convenient supply of a U(IV)-U(VI) mixture(8). In each case the reaction rates were also followed with a glass-electrode calomel electrode assembly. However, the data have not yet been completely tabulated. In those cases where calculations have been completed, the assumptions of the species previously suggested have been further confirmed. A typical set of data is as follows:

The initial slope of a plot of log [U(IV)]/[U(VI)] *vs* time permits the approximate calculation of the rate constants k_2. A 5.27×10^{-3} *M* U(VI) solution of ionic strength 0.5 (KCl-HCl) was made 1.47×10^{-3} *M* in UCl_5. From the plot of log [U(IV)]/[U(VI)] *vs* t, $k_2 = 0.458$ (moles/l)$^{-1}$ sec^{-1} was found at an HCl concentration of 5.1×10^{-3} *M*. Using the $K_{eq} = 2.12$, determined for steady state conditions, the disproportionation constant $k_1 = k_2K_{eq} = 0.97$ (moles/l)$^{-1}$ sec^{-1} was found. This is in fair agreement with the value 1.05 (moles/l)$^{-1}$ sec^{-1} found by extrapolation of the data presented in the previous quarterly report. It is of interest to note that even at this low acid concentration, the mechanism proposed in the previous paper still applies.

SPECTROPHOTOMETRY OF THE U(VI)-CHLORIDE SYSTEM

G. W. Smith and K. A. Kraus

Spectrophotometry of U(VI) in chloride solutions is now under way with the objective of determining the association constants of some of the U(VI)-chloride complexes. The spectrophotometric work is almost complete, but the data have not yet been completely tabulated and analyzed. It is expected that a completion report will be issued in the near future.

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(8) K. A. Kraus and F. Nelson, ORNL 189, December 1948.

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SPECIAL INSTRUMENTATION

Precision Alpha-Counting of Liquid Samples (K. A. Kraus and H. H. Miller). Work on this problem has been concluded and a progress report is in preparation.

Precision of pH Measurements with Glass-Electrodes and a Vibrating Reed Electrometer (K. A. Kraus and R. W. Holmberg). Work regarding the evaluation of the "routine" precision of the glass electrode-calomel electrode vibrating reed assembly, which was described in the previous quarterly report, has been continued and is practically complete. A report on this work is in preparation and therefore no discussion of this problem and the later results will be given here. Suffice it to say, that it was found possible to decrease further the standard deviation of a series of determinations of voltage differences for acid pairs. At present, standard deviations of the order of 0.015 mv can be obtained for such voltage differences with determinations extending over several days.

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II. PHASE RULE STUDIES

THE SYSTEM UO_3-UO_2SO_4-H_2O

C. H. Secoy

A phase study of the three-component system UO_3-UO_2SO_4-H_2O was started during the past quarter but has not progressed very far. One set of data has been obtained at 25° C for solutions dilute with respect to the sulfate.

The two main problems in the selection of a fluid system for a homogeneous reactor are the corrosion problem and the bubble problem. There is a possibility that corrosion effects might be decreased in the uranyl sulfate system by adding UO_3 to the solution since this shifts the *p*H of the solution to higher values. The effect of the excess UO_3 on the radiation bubbling of the solution is not known but might possibly be in the beneficial direction. For these reasons a study of the solubility of UO_3 in solutions of varying UO_2SO_4 concentration and at temperatures varying from room temperature to perhaps 300° C was initiated.

The experimental procedure for the lower temperatures has been to equilibrate a solution of known UO_2SO_4 content with an excess of solid UO_3 in a temperature bath. The liquid and the wet residue were then analyzed for UO_2^{++} and $SO_4^{=}$. At the same time the density and *p*H of the original UO_2SO_4 solution and of the UO_3-saturated solution were determined.

At this time only four samples at 25° have been completed. The analytical data, *p*H, and density measurements for these are given in Tables IX, X, and XI. The last column in Table X gives the ratio of the grams of uranium per liter in the final solution to that in the initial solution. It is evident from these figures, if the data are not in error, that something must happen at a concentration between that of the second and third samples. The analysis of the wet residues indicates that a solid phase transition must occur in this interval. Figure 9 shows the plot of the solubility and the extrapolation to determine the composition of the solid phases. For samples 1 and 2, the solid phase is unquestionably $UO_3 \cdot 2H_2O$. For samples 3 and 4, the solid phase has a mole ratio of 5 and 6 moles UO_3 to one of UO_2SO_4. This ratio and the amount of H_2O in the solid cannot be fixed with certainty until several additional points are obtained. The break in the solubility curve at the

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TABLE IX

Initial UO_2SO_4 solutions

WEIGHT PERCENT of UO_2SO_4	g. U/L	pH	ρ
1.060	6.96	2.89	1.010
2.045	13.54	2.67	1.018
4.135	27.93	2.39	1.039
6.528	44.99	2.17	1.060

TABLE X

Solutions saturated with UO_3

PERCENT of UO_3	g. U/L	pH	ρ	$\frac{\text{g. U/L FINAL}}{\text{g. U/L INITIAL}}$
1.385	11.68	4.07	1.0133	1.68
2.779	23.78	4.01	1.0284	1.76
4.205	36.53	3.80	1.0448	1.31
6.783	60.68	3.61	1.0750	1.35

TABLE XI

Wet residues

PERCENT of SO_3	PERCENT OF UO_3
0.127	33.07
0.242	27.08
1.383	20.39
1.813	21.94

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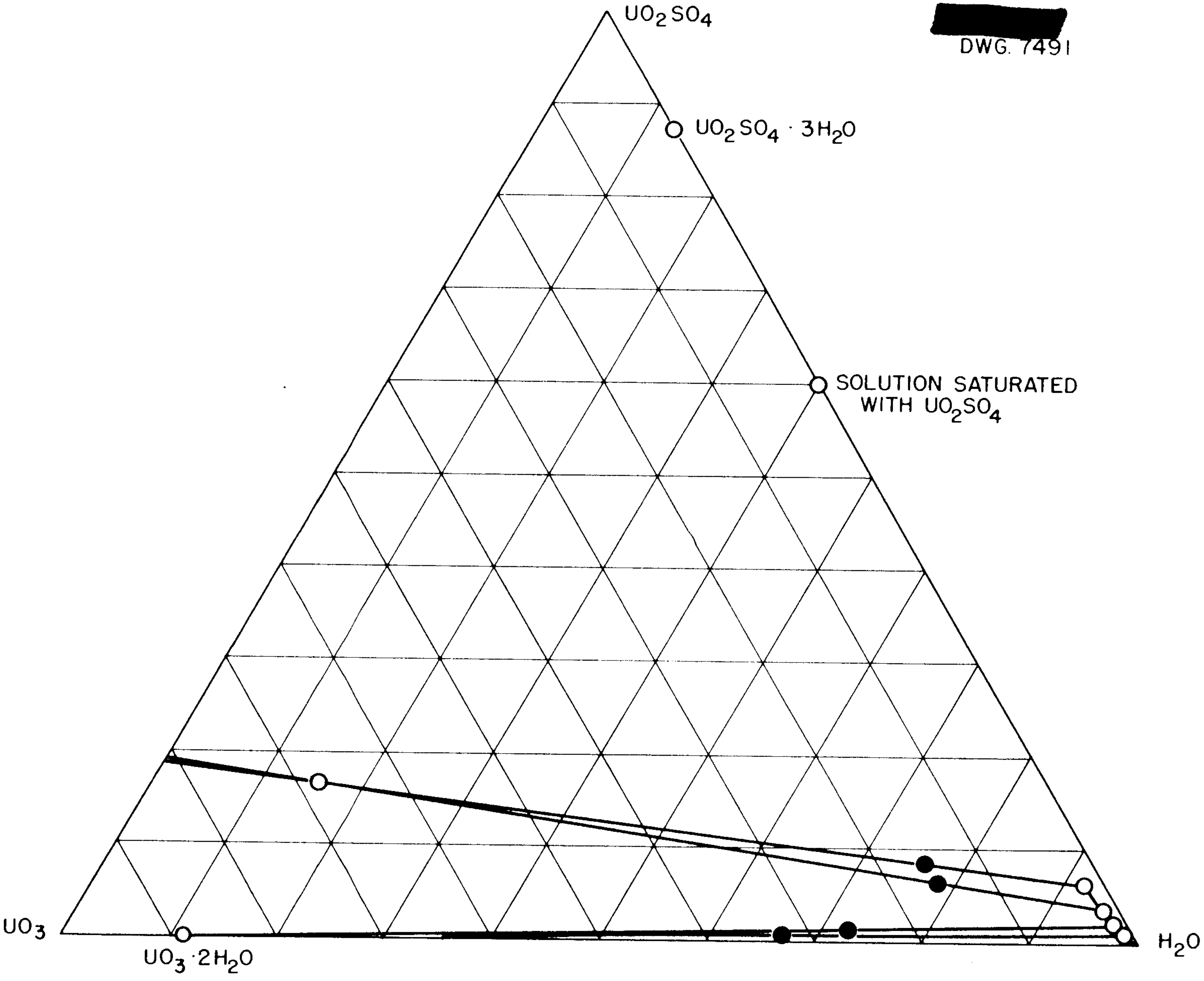

FIG. 9

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transition point can scarcely be detected on the graph as shown. However, if the data are plotted on a much enlarged scale, it is clearly evident at approximately 1.3% UO_3 and 3.13% UO_2SO_4.

APPLICATION OF KINETIC THEORY TO THE CRITICAL CURVE FOR AQUEOUS SOLUTIONS OF 1-1 ELECTROLYTES

C. H. Secoy

Aqueous solutions of 1-1 electrolytes, insofar as they have been studied, undergo critical change without phase separation at all concentrations. The critical temperature is elevated by the presence of the salt. Schröer(9), in 1927, found that log Δ T plotted against log X gave a straight line where X is the salt concentration in moles per liter. He attempted to explain his results in very general terms as a physical adsorption because of the analogy in the form of his equation with the Freundlich adsorption isotherm equation. His explanation seems hardly adequate since in a term by term comparison the analogy fails.

An equation based on kinetic theory has been derived which describes the available data more precisely than Schröer's and in which the constants all have a definite physical significance. The equation is of the form,

$$T^n = \frac{a + k_1 \gamma + k_2 \gamma^2}{k_3 + k_4 \gamma} .$$

The constants a, k_3, and k_4 can be estimated *a priori* from known physical quantitites for a given salt. T is the critical temperature of a solution in which the mole fraction of positive ion is γ. The quantities n, k_1, and k_2 are also related to definite physical quantities but cannot be given *a priori* values with our present knowledge. They must be determined from the data at hand.

The development of the equation and its application will be described in detail in a project report to be issued shortly (ORNL 247). The equation is applied successfully to data from Schroer's paper and to data obtained in this laboratory for solutions of NaCl, KCl, KBr, and KI. The values of n, k_1 and k_2 obtained for these four salts are shown to be of the expected magnitude and to lie in the expected order.

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(9)Erich Schröer, Z. physik. Chem., **129**, 79-110 (1927).

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NUCLEAR AND CHEMICAL PROPERTIES OF ELEMENTS IN THE FISSION PRODUCT REGION

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CHARACTERIZATION OF Cs^{135}

H. Zeldes, A. R. Brosi, G. W. Parker,
G. M. Herbert and G. E. Creek

Inasmuch as the large quantities of Xe^{135} prepared for cross-section measurements (ORNL 336) were retained in closed containers, it seemed feasible to isolate and characterize the long-lived Cs^{135} daughter. Accordingly, preparations were made about a year ago to uncap, discharge and wash the highly radioactive containers by remote control and also to remove safely the high level iodine activities so that the Cs containing materials might be handled easily.

The closed containers, referred to as wafers in the Xe^{135} cross-section work, contained about 10 mg iodine in the form of PdI_2 from which the Xe^{135} grew and decayed. In order to be certain that all the Cs was recovered, the solid PdI_2 was pushed from its capillary holder and the holder then washed with aqueous $NH_3 \pm H_2O_2$, which is a good solvent for PdI_2. The washing procedure introduced several milligrams of metal ions from the metal wafer and also variable amounts of silicone stopcock grease. After the first few relatively low level runs, it was learned that in addition to the Cs^{135} activity, which is the only possible Cs activity from this source, there were present several million disintegrations of a variety of other activities, possibly arising from the daughters of short-lived gaseous activities or spray in the iodine separation process. The presence of this activity which was thousands of times more intense than the Cs^{135} activity, together with the large mass of material with which the mass ($<10\ \mu g$) of Cs^{135} was associated, made it almost imperative to use carrier Cs to isolate the Cs^{135} activity.

Cs^{135} activity was isolated with carrier from six Xe runs. The procedure was to uncap the wafer, push its contents into a glass container into which aqua regia was added and then to evaporate dry to remove iodine. The wafer capillary was then washed with aqueous $NH_3 \pm H_2O_2$ which was also carefully evaporated dry. The residue was then dissolved in aqua regia and evaporated dry again. The two residues, which were relatively inactive, were dissolved in 6 *N* HNO_3 and transferred to a volumetric flask to which Cs carrier was also added. The Cs was isolated as $CsClO_4$. It was felt that no other activity was carried along, as successive precipitations did not alter the specific activity.

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Also, similar absorption curves were always obtained.

Al absorption curves for four of the experiments at 30% geometry with a mica end window (3.1 mg) tube are shown in Fig. 10. The beta energy is about 0.19 Mev. No gamma or X-ray radiation was detected when a G-M counter and an argon and methane-filled counter were used.

The number of Cs^{135} atoms was known from the Xe^{135} assays in the cross-section work.

The half-life of Cs^{135} was established by determining (gravimetrically) the recovery of Cs carrier and by absolute beta counting the fraction recovered. The half-life so determined is $2.95 \pm 0.3 \times 10^6$ years.

The absolute beta counting was done with a slide chamber proportional counter. The samples were mounted on 4 mil Pt discs. The counting efficiency of this arrangement (assuming no self-absorption) is reported elsewhere in this report and turned out to be 65%.

The major source of error in the half-life determination is probably the uncertainty in the large self-absorption correction to the counting rate because of the relatively large mass of $CsClO_4$. To make this correction, counts were made for a range of masses of counting samples. In order to get a sufficient number of points, and at the lowest attainable masses of $CsClO_4$, most of the $CsClO_4$ samples obtained from individual runs were divided into fractions by aliquoting methods. From each of the resulting counting rates the Cs recovery data and the Xe assay values, and "apparent" value of the half-life of Cs^{135} was computed and plotted versus the mass of the sample counted. The "apparent" half-lives thus computed are uncorrected for self-absorption. This correction goes to zero at zero mass, and hence the "apparent" half-life at zero mass is the correct one. This plot is shown in Fig. 11, and a summary of the data in Table I. In Table I, $(D^{Cs^{135}})$ means the "apparent" disintegration rate of Cs^{135} for the entire run, that is, with no self-absorption correction. $D_0^{I^{135}}$ gives at time zero the d/m of the parent I^{135} as determined from the assay in the Xe^{135} cross-section work.

Recently, N. Sugarman [Phys. Rev. 75, 1473 (1949)] has reported 0.21 Mev for the maximum beta energy and $2.1 \pm 0.7 \times 10^6$ years for the half-life of Cs^{135}. The value for the half-life reported here and that reported by Sugarman fall within the error assignments. However, we believe that the errors in our half-life measurements are considerably smaller than those obtained by Sugarman.

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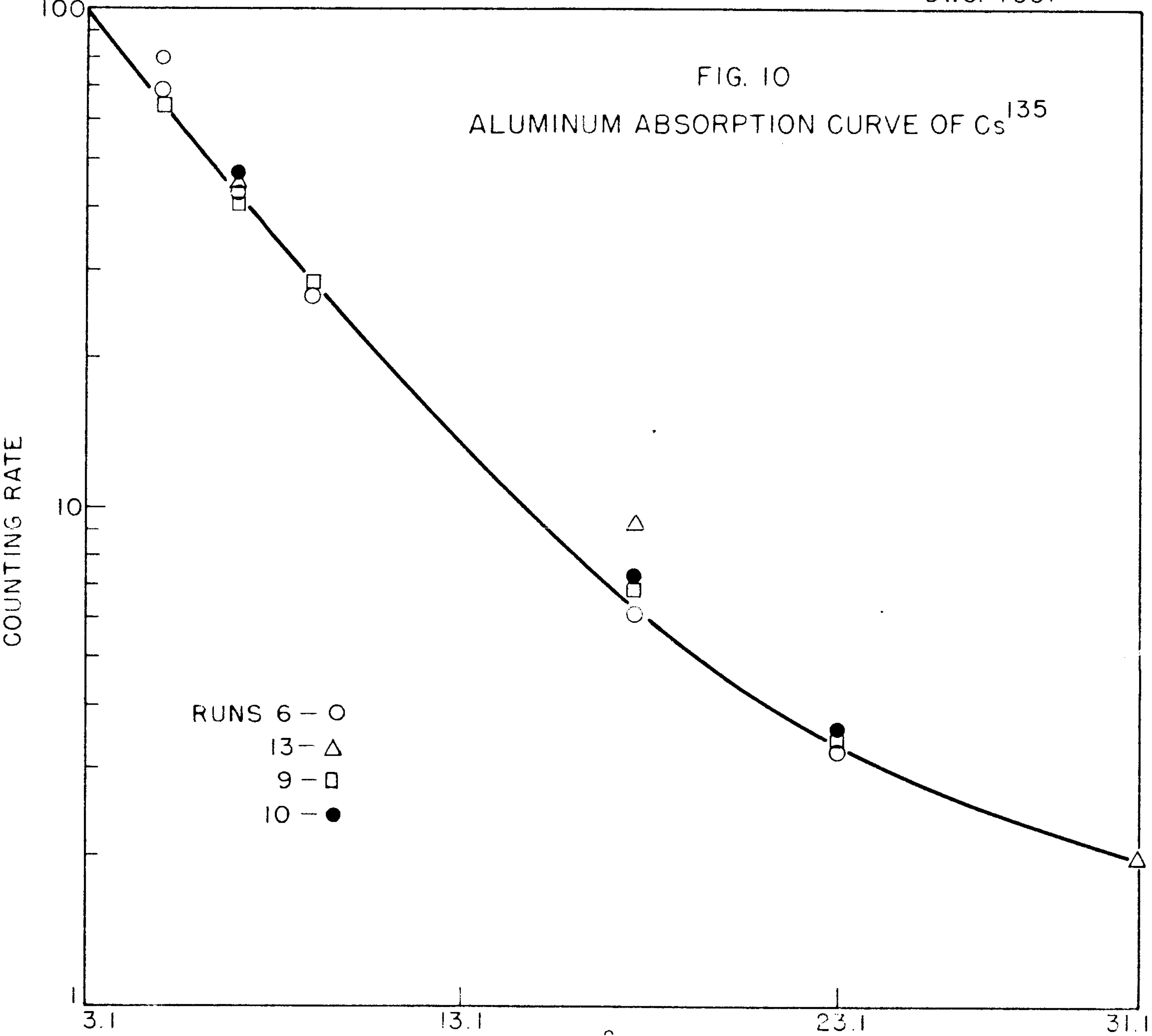

FIG. 10

ALUMINUM ABSORPTION CURVE OF Cs^{135}

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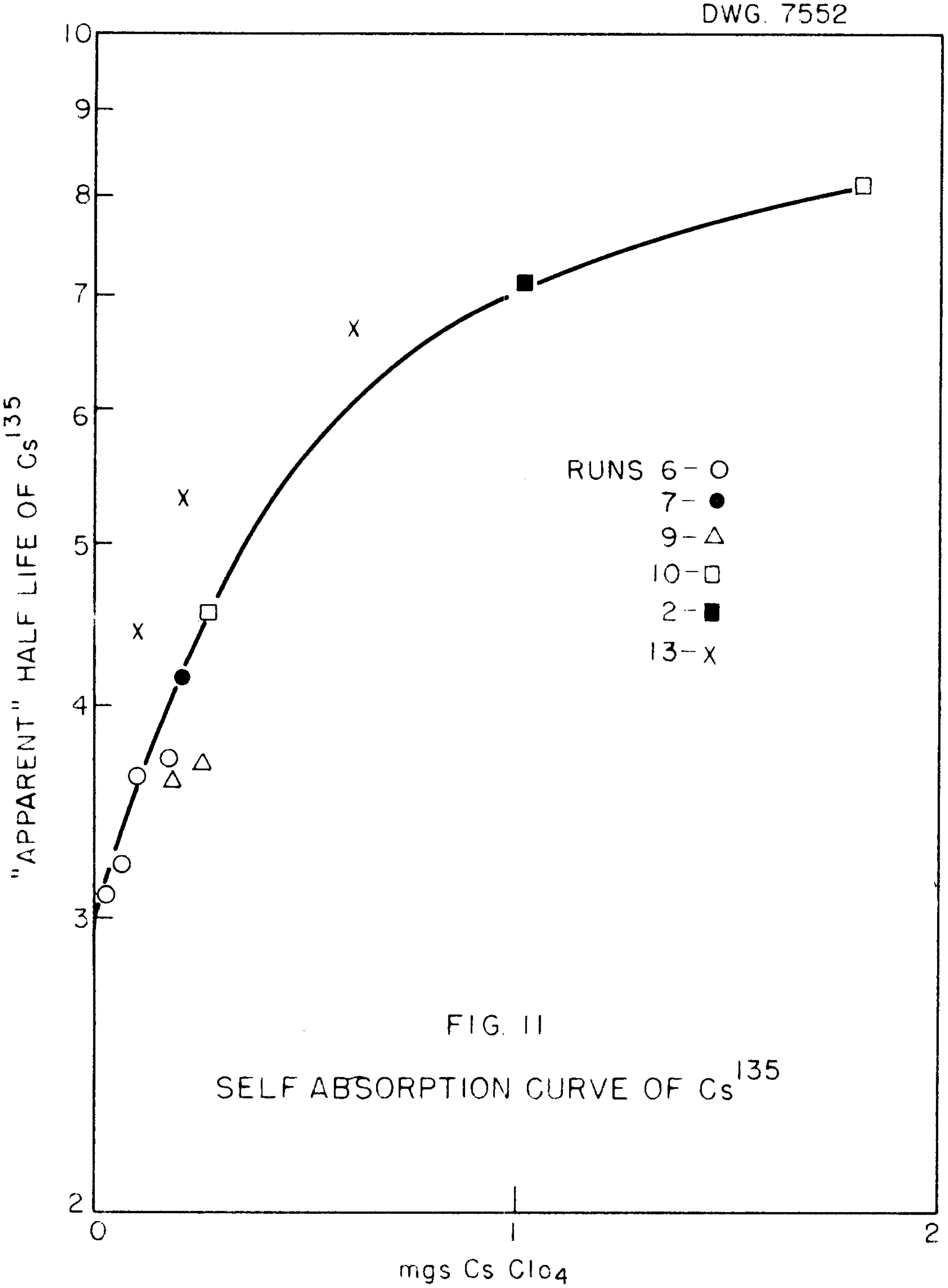

FIG. II

SELF ABSORPTION CURVE OF Cs^{135}

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TABLE I

Summary of data for half-life of Cs^{135}

RUN	2	6	7	9	10	13
Fraction of run measured	0.80	0.90	0.84	0.80	0.80	0.50
Wt. of Cs carrier (mg)	2	1.5	1.5	1.5	2	2
Wt. of $CsClO_4$ counted (mg)						
(1)	2.935	0.1048	0.208	0.261	1.815	2.109
(2)	1.185	0.180		0.189	0.272	0.608
(3)		0.0360				0.213
(4)		0.0720				0.1055
Prop. Count on Pt (c/m)						
(1)	121	101	171	207	208	489
(2)	73	170		154	56	130
(3)		41				57.5
(4)		79				34
$D^{Cs^{135}}$ (c/m)						
(1)	275	4290	3970	4020	772	2490
(2)	418	4250		4120	1385	2300
(3)		5120				2900
(4)		4910				3470
$D_O^{I^{135}}$ (d/m)	3.91×10^{12}	2.08×10^{13}	2.17×10^{13}	1.96×10^{13}	8.25×10^{12}	2.02×10^{13}
Apparent $t_{½}^{Cs^{135}}$ (yr)						
(1)	1.08×10^{7}	3.69×10^{6}	4.16×10^{6}	3.71×10^{6}	8.11×10^{6}	6.18×10^{6}
(2)	7.1×10^{6}	3.72×10^{6}		3.62×10^{6}	4.53×10^{6}	6.68×10^{6}
(3)		3.09×10^{6}				5.30×10^{6}
(4)		3.22×10^{6}				4.43×10^{6}

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PRELIMINARY REPORT ON THE ISOLATION AND CHARACTERIZATION OF LONG-LIVED I^{129}

G. W. Parker, G. E. Creek, G. M. Herbert
P. M. Lantz, and W. J. Martin

Introduction. Previous investigations of the long-lived fission-produced iodine have resulted in the proposals of lower limits of 10^8 y for the half-life of I^{129} (1), (2). No prior report, however, has claimed observation of the radiations.

The existence of an isotope of mass 129 in old fission iodine has been assured by the identification of the parent isotopes of Sb and Te in the fission chain (3), by the complete absence of the daughter Xe in the fission gases (4), and by Katcoff's (5) identification of the neutron absorption product, the 12.6 hr I^{130} in samples of fission iodine isolated by Seiler. More recently Leader and Sullivan upon the examination of the residue from the decay, after one year of cooling, of a fission source of 40 curies of 8 day I^{131}, found a remaining activity of only about 30 counts per minute. Since this small counting rate indicated a half-life in excess of 10^9 years which would require that the isotope occur to an appreciable extent in nature, it was necessary for them to conclude that even this small amount of radioactivity was due to an impurity. They also concluded that any beta radiation due to radioisotope I^{129} must either be very soft (less than 0.1 Mev) or is not observable. The fact that Leader and Sullivan were not able to characterize beta radiation of much less than 0.1 Mev is significant.

The upper limit of the natural occurrence of I^{129} was first shown to be less than 25 parts per million (6), and has more recently been lowered to one part per million (7). Katcoff and Boyd have each reported a trace of 12 hour activity as a result of neutron bombardment of natural iodine. This, it is proposed, may be the known I^{130} (8). Katcoff estimated that this limit of

(1) G. R. Leader and W. H. Sullivan, Report (H) CN-3466, Jan., 1946; PPR Vol. 9B 7.36 (1946).

(2) Seiler, J. A., Report CN-1998 (1946).

(3) The Plutonium Project, "Nuclei Formed in Fission", J. Am. Chem. Soc. 68, 2411-2442 (1946).

(4) Arrol, W. J. Chackett, and S. Epstein, CRC-297 (1947).

(5) Katcoff, S., Phys. Rev. 71, 826 (1947).

(6) Nier, A.O.C. Phys. Rev. 52, 937 (1937).

(7) Boyd, G. E., Private Communication.

(8) Livengood and Seaborg, Phys. Rev. 54, 775 (1938).

[redacted]

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observed activity, if it resulted from neutron capture in 10^8 y I^{129}, indicated the possible natural existence of the isotope to the extent of about 0.3 parts per million in order to be consistent with his determination of an approximate cross-section value of 8 barns for I^{129} in samples of fission iodine.

Summary. Characterization of the radiations, half-life and neutron cross section of I^{129} has been attempted and preliminary data are reported. Iodine in milligram quantities has been obtained nearly isotopically pure by three separate processes. From one source, I^{131} masked the soft radiations of the 129. The other samples showed a consistent amount of an electron of 100-130 Kev and a gamma or X-ray of 28-32 K.ev. The half-life is estimated at 2-4 × 10^7 years. The neutron absorption cross section was observed to be of the order of 15 barns in agreement with published work.

Experimental. The most abundant source of the longer-lived fission iodine isotopes has been found in the strong nitric acid condensate from waste gases from pilot plant dissolver operations. An efficient chemical recovery from these condensates has been made by means of large scale distillations with H_2O_2 into dilute alkaline sulfate. Unfortunately, however in the iodine from the existing by-product sources it was found that a very small content of 8 day I^{131} was sufficient to mask differences in the absorption curves which might be attributable to I^{129}.

Therefore, it was necessary to make special dissolvings of long-irradiated, long-cooled metal from which the off-gases, NO_2, I_2, etc., were scrubbed out in alkali. From two of these dissolvings about 2 milligrams of total iodine were finally extracted. For these samples absorption curves were obtained and decay observed. Again, however, the iodine contained small amounts of 8 day activity, but with time the initial portion of the absorption curve indicated an increasing amount of a 100-120 Kev radiation corresponding to a very low specific activity in the total amount of iodine.

A second series of dissolvings was undertaken, avoiding the use of the alkaline scrubber into which it was assumed that locally contaminated air containing I^{131} was being drawn. In this case, the metal was dissolved in hydrochloric acid and after the oxidation of UCl_4 with H_2O_2 and the addition of $Fe_2(SO_4)_3$, iodine was distilled into SO_2-solution. In the new absorption curves of the iodine obtained, it was immediately observed that none of the radiations of 8 day iodine was present.

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Radiation and Half-Life of Long-Lived Iodine. In order to establish the energy of the radiation and to arrive at a preliminary value for a half-life, on the assumption that the radiations observed were indeed from I^{129}, small disks of silver foil were weighed and coated with AgI by simply shaking the silver in contact with a moist CCl_4 extract containing an amount of iodine previously determined polarographically(9).

Plates of AgI made in this way were counted with a minimum of self-absorption. As a further check on the mass, it was convenient to remove the AgI by washing with 10% NH_4OH and to re-weigh the plate and obtain a value for the difference.

The range of the soft electron in aluminum has been roughly estimated at 15 to 22 milligrams corresponding to 100-135 Kev (Fig. 12). The proportion of the gamma fits reasonably to a 1:1 ratio with the beta assuming a counting efficiency of about 2% in the 90% argon-10% methane mixture used in the proportional counter(10). The half-thickness of the gamma in aluminum (600-700 mg) corresponds to an energy of 28-33 Kev (Fig. 13). Since this value is quite close to the energy of the iodine X-ray, more work will be expended in verifying its association with the iodine and the beta and also in further determining its identity. Samples are being prepared for study of the beta spectrum on the scintillation counter by P. R. Bell of the Physics Division.

The specific activity in the pure samples has been estimated at 1-2 disintegrations/second/microgram of 129. Since precise spectrometric data are not yet available, we have assumed 75% isotopic abundance from microwave data furnished by Livingston. The half-life corresponding to the above activity is about $2\text{-}4 \times 10^7$ years. The inconsistency with a longer half-life proposed as a lower limit is ascribed to the former limitation in counting radiation below 0.1 Mev.

The thermal neutron absorption cross section has been roughly determined to be approximately 15 barns in agreement with Katcoff within a factor of two. Further work should give a more reliable figure.

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(9) Thomason, P. F., and Davenport, W. T., Private Communication.

(10) Winsberg, L., Lecture No. 10, Treatment of Experimental Data - Radiations, AECD 2047, 1948.

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[redacted]

Chemical Procedure for Fission Iodine. An outline of one of the chemical extractions and the purification procedures for the iodine is given as follows:

Source	Uranium metal (long-irradiated) cooled three years. Dissolve in glass using minimum of conc. HCl.
UCl_4 Slurry	Add $Fe_2(SO_4)_3$ to about 10 mole percent of the uranium. Oxidize barely to UO_2Cl_2 by careful addition of 10% H_2O_2 (disappearance of green color).
UO_2Cl_2	Add same amount of $Fe_2(SO_4)_3$ after the endpoint of the oxidation. Distill strongly for several hours with sufficient reflux condenser to give a minimum volume of distillate. Keep distillate saturated with SO_2. Add small amount of NaOH.
Distillate	Boil out excess SO_2. Extract iodine into CCl_4 with addition of $NaNO_2$ and HNO_3. Wash CCl_4 layer with H_2O.
CCl_4 Extract	Reduce with $NaHSO_3$ and extract into small volume H_2O. Repeat oxidation-reduction cycle.
$NaHSO_3$ Extract	Add solution to small glass still. Add few drops of $KMnO_4$ to permanent color. Make about 6 N in H_2SO_4. Add H_3PO_3 solution and heat until free of MnO_2 color. Distill about one-third of aqueous volume into $NaHSO_3$ solution.
Distillate	Repeat the $NaNO_2$ oxidation and CCl_4 extraction. Wash with H_2O. Separate CCl_4 layer.
CCl_4 Extract	Clean a 1 cm silver plate in dilute HNO_3. Wash and weigh and drop into an aliquot of the CCl_4 extract. Shake occasionally until iodine color has been dissipated.
Ag-AgI Disk	Wash and dry. Weigh for mass of iodine collected. Cover and mount for counting.
Ag-AgI	Place in warm 10% NH_4OH sufficient to complex AgI. Remove and reweigh disk or collect AgI on weighed filter after acidification with HNO_3 or by boiling out excess NH_3.

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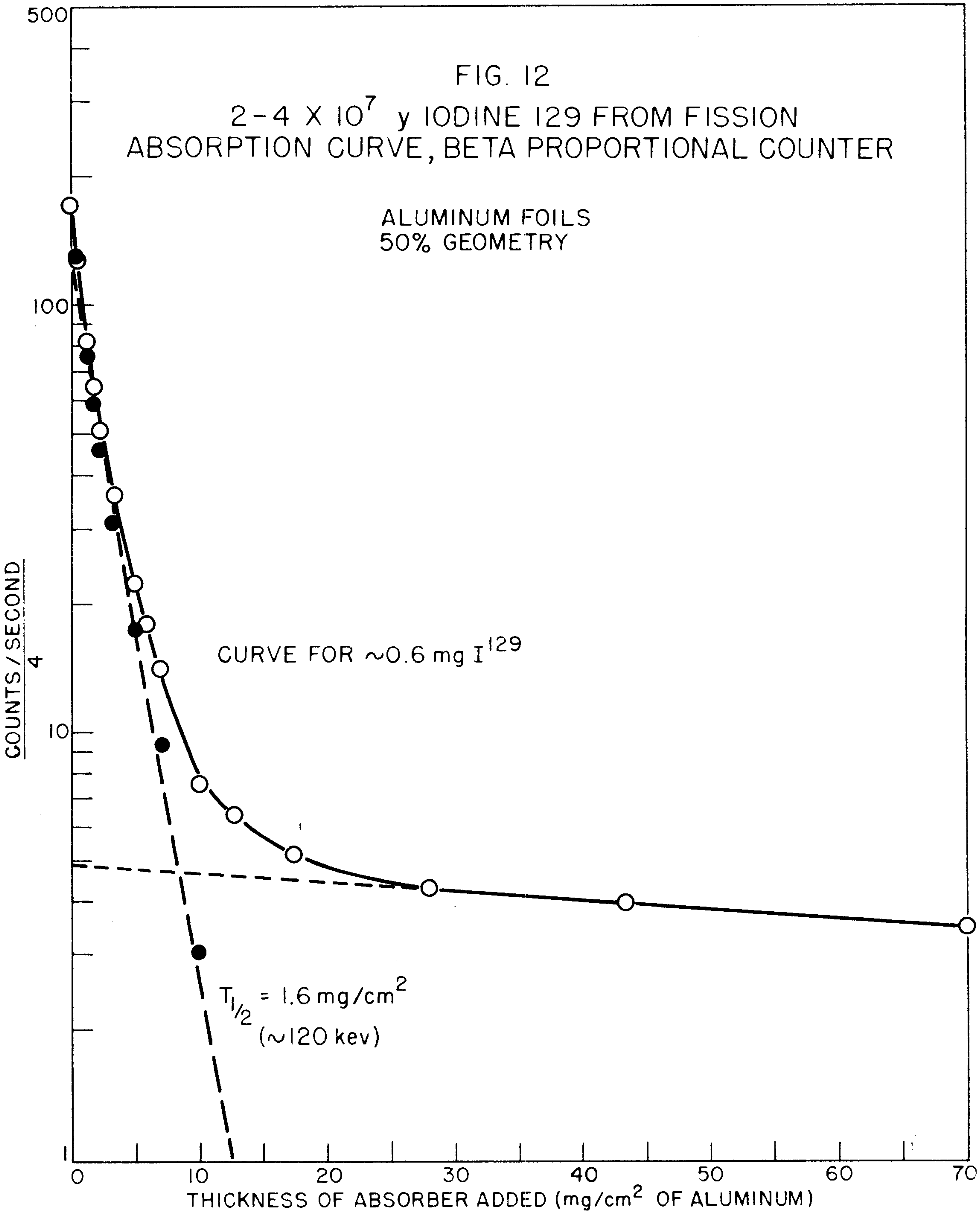

FIG. 12

2-4 X 10^7 y IODINE 129 FROM FISSION
ABSORPTION CURVE, BETA PROPORTIONAL COUNTER

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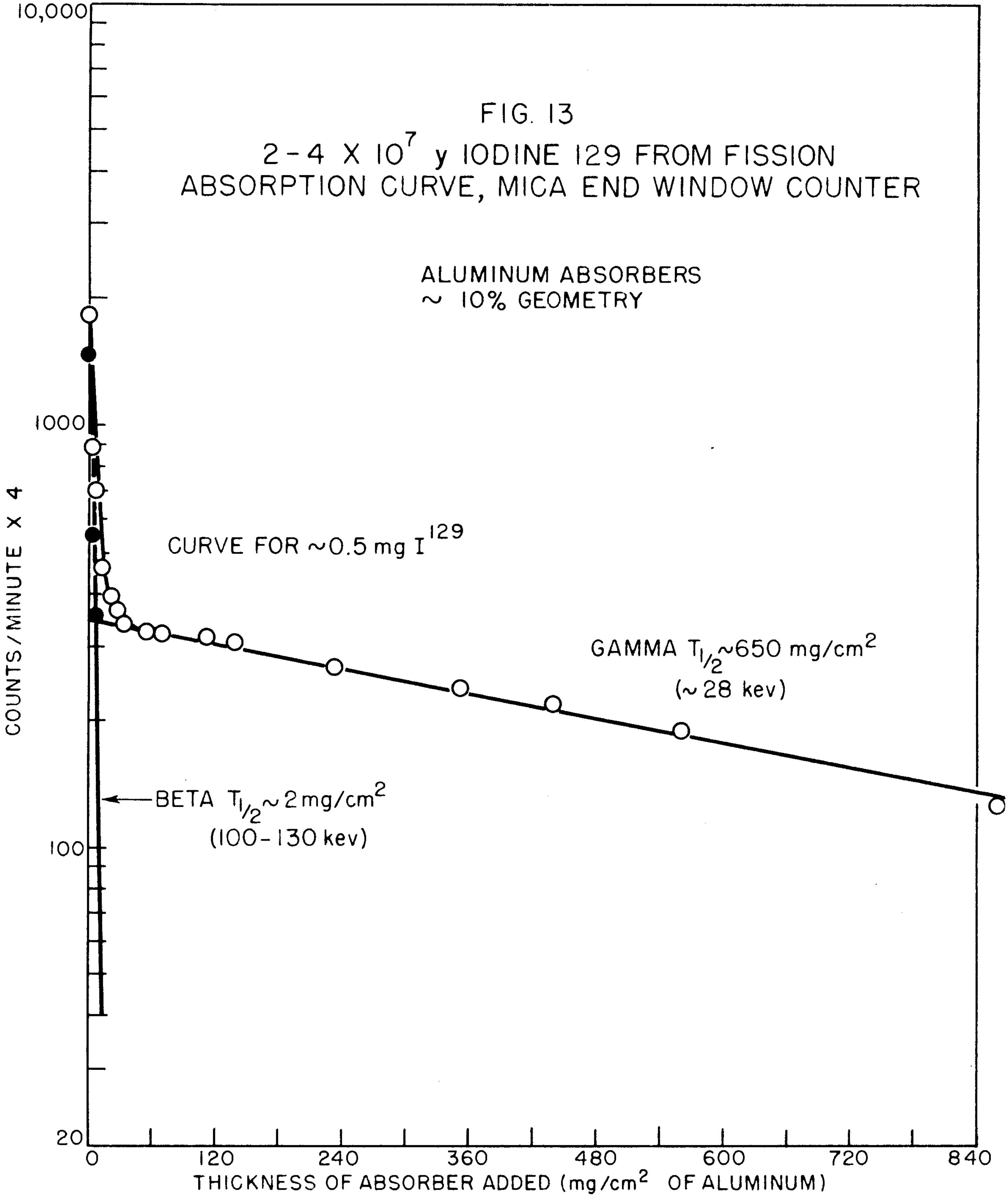
FIG. 13
$2-4 \times 10^7$ y IODINE 129 FROM FISSION
ABSORPTION CURVE, MICA END WINDOW COUNTER

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THE ABSORPTION SPECTRUM OF ELEMENT 61*

G. W. Parker, P. M. Lantz

1. *Introduction.* Since the isolation of milligrams(11) of the element 61 in chemically pure state is now almost routinely performed in this laboratory, advantage has been taken of the opportunity to investigate some of the properties of the synthetic element. Among the investigations conducted was a study of the absorption of light in the visible spectrum as ordinarily done with the rare earth elements by means of the quartz spectrophotometer.

In the fission products of uranium resulting in the chain reacting pile the 4 year isotope 147 of element 61 has been shown to occur with a yield of about 2.5%(12). Sources of mixed fission products sufficient to yield milligrams of element 61 have been isolated and the rare earth elements individually separated by ion-exchange methods to produce the first recognizable quantities of the substance of atomic number 61. While the 4 year half-life of the isotope is sufficient to permit freedom in time for handling and experimentation, in order to make investigations involving milligrams of mass it was necessary to work with curies of radioactivity.

J. A. Marinsky and L. E. Glendenin reported in 1945 the isolation and radiochemical identification of the synthetic rare earth element 61 in the uranium fission products. Later Winsberg(13) estimated its half-life through observed decay to be 3.7 years which would indicate its specific activity to be approximately 0.8 curies per milligram.

Improvements in separation techniques having made available milligram quantities of this element, determination of its specific activity (approximately 0.6 curies per milligram) by weighing and absolute beta counting was performed during the course of this absorption study.

2. *Experimental Details.* (a) Material: Prior to this absorption study, the same sample in the form of $(61)Cl_3$ was used by L. E. Burkhart, W. F. Peed,

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(11) G. W. Parker and P. M. Lantz, Oak Ridge National Laboratory Report, ORNL-75, 'The Separation of Milligram Quantities of Element 61 from Fission', June, 1948; AECD-2160, May 27, 1949.

(12) J. A. Marinsky and L. E. Glendenin, J. Am. Chem. Soc. 69, 2781 (1947).

(13) J. A. Seiler, and L. Winsberg, PPR Vol. 9B, 7.54.2 (1946).

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and E. J. Spitzer(14) (Oak Ridge Electromagnetic Plant) to record the K and L emission lines of the X-ray spectrum of element 61. About 3 mg of the sample of 61 was recovered from the X-ray tube and was tested for purity(15) before spectrophotometric study was made, by comparing copper-spark spectrograms with the known lines of the other rare earths and those characterized at this laboratory for element 61(16). Part of this sample was used by C. Feldman(17) (this laboratory) to look for "Illinium" lines reported by Harris, Hopkins, and Yntema(18).

The results of the spectrographic purity test are given in Table II.

In preparation for absorption study, the portion of the sample remaining after applying the spectrographic test above was analyzed for gross beta activity by absolute beta counting techniques(19) and was found to be 822 mc. It was then converted to the $(61)(Cl)_3^{--}$ and was transferred in 0.2 ml of 0.1 *N* HCl solution to a calibrated semi-micro quartz cell 2.5 mm × 10 mm (10 mm length of light-path).

After the study was completed the 61 was converted to the oxalate and weighed. Then the oxalate was ignited to the oxide and reweighed.

The 61 (calculated as 0.926 mg of the element) obtained as the oxide was then found to be 551 mc. On the basis of this weight-activity ratio applied to the original 822 mc the molarity (0.0472) of the solution employed in the absorption band study of the chloride was calculated.

(b) Apparatus: For this investigation a Beckman Spectrophotometer Model LD was employed using a special RCA C7032 photo-tube for measurements below 625 millimicrons and an RCA Type 919 cesium oxide photo-tube for measurements above 625 millimicrons. A defining slot 1 × 2 mm, punched from a piece of 0.004 in. steel shim stock, was inserted on the light source side of the cell, being held in place with tape. The defining slot was necessary to diminish the standard 3 × 6 mm light beam so that it would fall within the limits of the small cross section of the solution exposed. Before securing the defining slot

(14) L. E. Burkhart, W. F. Peed and E. J. Spitzer, 'The K Spectra of Element 61', Phys. Rev. 75, p. 86 (1949); 'The L Spectra of Element 61', AEC Res. Paper Y-355, February 24, 1949, to be published.

(15) Private Communication from M. Murray, Oak Ridge National Laboratory, April, 1949.

(16) D. Timma, 'The Spark Lines of Element 61', AEC Report, MonC-166, (to be published).

(17) C. Feldman, 'Note on the Arc Spectrum of Element 61', to be published (work completed April 6, 1949).

(18) J. A. Harris and B. S. Hopkins; J. Am. Chem. Soc. 48, 1585 (1926). L. F. Yntema, J. Am. Chem. Soc. 48, 1598 (1926).

(19) P. M. Lantz and G. W. Parker, to be published.

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TABLE II

Impurities found in element 61 (20-30 micrograms)

(Analyzed by the copper spark
method on a Jarrell-Ash grating
spectrograph)

ELEMENT	DEGREE OF IMPURITY	ELEMENTS NOT FOUND
Al	Trace	Ag, As, Au, B, Be, Bi
Ca	Strong	Cd, Ce, Co, Dy, Er, Eu,
Cr	Moderate	Ga, Gd, Ho, K, La, Li,
Fe	Faint Trace	Lu, Mn, Mo, Nd, Ni, Pr,
Mg	Moderate	Rb, Sb, Si, Sm, Sn, Sr,
Na	Trace	Ta, Ti, Tm, V, Zn
Pb	Very Weak	
Pt	Presence Questionable	

TABLE III

Principal absorption bands of element 61

WAVE LENGTH (m)	MOLAR EXTINCTION COEFFICIENT ($\epsilon \times 10^3$)
459.5 ± 0.5	0.7
493 ± 0.5	1.2
548 ± 0.5	2.3
629.0 ± 1.0	0.5
568 ± 0.2	2.3
685 ± 0.2	1.3
702.7 ± 0.3	1.6
737.2 ± 0.2	1.9
785.0 ± 0.2	1.1
810.0 ± 0.1	0.6

[redacted]

it was so aligned that the light emanating from it would pass directly through the liquid column in the positioned quartz-cell, without interference from the sides of the cell.

Wavelength calibration of the Beckman Spectrophotometer was done with both mercury and hydrogen arc lamps, after the instrument had been adjusted for focus of maximum light. For two of the mercury emission lines, 253.6 mμ and 546.0 mμ, and also for one of the strongest hydrogen lines, 656.27 mμ, agreement within 0.5 mμ was obtained, while for the 1014 mμ mercury line the best instrument value was 1020 mμ. This agreement in calibration seemed to be satisfactory since the most prominent absorption bands in the visible spectrum for element 61 appear in the region from 400 μu to 790 μu.

(c) **Procedure**: After the $(61)(Cl)_3$ solution was transferred to the quartz cell and the blank prepared, the cells were sealed with tape to prevent evaporation in order to insure maintenance of a constant concentration throughout the period of measurement. Transmission readings on the Beckman Quartz Spectrophotometer were taken from 350-1000 mμ at 5 mμ intervals except when a change in absorption was indicated, at which time readings at 1 mμ intervals were taken to determine accurately the wavelength at which maximum absorption was obtained.

In order to provide data on the concentration of the material used in this absorption study it was put through another purification, preparatory to weighing, by means of several reprecipitations as the oxalate and hydroxide. This repurification was considered necessary because of the contamination contributed by atmospheric dust during the transfer of solutions. Finally the oxalate was transferred to a Gooch-type 2 ml platinum crucible in which it was weighed on the basis of an assumed formula as $(61)_2O_3$ following the ignition of the oxalate in an oxygen atmosphere at 650° C. The weights obtained for 61 present, weighing as $(61)_2(C_2O_4)_3 \cdot 10\,H_2O$ and as $(61)_2O_3$, agreed within 0.3%.

Absorption studies have been made of approximately twelve different 61 preparations of various concentrations of chloride and nitrate solutions on the same calibrated spectrophotometer with remarkably good agreement. For the sake of further comparison several samples of spectrographically pure neodymium nitrate of known concentration were examined on the same instrument, and the absorption bands obtained compared favorably with those published by Rodden(20).

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(20) C. J. Rodden, J. Nat. Bur. Stds., 26, Research Paper 1395, June, 1941.

[redacted]

In order to show more clearly the weak, as well as the more prominent absorption bands, a molar extinction coefficient plot was made in the manner according to Brode$^{(21)}$ (Fig. 17). For a comparison of the bands of absorption of $Nd(NO_3)_3$ and $(61)(NO_3)_3$ relative to their position and intensities, reference is made to Fig. 16.

3. *Experimental Results.* Absorption data obtained in studies of both the $(61)Cl_3$ and $(61)(NO_3)_3$ seem to indicate that they possess the same absorption characteristics in solution, Figs. 14 and 15.

It is interesting to note in Fig. 17 that the major bands of absorption of element 61 are approximately the same in number and have the same general location in the visible spectrum as those of its rare earth neighbor, neodymium. However, by referring to Fig. 16, it is evident that the closest any of the prominent bands for neodymium approach those of element 61 is of the order of 8 mμ which is considerably outside the limits of experimental error. The maximum deviation observed in the location of the ten major absorption bands was less than 1.0 mμ.

Table III summarizes the positions and relative intensities of the ten major bands observed. Bands 548.5 ± 0.5 mμ, 568.2 ± 0.2 mμ, and 737.2 ± 0.2 mμ due to their greater intensity could conceivably be used for the purpose of identification of very low concentrations of element 61 solutions.

No investigation was made to determine whether the molar extinction coefficients changed with concentration.

The very weak band appearing at 402.5 ± 0.5 mμ is assumed to be contributed by the stable samarium isotope 147 resulting from beta decay of 4.0 yr element 61. This particular spectral band is reported by Yntema$^{(22)}$ as being the most prominent of the samarium bands. The remaining spectral bands of samarium, however, do not appear in concentrations of element 61 which are three to four times as high as is illustrated in Fig. 17. Due to the fact that measurement of absorption in solution does not distinguish between two adjacent absorption bands separated by only a few Angstroms, comparison with the absorption by the crystals will be undertaken soon. It is hoped that this would also establish whether this weak band at 402.5 ± 0.5 mμ belongs to samarium or to element 61.

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(21) W. R. Brode, "Chemical Spectroscopy", John Wiley, New York, Second Edition (1943).

(22) L. F. Yntema, J. Am. Chem. Soc. 48, 1598 (1926).

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NOT CLASSIFIED
DWG. 7207

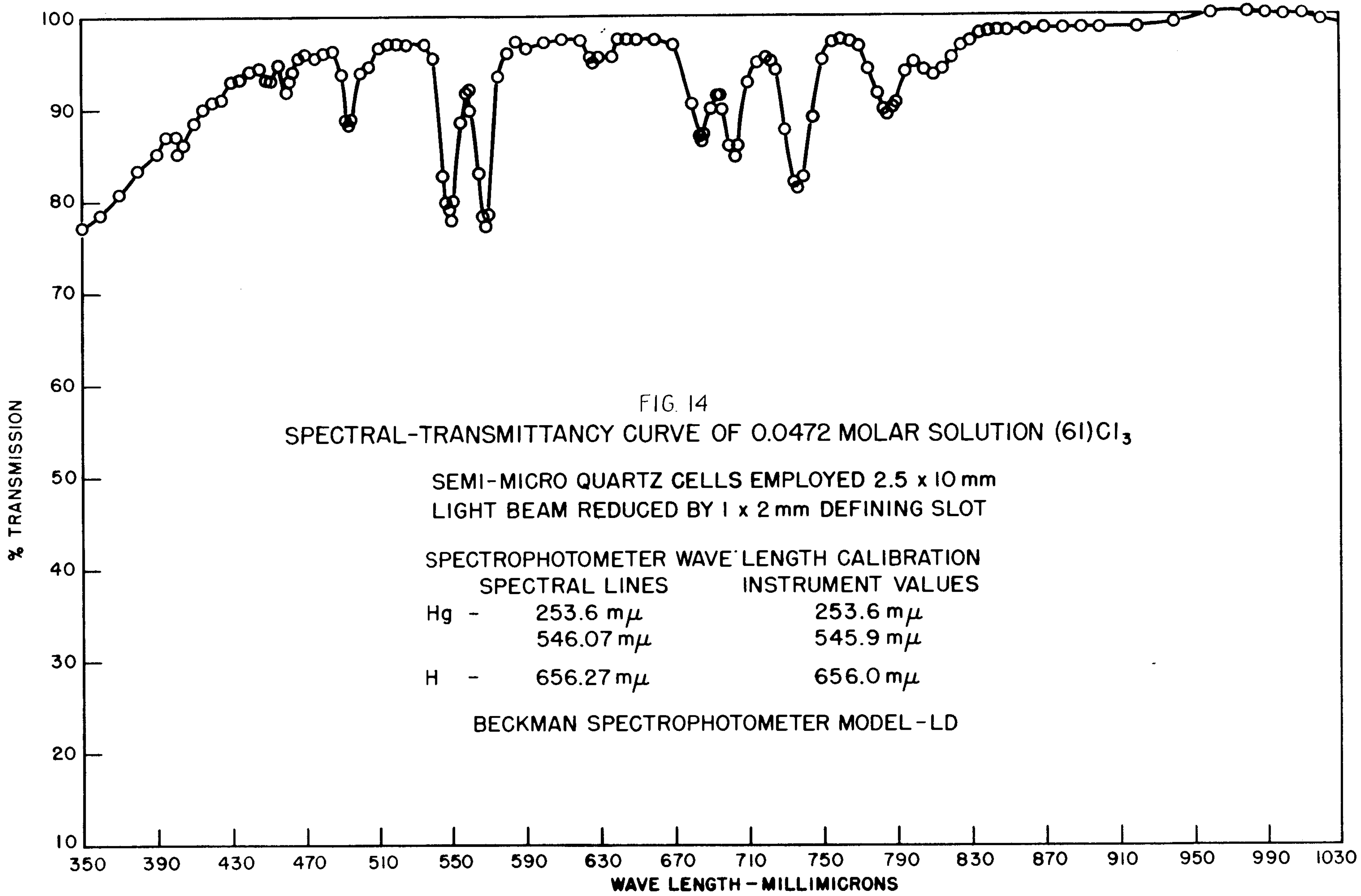

FIG. 14

SPECTRAL-TRANSMITTANCY CURVE OF 0.0472 MOLAR SOLUTION $(61)Cl_3$

SEMI-MICRO QUARTZ CELLS EMPLOYED 2.5 x 10 mm
LIGHT BEAM REDUCED BY 1 x 2 mm DEFINING SLOT

SPECTROPHOTOMETER WAVE LENGTH CALIBRATION

	SPECTRAL LINES	INSTRUMENT VALUES
Hg –	253.6 mμ	253.6 mμ
	546.07 mμ	545.9 mμ
H –	656.27 mμ	656.0 mμ

BECKMAN SPECTROPHOTOMETER MODEL-LD

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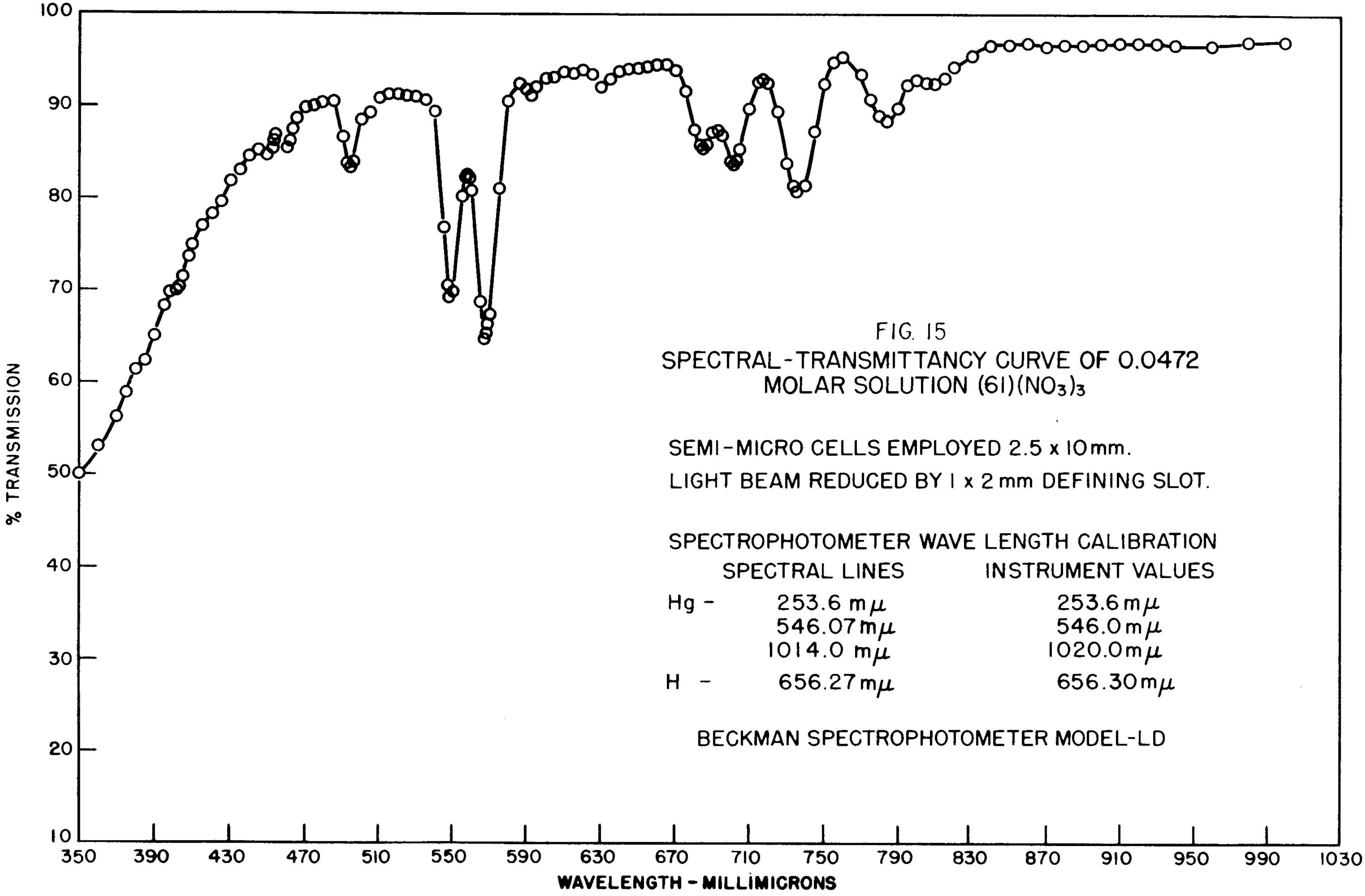

FIG. 15

SPECTRAL-TRANSMITTANCY CURVE OF 0.0472 MOLAR SOLUTION (61)$(NO_3)_3$

SEMI-MICRO CELLS EMPLOYED 2.5 x 10 mm.

LIGHT BEAM REDUCED BY 1 x 2 mm DEFINING SLOT.

SPECTROPHOTOMETER WAVE LENGTH CALIBRATION

	SPECTRAL LINES	INSTRUMENT VALUES
Hg -	253.6 mμ	253.6 mμ
	546.07 mμ	546.0 mμ
	1014.0 mμ	1020.0 mμ
H -	656.27 mμ	656.30 mμ

BECKMAN SPECTROPHOTOMETER MODEL-LD

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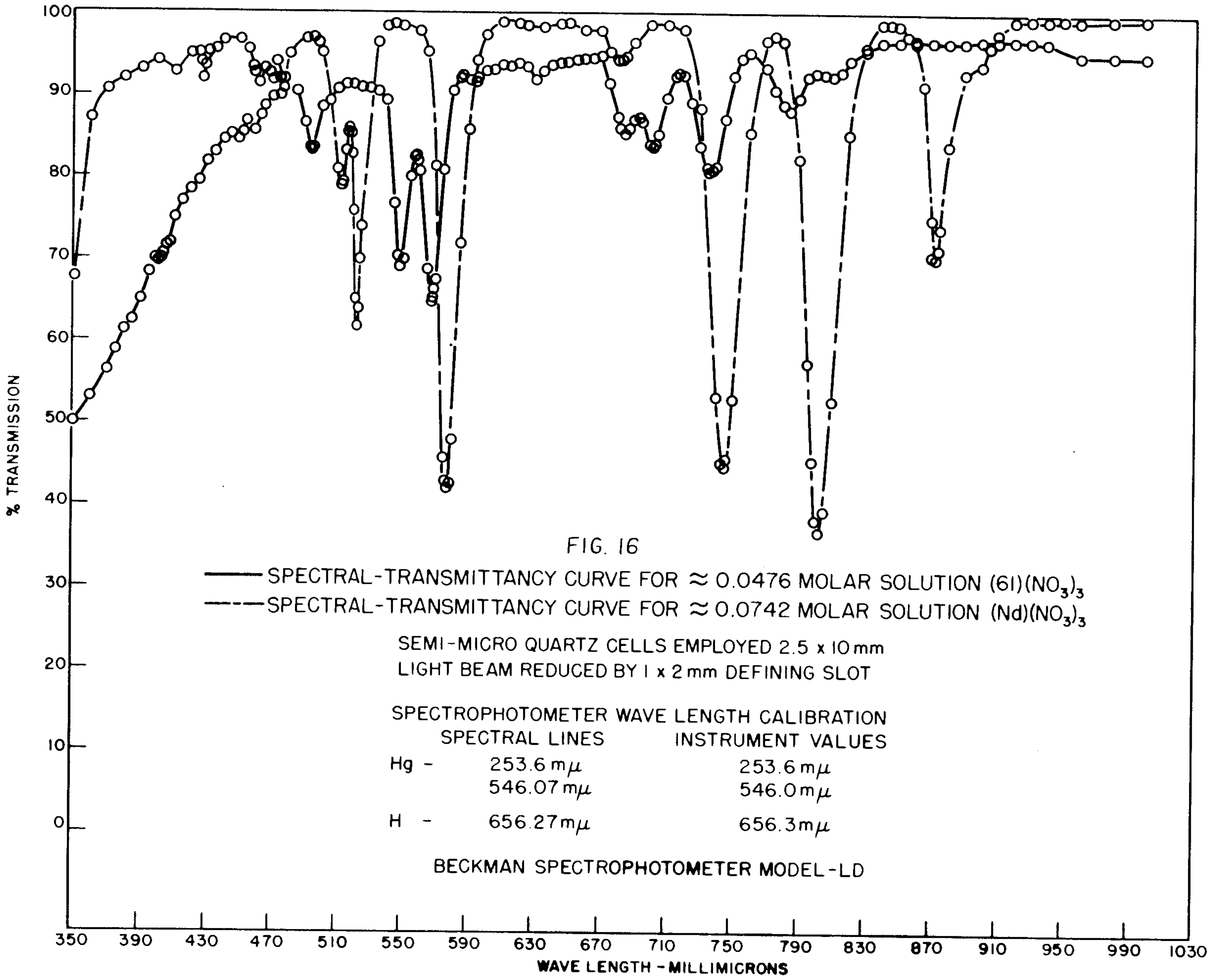

FIG. 16

——— SPECTRAL-TRANSMITTANCY CURVE FOR ≈ 0.0476 MOLAR SOLUTION $(61)(NO_3)_3$

– – – SPECTRAL-TRANSMITTANCY CURVE FOR ≈ 0.0742 MOLAR SOLUTION $(Nd)(NO_3)_3$

SEMI-MICRO QUARTZ CELLS EMPLOYED 2.5 x 10 mm
LIGHT BEAM REDUCED BY 1 x 2 mm DEFINING SLOT

SPECTROPHOTOMETER WAVE LENGTH CALIBRATION

	SPECTRAL LINES	INSTRUMENT VALUES
Hg -	253.6 mμ	253.6 mμ
	546.07 mμ	546.0 mμ
H -	656.27 mμ	656.3 mμ

BECKMAN SPECTROPHOTOMETER MODEL-LD

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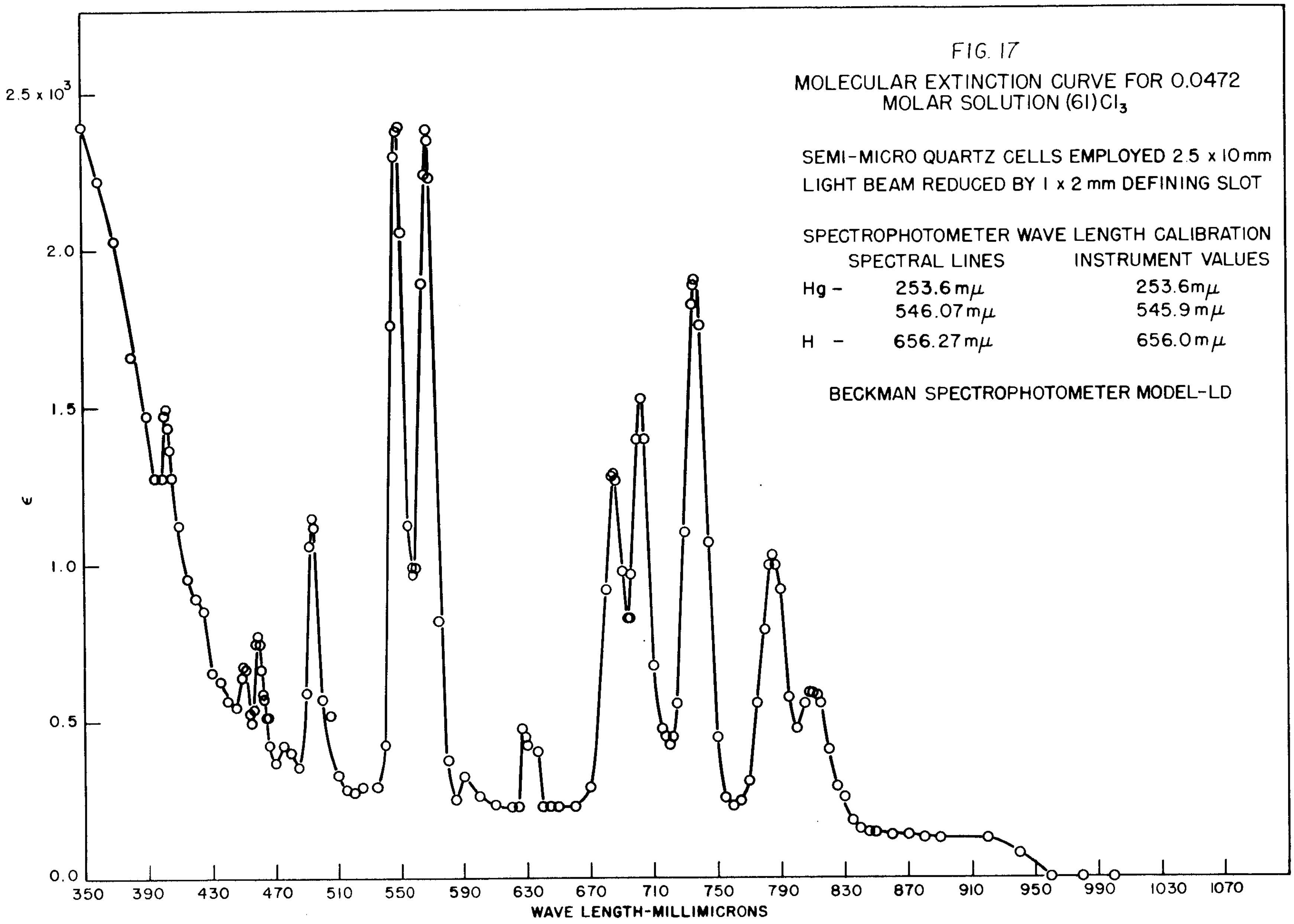

FIG. 17

MOLECULAR EXTINCTION CURVE FOR 0.0472 MOLAR SOLUTION $(61)Cl_3$

SEMI-MICRO QUARTZ CELLS EMPLOYED 2.5 x 10 mm
LIGHT BEAM REDUCED BY 1 x 2 mm DEFINING SLOT

SPECTROPHOTOMETER WAVE LENGTH CALIBRATION

	SPECTRAL LINES	INSTRUMENT VALUES
Hg -	253.6 mμ	253.6 mμ
	546.07 mμ	545.9 mμ
H -	656.27 mμ	656.0 mμ

BECKMAN SPECTROPHOTOMETER MODEL-LD

[redacted]

It was observed that the crystalline salts, chloride and nitrate, of element 61 displayed different colorings. This introduced the question of whether in solution these salts would have the same optical absorption characteristics; however, when this test was made, it was noted that the coloring of the solutions was visibly the same, i.e., pink or rose. This fact was later indicated by the failure to find any apparent difference in the two spectra.

Other chemical forms of element 61, such as the hydroxide, oxalate and oxide all appear pink or rose.

It was of interest to compare the results of this study of the synthetic element with those reported in 1926 on natural material by B. S. Hopkins, et al$^{(18)}$. Harris and Hopkins concluded that the most probable bands were in the positions 5816 Å and 5123 Å. A description of the methods used by Hopkins, et al., in studying absorption is not given in the papers cited. The absorption data presented here were obtained with the element in solution and in that form the presence of these lines is not indicated.

4. *Summary.* (a) The absorption bands of element 61 in the visible spectrum are observed to resemble those of neodymium, both in number and in intensity but are distinctly separable from the neodymium bands by at least 8 mμ.

(b) The absorption bands of element 61 are in the same position and of the same magnitude for both the chloride and nitrate solutions.

(c) The most prominent absorption bands for a solution of element 61 are to be found in positions 493.5 ± 0.5 mμ, 548.5 ± 0.5 mμ, 568.0 ± 0.2 mμ, 685.0 ± 0.1 mμ, 702.7 ± 0.3 mμ, 737.2 ± 0.2 mμ, and 785.0 ± 0.1 mμ.

SEARCH FOR Mo^{93}

G. E. Boyd and Q. V. Larson

Further attempts have ceen carried out during the pass quarter to produce Mo^{93} by neutron irradiation of enriched Mo^{92}. It may be reported immediately that thus far no indication of the reported 6.7 h activity attributed to Mo^{93} has been obtained. It is of interest, however, that this period, reported to be produced by Cb(d,2n), Cb(p,n) and Zr(α,n), is now regarded as an excited

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state of Mo^{93} which decays with the emission of conversion electrons and a 1.6 Mev gamma ray. [Kundu and Pool, Bull. Am. Phys. Soc., **24**, (4) 31 April 28-30 (1949)]. These characteristics are notably different from the 0.3 and 0.7 Mev β^+ particles previously reported by these authors, and may serve to explain the failure of our attempts (ORNL 336, p.38) to find a Mo decay with the emission of positively charged particles. In view of the newly purported radiation characteristics of Mo^{93} several more neutron bombardments of Mo^{92}, without and with chemistry, were made and a ~7 hour period was sought in the decay of the gamma radiations measured through 5 g Pb/cm^2. An entire 10 mg Mo^{92}O$_3$ sample irradiated for seven hours gave a counting rate of only about 1500 c/m (sample at 10% geometry) under these conditions. The decay of this sample upon which no chemistry was done was resolvable into two periods: 17.1 h and 67 h, the counting rates being 1450 and 200 c/m at the end of bombardment.

A second bombardment of 17 h on a 10 mg aliquot of Mo^{92}O$_3$ was made so as to enhance the indicated 17.1 h period and chemistry was performed. Only about 230 c/m were observed through 5 gm Pb/cm^2 and this decayed with an approximate 67 h half-life. It is concluded that either the 6.7 h Mo^{93} does not exist, or that the cross section for its formation by slow neutron capture in Mo^{92} is less than 10 μb.

In order to investigate the possibility that Mo^{93} may possess a very long half-life, 500 mg samples of Mo metal which had been irradiated in the ORNL pile for one year (Tc production bombardment #2) and had cooled for over 700 days were purified chemically to remove the Tc, Re, W, Fe and Cb contaminants known to be present from earlier studies. An aluminum absorption curve has indicated Cb Kα X-rays in high relative abundance together with conversion electrons and a small amount of gamma radiation. The age of the sample allows a lower limit of >70 d to be set as the half-life. The study of this seemingly new long-lived Mo activity will continue.

SHORT-LIVED TECHNETIUM ACTIVITIES IN U^{235} FISSION

G. E. Boyd and Q. V. Larson

Work during the past quarter on the program of identifying some of the short-lived, fission produced Tc isotopes has consisted mainly in the repeated

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rapid isolation of a molybdenum fraction from 500 mg amounts of uranium irradiated in the pile for several minutes followed by measurements of the growth and decay of the radiations from these fractions through varying thicknesses of Al and-or Pb. No new Mo activities have been observed, although the existence of an 11 m $Mo^{(102)}$ [O. Hahn and F. Strassmann, Naturwiss., 29, 285 (1941) in U^{235} fission has been confirmed. The Tc^{102} daughter of this activity possesses a half-life of <25 s and appears to decay with the emission of β^- particles of about 1900 mg Al-cm^2 range (e.g., about 3.7 Mev). The slightly different half-lives of 17 m and 15 m were observed for the 14.6 m Mo^{101} and 14.0 m Tc^{101} activities, respectively. The radiation characteristics of these latter nuclides appear to agree fairly well with those previously reported. Further characterization of the energies of the radiations of both the 17 m Mo^{101} and its 15 m Tc^{101} daughter is intended, however.

From the experiments with Mo it is possible to state that those radionuclides of mass >102 probably possess half-lives of <2 m. No periods in fission Mo longer than 67 h have been observed.

THE RADIONUCLIDES OF TIN

C. M. Nelson and G. E. Boyd

A preliminary survey of the activities produced by the neutron irradiation of the calutron enriched stable tin isotopes has now been completed using the $Sn^{112}O_2$, $Sn^{114}O_2$, and $Sn^{115}O_2$ preparations. By means of a 30 minute irradiation of each of these enriched samples it has been possible to assign the 30-33 m period noted earlier in the bombardment of $Sn^{116}O_2$ and $Sn^{117}O_2$ to mass 113. An attempt was made to determine the energies of the radiations associated with this period but the growth of a short-lived indium daughter activity into the irradiated sample made difficult the interpretation of the gross absorption in aluminum. Apparently the 30 m activity decays with charged particles of 1.2 Mev energy and possibly also by K-capture since X-rays in the In-Sn region were found in good yield. Evidently the 30 m Sn^{113} is isomeric with the known long-lived period at mass 113. Approximately 80 days after irradiation the same $Sn^{112}O_2$ sample which gave the 30 m activity in maximum yield has exhibited an almost pure 120 day decay.

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No chemical separations or purifications have been conducted with the samples irradiated thus far. In all cases, the spectrochemical analyses from the Y-12 group (Keim, Weaver and co-workers) have indicated the enriched tin preparations to be remarkably free from impurities. Immediately in the future, however, chemistry will be employed to determine if the as yet unassigned 80 m, 3 h, 17 h, and 13-17 d periods belong to tin.

Two further incidental experiments have been conducted to determine if there were any highly energetic gamma radiations associated with the tin activities. Approximately a 20 gm sample of ordinary (C.P. grade) SnO_2 was irradiated in the pile for 3 hours and then placed in the D_2O-photoneutron apparatus of Dr. M. H. Feldman. Since the (γ,n) threshold for deuterium is known to be 2.2 Mev, quantum radiations emitted by Sn of greater energy than this value should produce neutrons which will be counted. The observed neutron counting rate, however, did not differ from the background for the apparatus. In a second trial, 50 gm of SnO_2 was irradiated for one week and then measured with a negative result.

HARD GAMMA EMITTERS IN FISSION

H. A. Levy and M. H. Feldman

1. *Radiation Characteristics of* I^{134}. The data on the decay of I^{134} through the various absorbers which were reported last quarter[23] have been re-analyzed by least squares procedures. The background of 22-hour I was estimated from the graph and subtracted. The differences were then fitted to an exponential with both half-life and initial activity treated as unknowns and with individual measurements suitably weighted, taking account of the variance of the counts and the estimated variances of the subtracted background. Plotting the initial activities against absorber thickness gives a revised absorption curve which is not significantly different from that obtained by graphical methods and reported last quarter. Results of this analysis may be summarized as follows:

(a) There is a hard β component, the maximum energy of which lies between 3.5 Mev and 4.2 Mev.

(b) There is a softer β component, the maximum energy of which lies between 1.5 and 1.75 Mev, depending on which of the limits is taken as the energy of

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(23) Levy, H. A. and Feldman, M. H., ORNL 336, p. 46 et seq.

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the harder component. Data taken on the β-ray spectrometer, less reliable because of low intensities and other uncertainties, indicate the energy to be 1.7 Mev.

(c) The half-life of this iodine nuclide has heretofore been taken as 54 minutes. Our data indicate a half-life of 50.8 minutes with a mean deviation, from 10 curves, of ± 1.4 minutes. Our decay curves(23) indicate a complete absence of 6.7 hr I and of 2.4 hr I, and it is assumed that the presence of small quantities of these species gave previous determinations a slightly high value.

2. *Absorption Coefficients of Hard γ Rays.* In order to determine the energies of hard γ's (above 2.2 Mev) such as the one found in I^{134}(23), it was necessary to construct an absorber rack over our heavy water tank. The shape of the heavy water tank was changed as was the construction of the fission chamber to obtain greater overall efficiency in counting (see Fig. 18 for schematic representation of this apparatus). In a measurement, the sample is lowered into the lead shield and absorbers, which may be 0.368 in. Al or 0.250 in. Pb sheets, are placed between the shield and the tank of heavy water. Neutrons ejected from the deuterium nuclei by the γ rays are counted by means of the fissions they cause in a layer of U^{235} in the fission chamber. The geometry of the sample position is adjustable by means of the threaded exterior of the lead shield which can be raised or lowered.

The advantage of this apparatus over an ordinary Geiger tube absorption set-up is that there exists a threshold energy of 2.2 Mev for countable γ's. Thus, degraded radiation softer than 2.2 Mev is not detected. This method gives an opportunity to check theoretical absorption coefficients of various materials for γ energies above 2.2 Mev. Heitler's(24) calculated absorption coefficients as a function of γ energy are plotted in Figs. 19-20. There is, of course, some uncertainty in the significance of the effective absorption coefficient we measure, because of the unusually large angle subtended by the detector. In any case, however, these measurements serve as a calibration of the method and apparatus.

The experiment has been carried out with Ga^{72}, Na^{24}, and Mn^{56} as γ sources; the gallium emitted two hard γ's.

(a) **Sodium:** The absorption curves for this hard γ emitter are given in Fig. 21. The usual corrections, such as that for decay, were applied, and the data were fitted to an exponential by a least squares procedure. The Al half

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(24) Heitler, W., The Quantum Theory of Radiation, Oxford Press, London, 1936.

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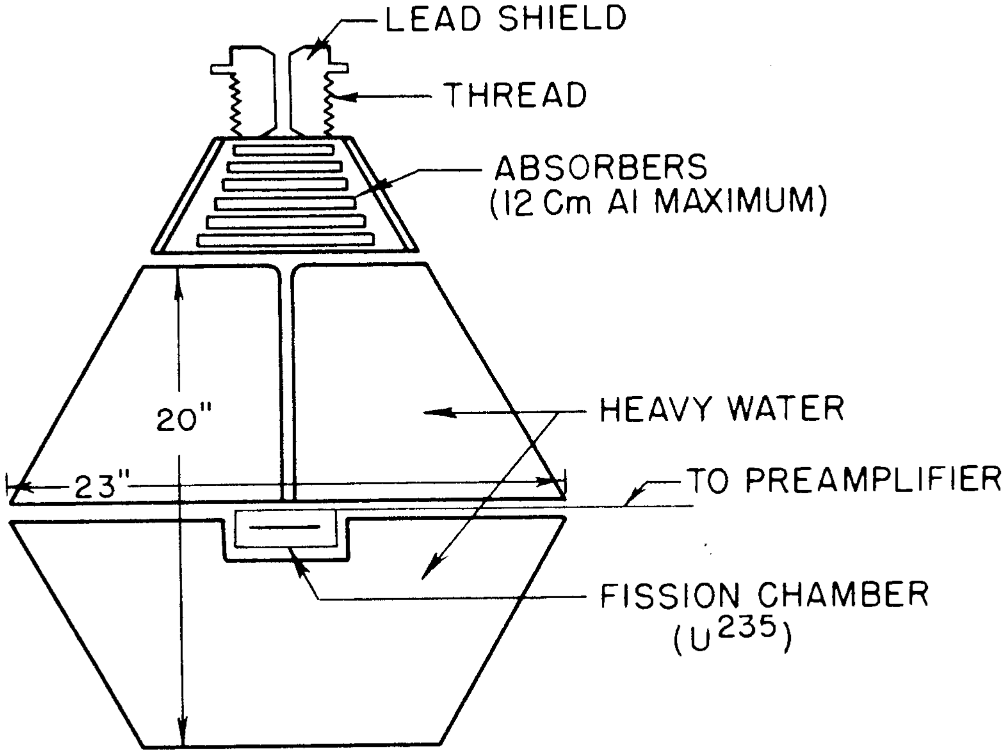

FIG. 18

GAMMA ABSORPTION APPARATUS

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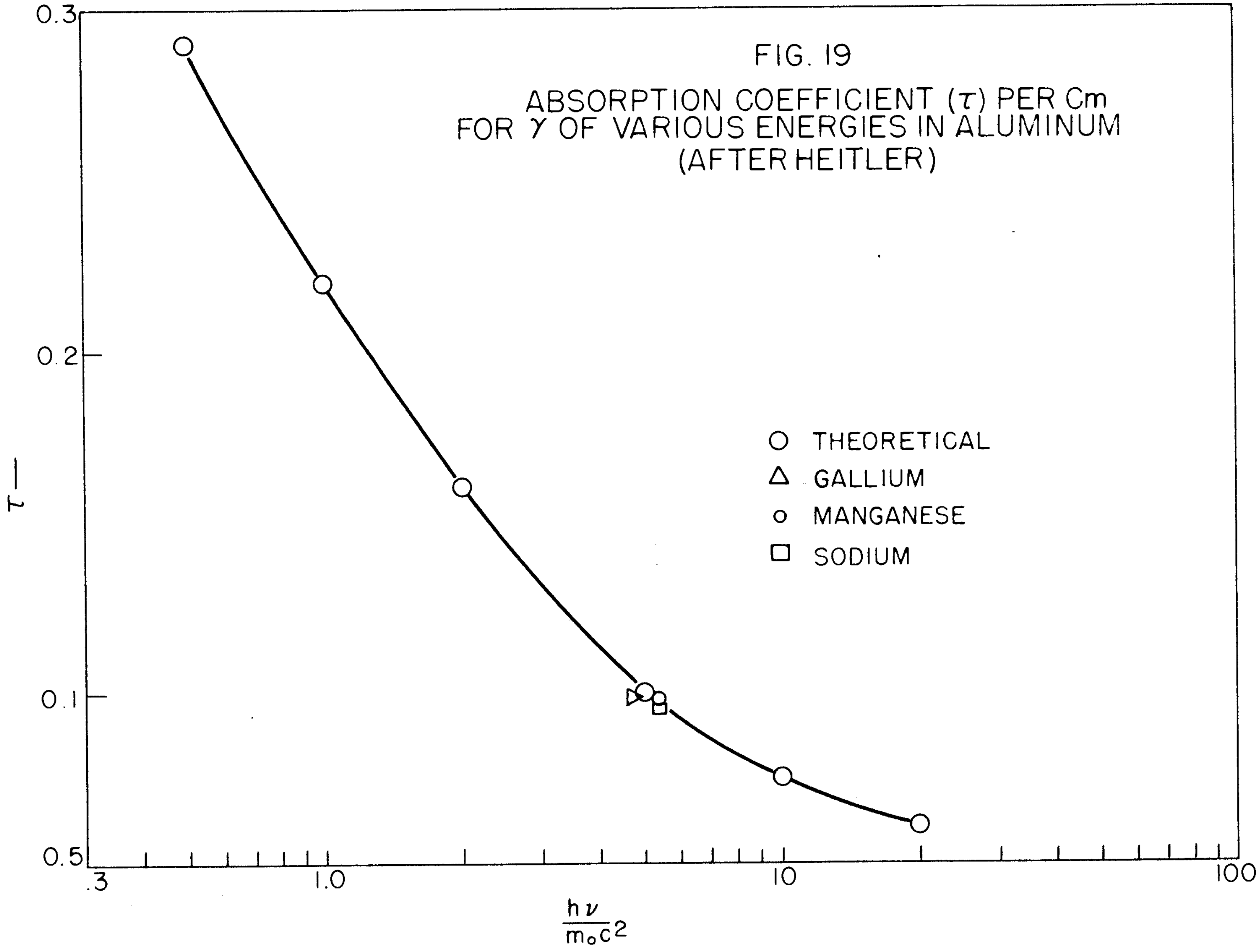

FIG. 19

ABSORPTION COEFFICIENT (τ) PER Cm FOR γ OF VARIOUS ENERGIES IN ALUMINUM (AFTER HEITLER)

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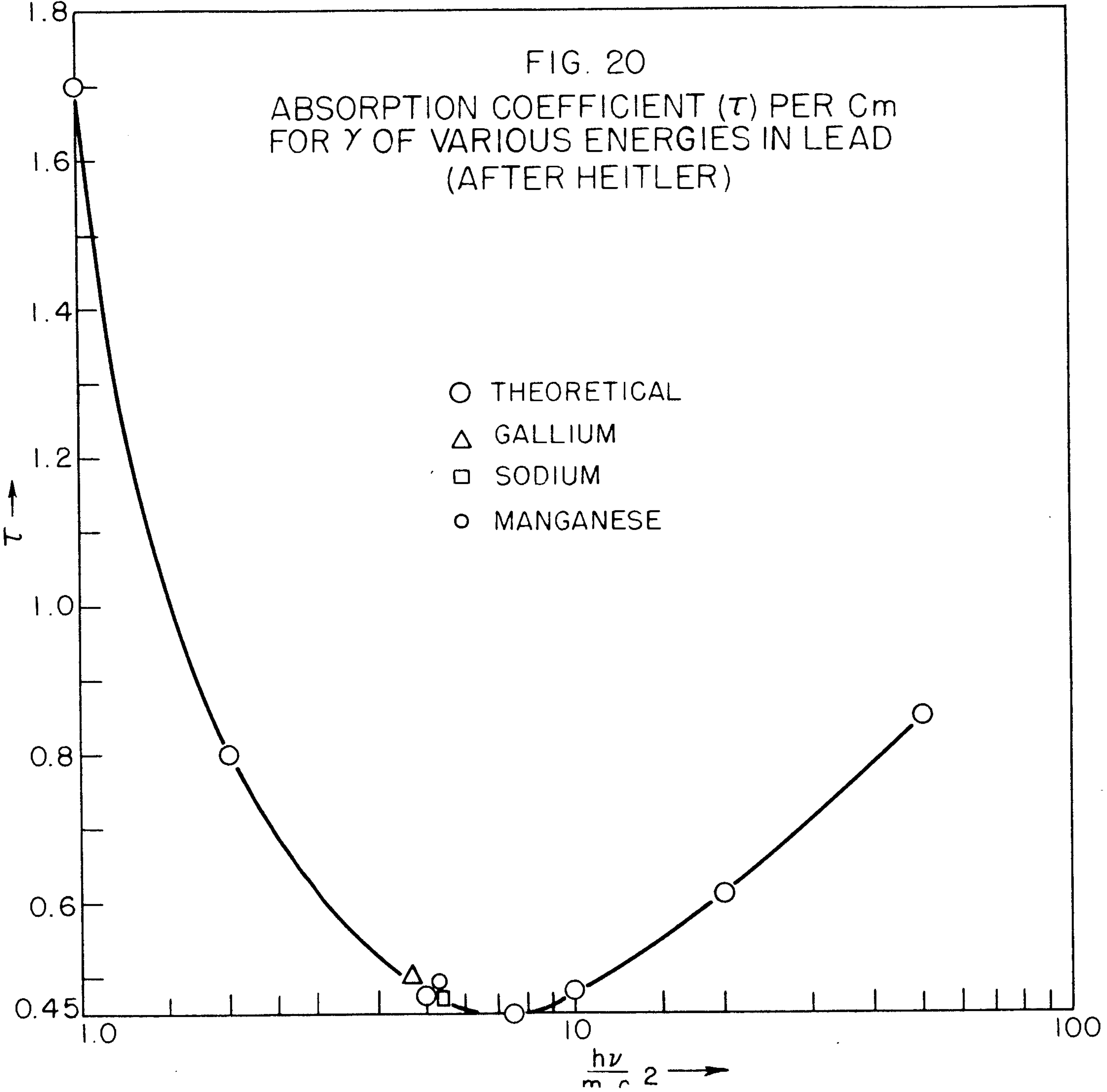

FIG. 20

ABSORPTION COEFFICIENT (τ) PER Cm FOR γ OF VARIOUS ENERGIES IN LEAD (AFTER HEITLER)

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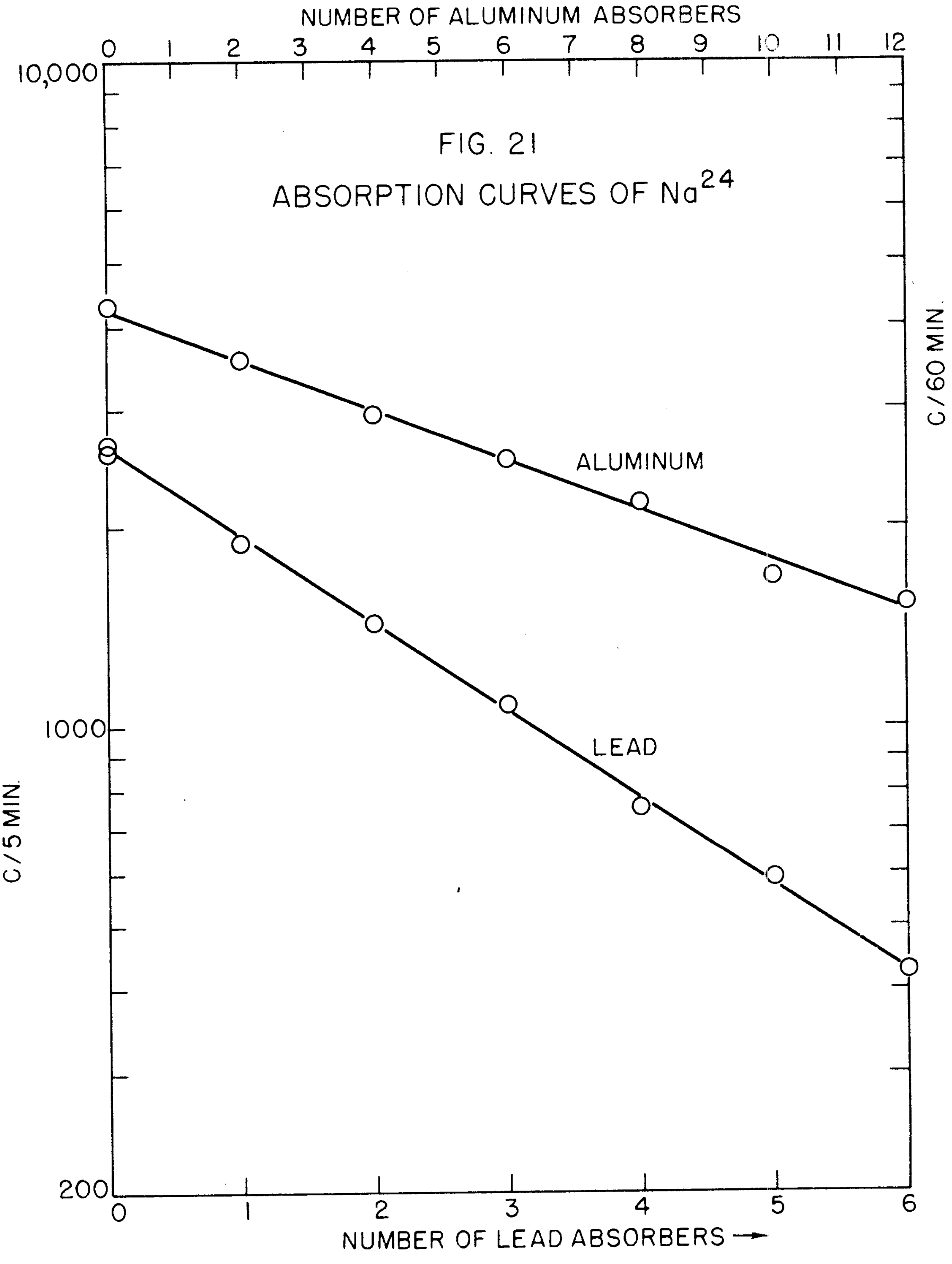

FIG. 21

ABSORPTION CURVES OF Na^{24}

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thickness, 7.80 absorbers, each 0.368 in. thick, corresponds to an absorption coefficient, τ of 0.951 cm^{-1} (see Fig. 19 for this point plotted on the theoretical curve). The Pb half thickness, 2.33 absorbers, each .250 in. thick, corresponds to a τ of 0.468 cm^{-1}. The Na samples gave a 14.8 hr half-life for the hard γ.

(b) Gallium: The absorption curves for this hard γ emitter are given in Fig. 22. The τ calculated from the Al absorption data is plotted in Fig. 19. This point, actually a composite for the two γ's(25), 2.51 and 2.21 Mev, fits the theoretical curve, assuming approximately equal abundances and counting efficiencies for the two γ's.

The decay curve for these hard γ's gave a half-life of 13.7 hrs which is within 4% of the value, 14.1, given by Seaborg and Perlman in their compilation(26) The decay was followed through one-half-life.

(c) Manganese: The absorption curves for this hard γ emitter are given in Fig. 23. The τ's calculated from these data are plotted in Figs. 19-20 and fit the theoretical curves very well.

The theoretical absorption coefficients are thus checked in the region 5 m_0c^2, where little or no experimental evidence was formerly available. In addition, we are able to make accurate γ energy measurements and have obtained some empirical calibrating points, relating known γ energies to an effective absorption coefficient.

It is hoped to check other hard γ emitters, such as La^{140}, by this means and also to use other materials, such as C and Fe, for absorbers.

3. *Hard γ from 6.7 hr I^{135}.* In an attempt to get a sufficient activity of the hard γ in 51 minute I^{134}, previously observed(23), so that an absorption curve might be taken, 5 slugs (1100 gms each) were irradiated in the Oak Ridge reactor for 4 hours. They were chemically processed* according to procedures previously used and described(27) by the Parker, Brosi, *et al.*, groups. This processing took about 7 hours from the time of pile shutdown to the time the sample was given to us. It was hoped that the activity of the I^{134} would still be appreciable, in spite of the long decay time, because of the large amount of material originally used.

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* This extremely high level sample was handled for us by G. W. Parker, G. Herbert, and G. E. Creek. We take this opportunity to thank them for their generosity.

(25) Haynes, S. K., ORNL 14 (1948).

(26) Seaborg, G. and Perlman, I. Rev. Mod. Phys. 20, (1948).

(27) Brosi, A. R., Mon-N-432, p. 70.

[redacted]

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DWG. 7324

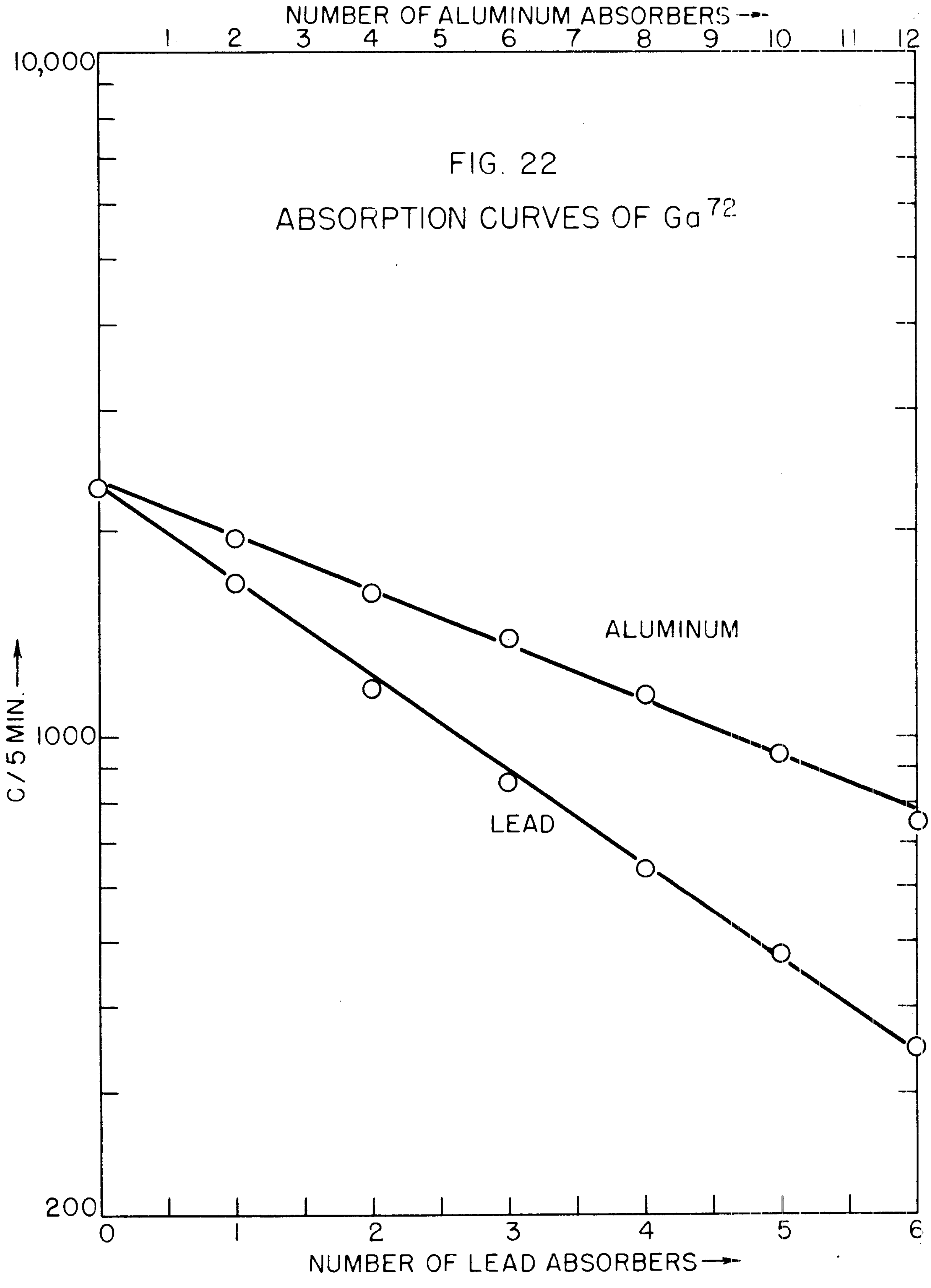
FIG. 22

ABSORPTION CURVES OF Ga^{72}

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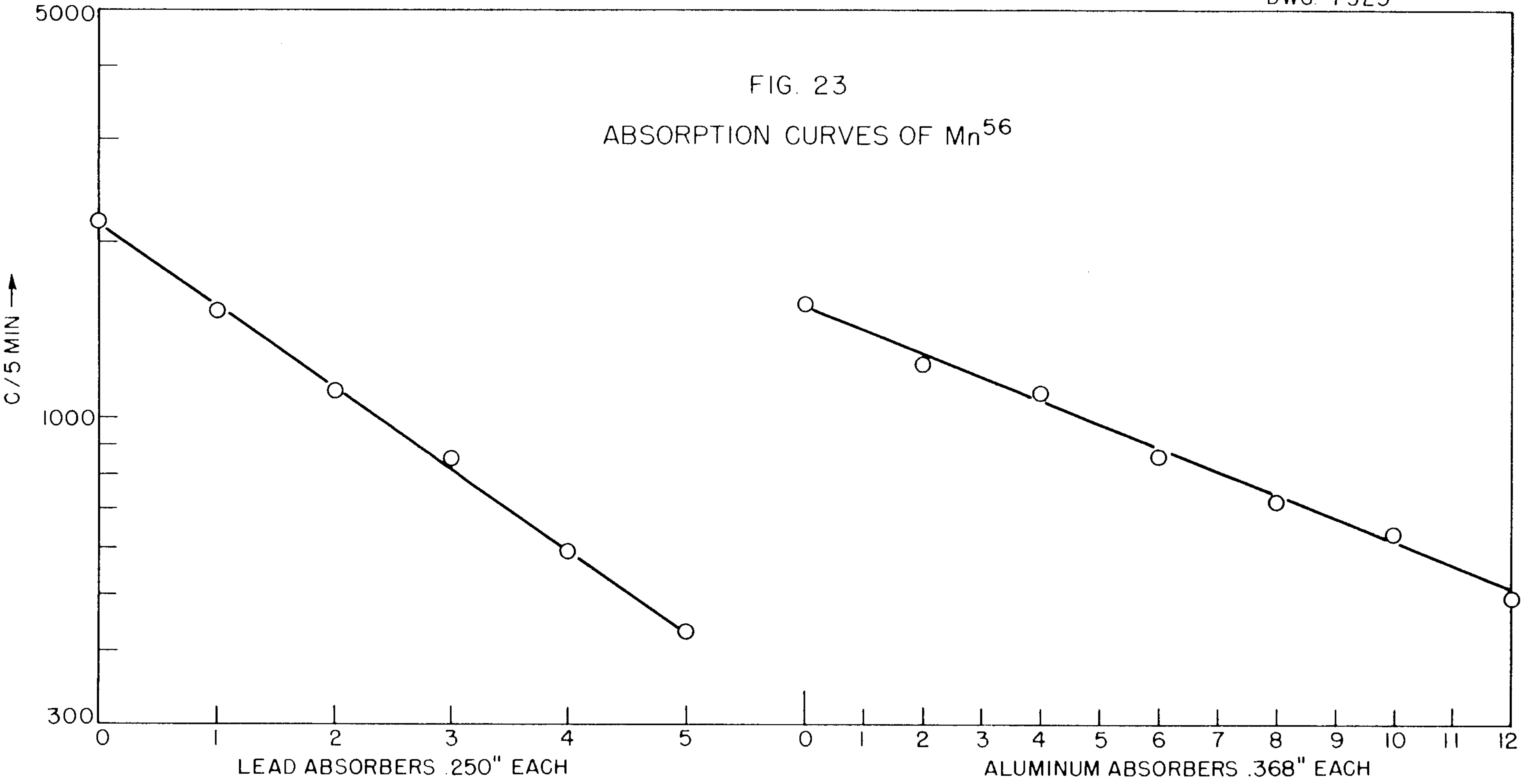

FIG. 23

ABSORPTION CURVES OF Mn^{56}

[redacted]

The sample, placed at the center of our tank (100% geometry) gave 4000 c/5 minutes. Absorption and decay curves were carried on simultaneously. The decay data taken with the sample at the center of the tank are given graphically in Fig. 24. It is immediately apparent that the activity is 6.7 hr rather than 51 minute I. The maximum activity to be assigned to the 51 minute I at the very beginning of the run was 500 c/5 min. This actually agrees very well with the activities we had previously been able to obtain using smaller quantities of uranium. Although the chemical procedures were different, the yields were probably comparable, and the yields in the present method are known to be high. The 6.7 hr half-life was assigned to the basis of the decay at center of tank, Fig. 24. The sample was also followed in a high pressure ion chamber, calibrated by A. R. Brosi for 6.7 hr I, after the hard γ measurements were completed. This gave an estimate of the absolute disintegration rate so that we could estimate the fraction of disintegrations giving a hard γ. From the disintegration rate of I^{135} in our sample at 5:18 AM, 5/22/49, 9.9 millicuries, the observed hard γ counting rate, 80 counts/5 minutes, and an estimated counting efficiency as measured with a similarly calibrated sample of Na^{24} 3.91×10^{-7} counts/hard γ emitted**, we estimate the abundance of hard γ's in I^{135} as 1.14% of the disintegrations. This constant, 1.14%, is of value in elucidating the decay scheme of 6.7 hr I^{135}.

In Fig. 25 are shown the measurements through the various absorbers. The 6.7 hr half-life was then superimposed on each set of points corresponding to a particular absorber decay curve; these were all extrapolated to a zero time, the initial amplitudes thus being determined. These initial amplitudes are plotted as a function of absorber thickness in Fig. 26. The half-thickness, 7.25 Al absorbers each 0.368 in. thick, corresponded to a γ of 0.102 which, on the theoretical curve (Fig. 19), corresponds to 2.4 Mev.

Previously observed γ's in I^{135} include 0.51 and 1.8 Mev. Of these, the 1.8 may be also a crossover γ. The 2.4 Mev γ ray may correspond to a crossover transition in competition with the two softer γ's in cascade.

** This value for the counting efficiency is higher than previously reported for our former equipment by the factor 1560/1079 which represents the increased over-all counting efficiency of our improved equipment as given by standard Ra counts.

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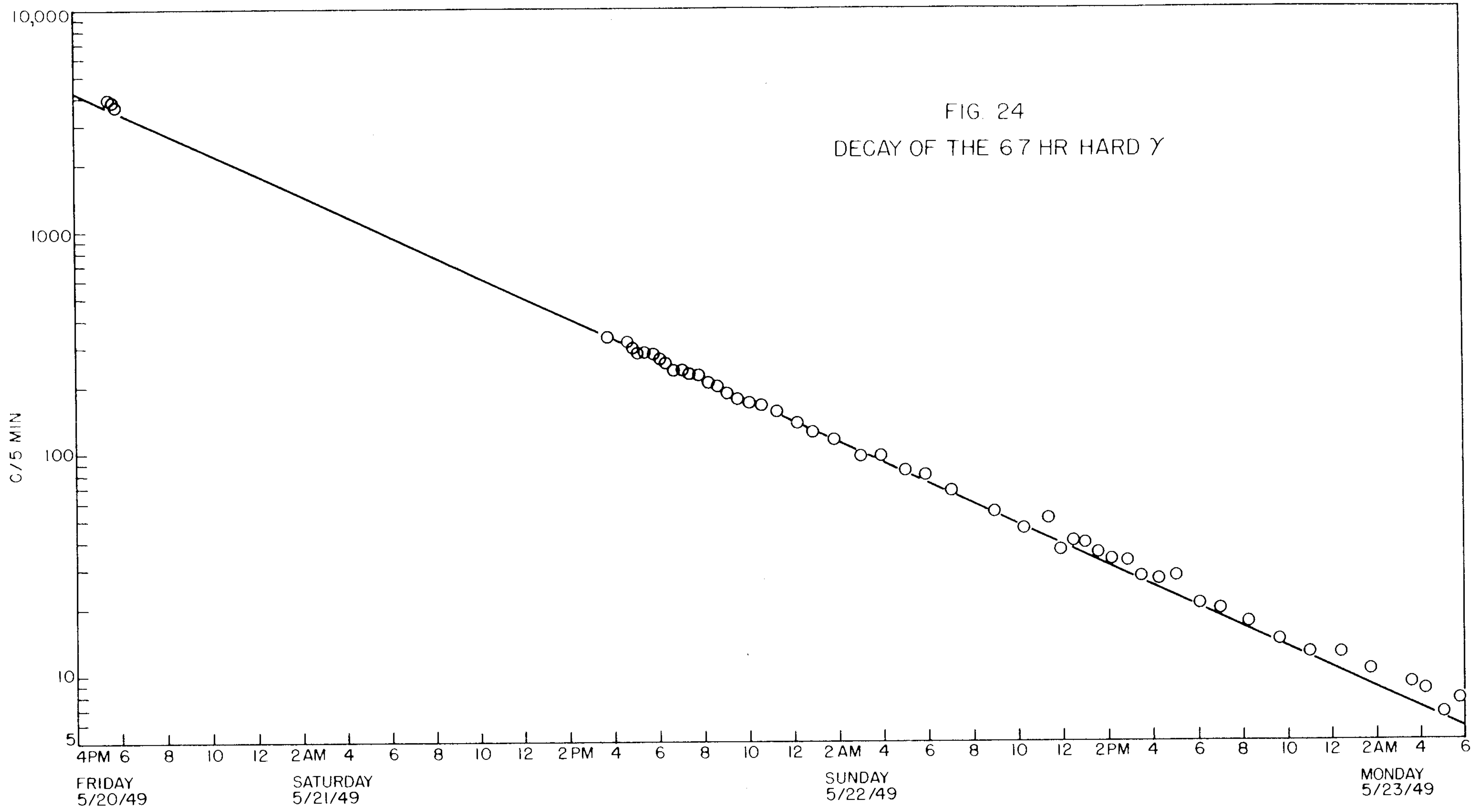

FIG. 24

DECAY OF THE 6.7 HR HARD γ

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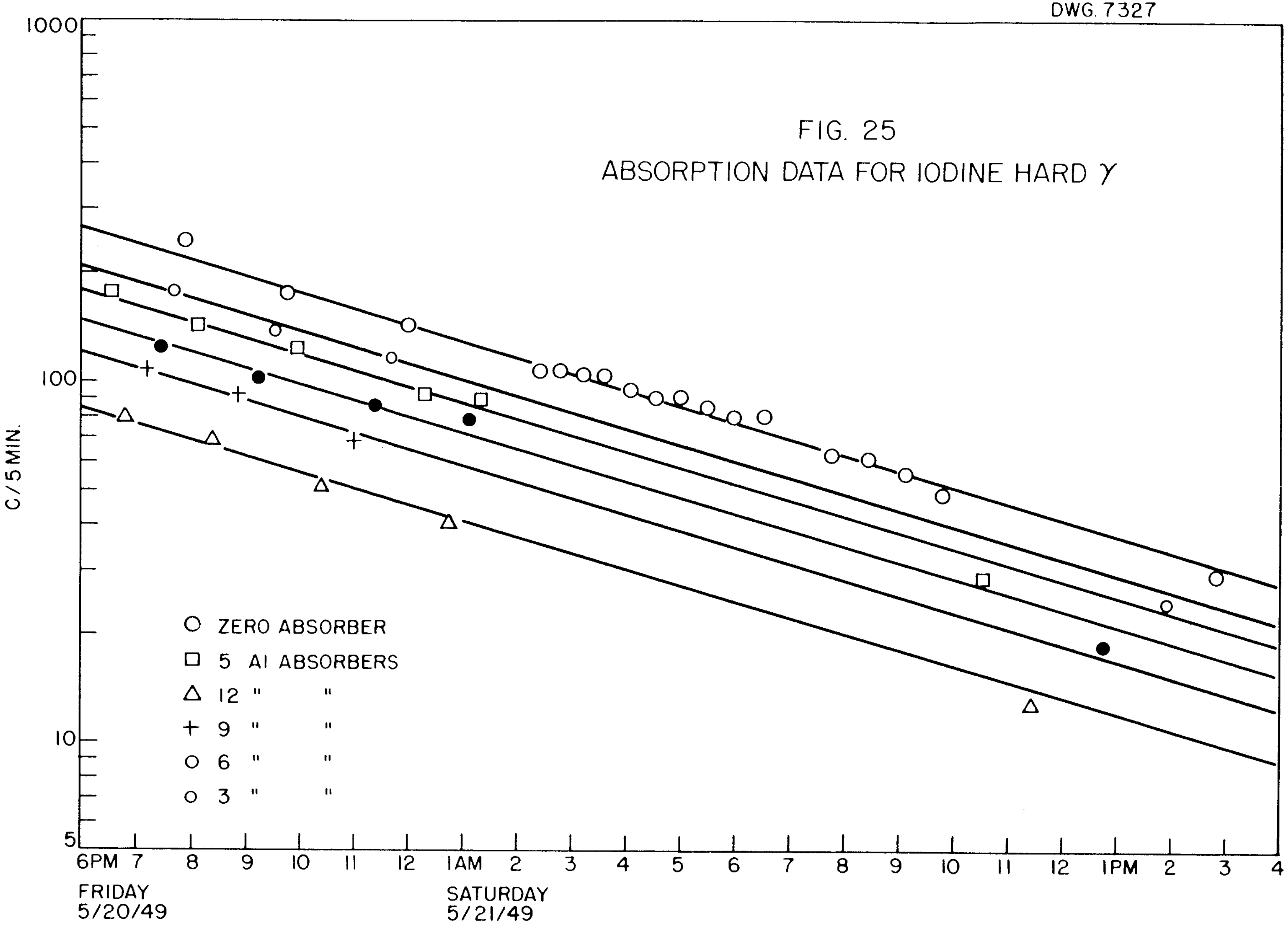

FIG. 25

ABSORPTION DATA FOR IODINE HARD γ

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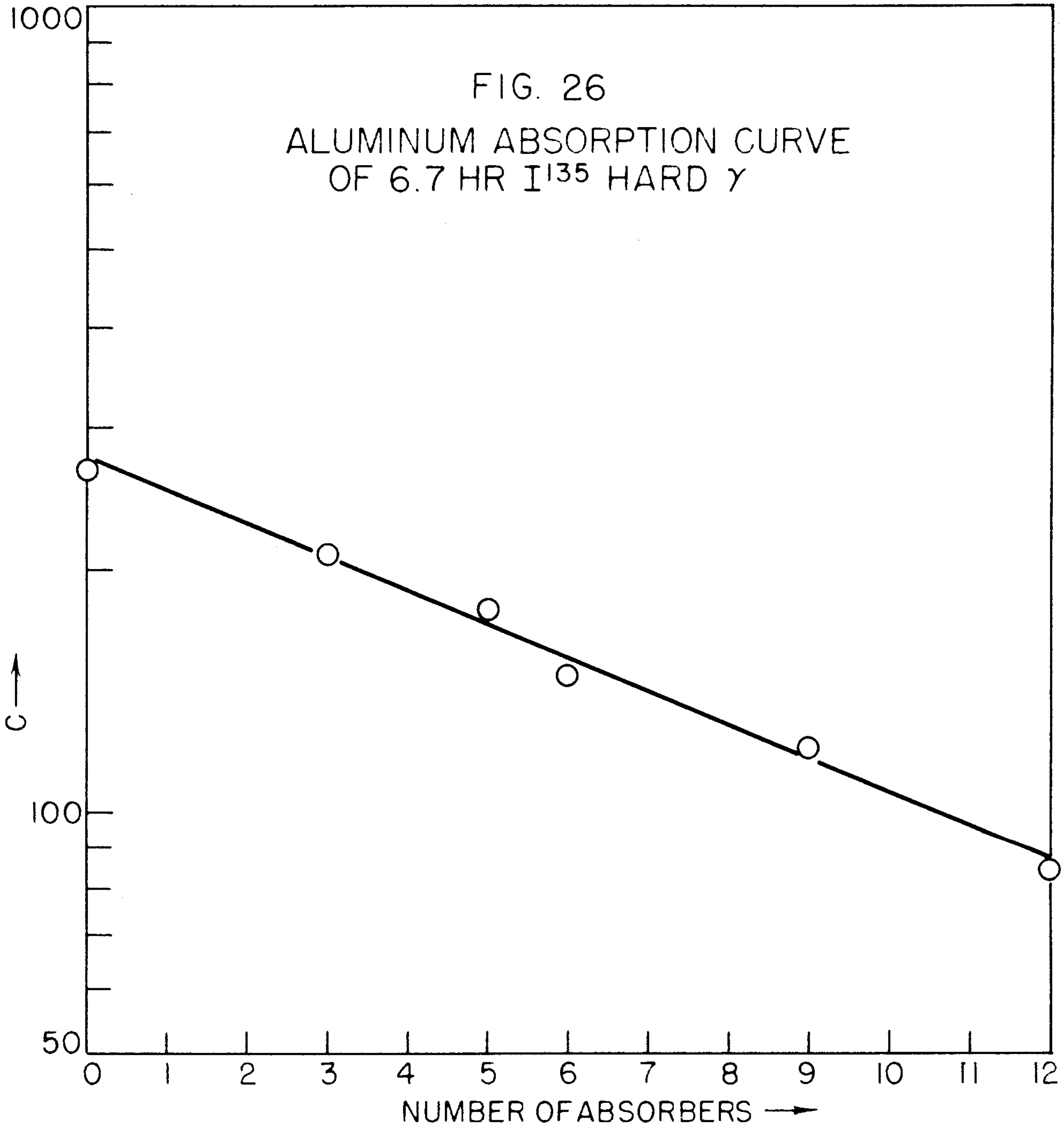

FIG. 26

ALUMINUM ABSORPTION CURVE OF 6.7 HR I^{135} HARD γ

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THE FUNDAMENTAL CHEMISTRY OF RUTHENIUM

M. D. Silverman

1. *Equilibrium Studies in the Upper Valence States.* Work on systems of the upper valence states of manganese which is reported in the literature has been reviewed in an earlier report(28). Previously reported qualitative inorganic and spectrophotometric tests indicated that an equilibrium, in complete analogy with manganese, might exist for the following reaction:

$$3K_2RuO_4 + 2H_2O \rightleftarrows 2KRuO_4 + RuO_2 + 4KOH$$

Furthermore, preliminary polarographic data indicated that the couple RuO_4^-, $RuO_4^=$, KOH might be a reversible one. If the potential for this couple were known in addition to an equilibrium constant for the above reaction, then the potential for the $RuO_4^=$, RuO_2 couple, which is almost certainly irreversible, could be calculated.

The above reaction was investigated approaching equilibrium from both sides of the equation. The experimental data indicate that equilibrium was not attained in the majority of cases. In the few instances where this possibility was present, the values obtained for the equilibrium constant differ widely. Because of the nature of the reaction the best available analytical methods were not sensitive enough to guarantee that in these few cases fortuitous results were not obtained due to analytical errors.

(a) **Experimental:** Sodium ruthenate (Na_2RuO_4) solutions were prepared by distilling ruthenium tetroxide into CO_2-free alkaline solutions. To these solutions, water or perchloric acid was added, as the case might be, to adjust the solution to the required *p*H and ionic strength. The solutions were put into flasks, the latter sealed, and then placed in a thermostat at 25° C for 5-7 days. The flasks were opened in a CO_2-free atmosphere (dry box), the solutions centrifuged to bring down any RuO_2 and aliquots were taken for analysis. An analysis for ruthenate and perruthenate was made in the following manner: An aliquot of the centrifuged reaction mixture was pipetted into a cold solution of KI in 2 *N* HCl. Ruthenium was reduced to the (III) state, and

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(28) ORNL 65, Quarterly Report of the Chemistry Division, March, April, May, 1948.

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the liberated iodine was titrated with 0.01 *N* sodium thiosulfate. Total ruthenium was first determined by the thiourea method developed by DeFord(29). Later, this was supplemented by a spectrophotometric method in which all the ruthenium was brought to the ruthenate (VI) state by pipetting aliquots of the reaction mixture into 1 *M* NaOH. Readings were taken for $RuO_4^=$ on the Beckman spectrophotometer at 4650 Å. This method first suggested as a possible analytical tool in MonN-432(30) was later developed by Marshall(31). Hydroxyl ion was determined by using a *p*H meter with a high *p*H Beckman blue glass electrode calibrated against standard buffers. It is estimated that the *pH* values obtained were accurate to ± 0.03 unit.

In attacking the reaction from the right side of the equation, solid $KRuO_4$, and RuO_2 were placed in CO_2-free alkaline solutions, the flasks sealed and then placed in a thermostat. RuO_2 was prepared in a manner similar to that employed by Schlesinger and Siems for MnO_2 (32), and pure $KRuO_4$ was prepared as previously described(33). The reaction mixtures were handled and analyzed in the manner described above.

The results are given in Tables IV and V. The following facts are noteworthy:

(1) When the reaction was attacked from the left hand side of the equation, analyses for total Ru by the thiourea method almost always showed more Ru present in solution than was given by the iodimetric method. This could be accounted for by the presence of colloidal RuO_2 which was not completely centrifuged out of the reaction mixture. The RuO_2, when dissolved in the iodide-HCl solution, would give a higher titer than that calculated on the basis of the solution containing only ruthenate and perruthenate.

(2) When the reaction was attacked from the right hand side of the equation, lower results for total Ru were obtained by the thiourea method than those calculated on the assumption that ruthenate and perruthenate were the only species present in solution. This could only be accounted for if there were a higher valence species of Ru present in solution, namely, RuO_4. This

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(29) DeFord, 'The Chemistry of Ruthenium', Doctoral Thesis, University of Kansas, Lawrence, Kansas, June, 1948.

(30) MonN-432, Quarterly Report on the Chemistry Division, September, October, November, 1947.

(31) K-392, Marshall and Rickard, 'Spectrophotometric Determination of Ruthenium', March, 1949.

(32) Schlesinger and Siems, J. Am. Chem. Soc. 46, 1965 (1924).

(33) CNL-37, Quarterly Report of the Chemistry Division, December, 1947 and January, February, 1948.

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TABLE IV

Approach to equilibrium from left hand side of equation,

$$3K_2RuO_4 + 2H_2O \rightleftarrows 2KRuO_4 + RuO_2 + 4KOH$$

SAMPLE NUMBER	pH	CONCENTRATIONS ALL IN MOLALITIES				μ NaClO$_4$	K (if any)
		OH Conc.	Total Ru (Thiourea)	If all $RuO_4^{=}$ (titer $Na_2S_2O_3$)	If all RuO_4^{-} (titer $Na_2S_2O_3$)		
1	11.00	1.01×10^{-3}	1.61×10^{-4}	1.24×10^{-4}	0.93×10^{-4}	7×10^{-3}	None
13	11.25	1.79×10^{-3}	1.82×10^{-4}	1.43×10^{-4}	1.08×10^{-4}	1.1×10^{-1}	None
14	10.60	3.26×10^{-4}	2.72×10^{-4}	2.21×10^{-4}	1.66×10^{-4}	1.1×10^{-1}	None
6	11.20	2.07×10^{-3}	2.93×10^{-4}	2.07×10^{-4}	1.55×10^{-4}	1.8×10^{-2}	None
11	10.35	2.26×10^{-4}	3.41×10^{-4}	4.48×10^{-4}	3.38×10^{-4}	3.7×10^{-2}	2.4×10^{-7}
12	10.90	8.00×10^{-4}	2.58×10^{-4}	3.05×10^{-4}	2.29×10^{-4}	3.7×10^{-2}	6.1×10^{-10}
3	11.80	6.35×10^{-3}	1.47×10^{-3}	1.02×10^{-3}	0.765×10^{-3}	2.4×10^{-2}	None
4	11.75	5.67×10^{-3}	1.40×10^{-3}	0.98×10^{-3}	0.735×10^{-3}	2.4×10^{-2}	None
5	12.10	1.27×10^{-2}	$\left.\begin{matrix}1.38\times10^{-3}\\0.89\times10^{-3}\end{matrix}\right\}$*	1.05×10^{-3}	0.785×10^{-3}	1.8×10^{-2}	7.9×10^{-5}
9	10.95	8.98×10^{-4}	3.16×10^{-3}	4.38×10^{-3}	3.28×10^{-3}	2×10^{-1}	None
10	10.80	6.35×10^{-4}	3.13×10^{-3}	4.45×10^{-3}	3.34×10^{-3}	2.6×10^{-1}	None
8	11.96	9.19×10^{-3}	5.08×10^{-3}	6.77×10^{-3}	5.08×10^{-3}	4.0×10^{-1}	None
7	12.20	1.60×10^{-2}	0.958×10^{-2}	1.28×10^{-2}	0.965×10^{-2}	2.1×10^{-1}	2.6×10^{-1}

* Two widely different analytical results on duplicate samples.

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TABLE V

Approach to equilibrium from right hand side of equation,

$$3K_2RuO_4 + 2H_2O \rightleftarrows 2KRuO_4 + RuO_2 + 4KOH$$

$$\mu = 0.15\ ClO_4$$

SAMPLE NUMBER	***pH***	**OH^- CONCENTRATION**	**TOTAL Ru (Thiourea)**	**IF ALL $RuO_4^=$**	**IF ALL RuO_4^-**	**K**
				titer $Na_2S_2O_3$		
5	9.55	3.58×10^{-5}	0.70×10^{-3}	1.19×10^{-3}	0.845×10^{-3}	None
6	9.55	3.58×10^{-5}	0.775×10^{-3}	1.23×10^{-3}	0.965×10^{-3}	None
1	10.05	1.13×10^{-4}	0.732×10^{-3}	1.13×10^{-3}	0.920×10^{-3}	None
2	10.20	1.60×10^{-4}	0.811×10^{-3}	1.28×10^{-3}	0.828×10^{-3}	None
3	10.48	3.04×10^{-4}	0.828×10^{-3}	1.23×10^{-3}	0.890×10^{-3}	None
4	10.50	3.19×10^{-4}	0.759×10^{-3}	1.10×10^{-3}	0.920×10^{-3}	None
7	11.56	3.66×10^{-3}	0.875×10^{-3}	1.20×10^{-3}	0.900×10^{-3}	None
8	11.63	4.30×10^{-3}	1.033×10^{-3}	1.39×10^{-3}	1.04×10^{-3}	None
9	10.62	4.20×10^{-4}	4.15×10^{-4}	6.13×10^{-4}	4.60×10^{-4}	None
10	10.64	4.40×10^{-4}	4.43×10^{-4}	5.94×10^{-4}	4.45×10^{-4}	None
11	10.38	2.42×10^{-4}	3.14×10^{-3}	5.55×10^{-3}	4.16×10^{-3}	None
12	10.40	2.53×10^{-4}	3.04×10^{-3}	5.15×10^{-3}	3.86×10^{-3}	None

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belief that RuO_4 was present in the reaction mixture was later verified by spectrophotometric data.

(3) It is believed that considerably greater accuracy is required in analyzing for total Ru. The thiourea method is not infallible and reproducibility is not always easily obtained. Furthermore, errors are additive in determining the concentration of ruthenate and perruthenate from a total Ru analysis and one employing a change in valence state upon titration.

(4) The error in determining the hydrogen ion concentration by means of *p*H measurements to ± 0.03 unit gives an error in the OH^- concentration of ~7%.

(5) The few values obtained for K show a considerable spread. They were calculated from the mass action equation,

$$K = \frac{(RuO_4^-)^2 \quad (OH^-)^4}{(RuO_4^=)^3}$$

Concentrations were employed, and not activities. Activity coefficients calculated by means of the approximate Debye-Huckel law, $-\log f = A\sqrt{\mu}$ gave values of $f = 0.637$ for RuO_4^- and OH^-, and $f = 0.406$ for $RuO_4^=$ based on $\mu = 0.15$. Raised to the appropriate powers, these values largely cancel out in the mass action equation.

2. *Spectrophotometry.* Over a year ago the first spectrophotometric curve for ruthenate ion, $RuO_4^=$, was published(30). The suggestion was offered that the 4650 Å absorption peak might be useful as an analytical tool. Since then, other workers(31) have investigated and verified the use of this absorption peak as an analytical method for ruthenium. The molar extinction coefficient of $RuO_4^=$ has been found to be 1735 at 465 mμ, in good agreement with their value of 1739.

Although an earlier curve for RuO_4 in H_2O was published(30), Wehner and Hindman(34) later published curves for RuO_4 in water, 1 *M* and 6 *M* perchloric acid. It has since been discovered that our earlier solution of RuO_4 contained impurities which affected the ratio of the peak heights at 3100 Å and 3850 Å, a fact which these investigators had noted. They also showed that the molar extinction coefficient for RuO_4 in 1 *M* and 6 *M* $HClO_4$ was not independent of concentration.

Pure H_2O solutions of RuO_4 were prepared and the spectrum re-determined.

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(34) ANL-4215, Summary Report for July, August, September, 1948, Chemistry Division, Section C-1.

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The ratio of the peak height at 3100 Å to that at 3850 Å is 3.12, in good agreement with their value of 3.2. Furthermore, in contrast with the results obtained in perchloric acid, aqueous solutions of RuO_4 follow Beer's Law in the concentration range, 0.4×10^{-4} to 1×10^{-3} *M*. The molar extinction coefficients obtained are $E_m(3100\ Å) = 2870$ and $E_m(3850\ Å) = 920$.

All attempts to obtain a pure spectrum for perruthenate ion, RuO_4^- failed. At first, this was difficult to explain. However, after completion of the equilibrium tests described above, this enigma was easily solved. Perruthenate ion is unstable in solution, so much so, in fact, that its life duration appears to be of the order of minutes. Furthermore, the products which result from its decomposition are dependent on the *p*H of the solution employed. Pure $KRuO_4$ has been prepared as previously described(33) and its identity verified by analysis and crystal structure. Therefore, it was possible to start with a pure solid compound of the (VII) state. When this compound is dissolved in H_2O (it might be called sparingly soluble), the perruthenate ion decomposes according to either of the following reactions:

$$(1)\quad 4RuO_4^- + 2H_2O \longrightarrow 3RuO_4 + RuO_2\downarrow + 4OH^-$$

$$(2)\quad 2RuO_4^- + 2OH^- \longrightarrow 2RuO_4^{=} + \tfrac{1}{2}O_2 + H_2O$$

Hence, the products of decomposition are dependent upon the *p*H of the dissolving solution. A spectrophotometric plot of optical density versus wave length is presented in Fig. 28 for solutions of varying *p*H. For solutions of *p*H >10, reaction (1) proceeds rapidly, so that within a few minutes the solution darkens perceptibly in color, and traces of solid RuO_2 can be detected coming out of solution. At *p*H $>10 <\sim 10.65$ reaction (1) proceeds at a much slower rate. The color of the solution darkens over a period of hours, and the RuO_2 is present as a colloid. At *p*H $\gtrsim 10.65$, reaction (2) starts to appear, as shown by the slight hump in Curve No. 3 at 4650 Å. At *p*H >10.65 reaction (2) predominates over reaction (1), and the color of the solution gradually turns to orange, visual evidence of ruthenate ion. The rate of reaction (2) increases considerably with increase in *p*H, so that at *p*H $\gtrsim 11.3$, the reaction appears to take place in the order of minutes. However, traces of RuO_2 still appear in the solution upon standing unless the *p*H is raised to ~ 12. Either reaction (1) still takes place to a slight extent until *p*H ~ 12, or as appears more likely, traces of RuO_2 appear due to decomposition or reduction of ruthenate ion. Close examination of the curves in Figs. 27-28 indicates that

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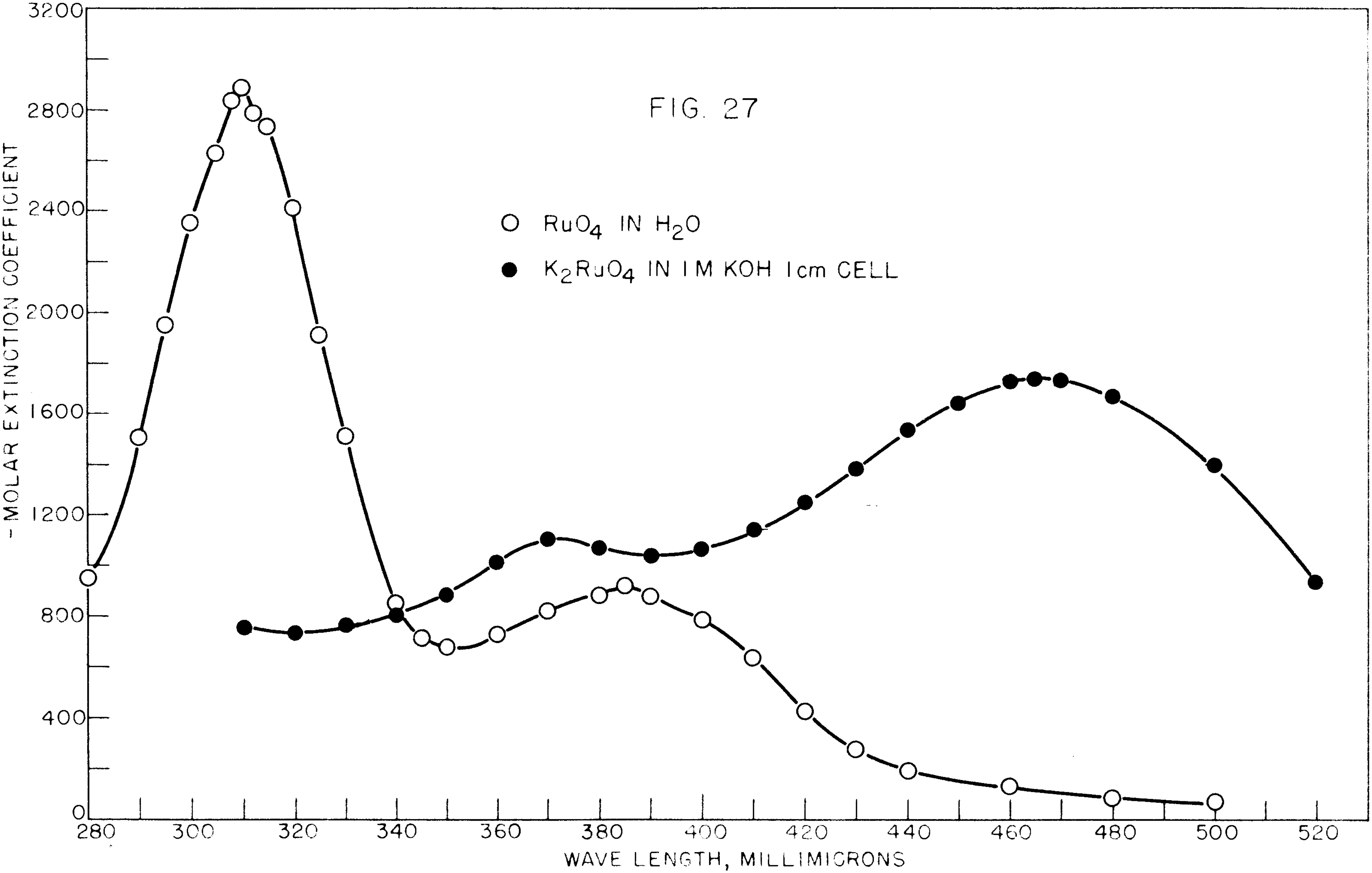
FIG. 27

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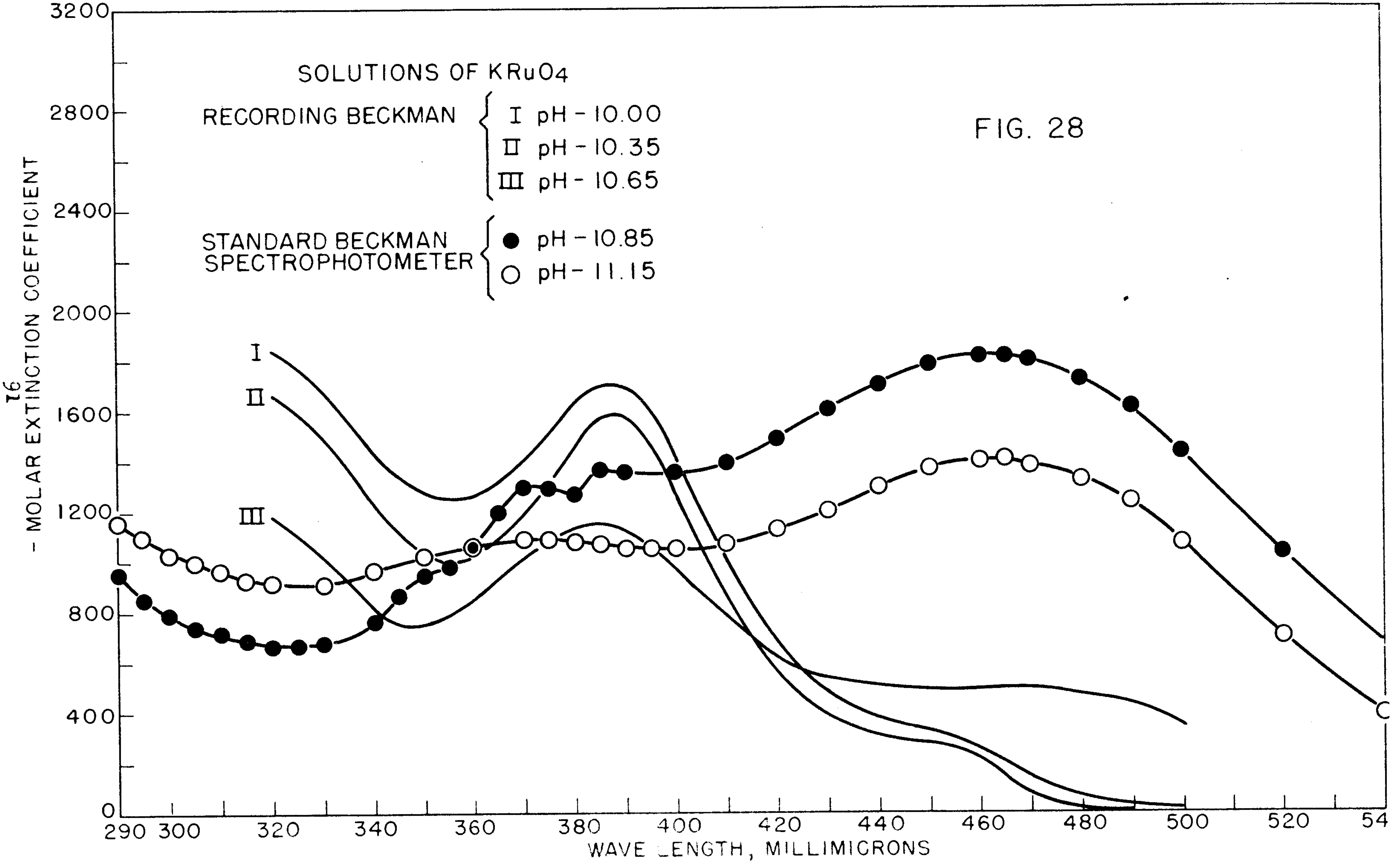

FIG. 28

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the (VII) state must have some type of absorption peak at 3850 Å, because addition of the pure (VI) and (VIII) curves cannot give a curve similar to those obtained. This is also evident in the ratio of the peaks' heights at 3850 Å to the troughs at ~3500 Å. An effort is being made to determine what amount of the (VII) state is present in solution by employing different analytical methods for ruthenium. It is noteworthy, however, that solutions (up to 0.1 *M*) of Na_2RuO_4 and K_2RuO_4 prepared by absorbing RuO_4 in CO_2-free redistilled H_2O have been kept in the ice box for months without any signs of decomposition or traces of RuO_2.

From the above spectrophotometric results it now appears possible to explain why no equilibrium was attained as described in the initial section of this report. Since it is possible for all these species (RuO_4, RuO_4^-, $RuO_4^=$, RuO_2, O_2, OH) to be present at one time in solutions of definite *p*H (~10.65 - 11.3), due to reactions (1) and (2) taking place, it would be very difficult to obtain equilibrium data. Moreover, analytical difficulties would make this task nearly impossible.

3. *Potentials*. After the failure to obtain equilibrium data for the (VI-VII) reaction postulated in Section 1 of this report, attention was given to the (VI-IV) couple, $RuO_4^=$, RuO_2, KOH which is almost certainly an irreversible couple. Attempts were made to bracket the potential for the couple by the use of other oxidizing-reducing couples, potentials for which are given by Latimer(35). The following agents oxidized RuO_2 to $RuO_4^=$ in 1 *M* NaOH: ClO^-, BrO_3^-, AgO, MnO_4^-, IO_3^-, Ag_2O. The following were unable to oxidize RuO_2 to $RuO_4^=$: $Co(OH)_3$, Ag_2CO_3, $Pd(OH)_2$, HgO(r). In almost every case where oxidation did take place, heating to 75-85° C was necessary and in some cases to the boiling point to accomplish the oxidation. The lowest couple accomplishing the oxidation was the Ag_2O, AgO couple whose potential is given by Latimer as -0.344 volts. However, the Ag_2CO_3, Ag couple in 1 *M* $CO_3^=$, which has a potential of -0.47 volts was unable to accomplish this oxidation. It is believed that diffusion and rate effects were quite pronounced in these tests. This mode of attack presented innumerable difficulties, so that further investigation along these lines was abandoned. About all that could be derived from this work is that the potential for the $RuO_4^=$, RuO_2 couple in 1 *M* KOH is less than -0.34 volts.

In CNL 37(33) preliminary polarographic data were presented for the upper valence states of ruthenium. Investigation along these lines is now being pursued anew, in view of the difficulties encountered in obtaining thermodynamic

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(35) Latimer, 'Oxidation Potentials in Aqueous Solutions', Prentice-Hall, N. 6. 1938.

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data from the work reported above. In earlier work, KCl was used as a background electrolyte in solutions prepared for polarograms. However, considerable difficulty was encountered when we attempted to use KCl in the present work. Solutions decomposed fairly rapidly, apparently due to the presence of Cl^-. Hence, ClO_4^- was later used as a background electrolyte. Because the potassium salt is not soluble enough in water to give low resistance bridges, $NaClO_4$ was employed. Actually a double bridge was employed; one of agar + KCl ran from the saturated calomel cell to the saturated $NaClO_4$ cell while the second went from the saturated $NaClO_4$ cell to the cell containing Ru in saturated $NaClO_4$ solution. Resistances in almost all cases were thus kept below 6000 ohms.

Some preliminary data can be presented at this time. The (VII-VIII) couple has been mainly investigated; oxidation waves starting with pure $KRuO_4$ dissolved in solution give a value of ~+0.7 volt (polarographic convention). Three reduction waves for RuO_4 dissolved in alkaline solution give values for the (VII-VIII) couple of 0.62, 0.63 and 0.66 volts. Furthermore, these reduction waves show the reduction of RuO_4 to RuO_2 in three distinct steps; the tetroxide to perruthenate (VIII-VII), the perruthenate to ruthenate (VII-VI), and the double electron jump (VI-IV) from ruthenate to tetravalent Ru in alkaline solution, probably RuO_2. Additional reduction waves for perruthenate and ruthenate solutions indicate that the value for the (VI-IV) potential lies ~+0.18 volts. These results are being checked further and the investigation is being continued along these lines.

It is hoped that one more point can be cleared up, i.e., to what extent does RuO_4 act as an acid in solution. *p*H measurements have indicated it to be a fairly strong acid, in direct contrast to previous work by Yost and White(36) on perperosmic acid, which has a dissociation constant of $\sim 10^{-12}$. It would be expected that RuO_4 should have an acid strength comparable to that of OsO_4 from the size of the ions and the similarity in their chemical behavior. Hence, oxidation of H_2O at the glass electrode by RuO_4 to give H^+ ions may account for the low *p*H values obtained. This will be checked further to permit a conclusion as to whether polarographic waves involving RuO_4 are to be based on the molecule or an anion involving Ru(VIII).

(36) Yost and White, J. Am. Chem. Soc. 50, 81 (1928).

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GENERAL NUCLEAR CHEMISTRY

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NUCLEAR CHEMICAL STUDIES OF THE RARE EARTHS

B. H. Ketelle

Forbidden Beta Ray Spectra of Y^{90} and Y^{91}. Because the aluminum adsorption curves of the beta rays of Y^{90} and Y^{91} appear to be abnormal, the spectra of these isotopes were studied using the thin lens spectrometer.

A sample of ion-exchange column purified Y^{91} obtained from I. R. Whitney was further purified on the heated Dowex 50 ion-exchange column. The source was essentially weightless and was mounted on a laminated polystyrene-formvar film 50 mg/cm^2 thick. The Y^{90} was prepared by milking a source of Sr^{90} which was adsorbed on a small ion exchange column. This source was also essentially free of mass and was mounted on a 50 mg/cm^2 film.

Figures 29-30 show the Kurie plots of Y^{90} and Y^{91}, respectively. These were computed using the Fermi functions for allowed transitions. These plots are definitely non-linear.

According to the Fermi theory of beta decay, a plot of $(N/c\phi WI^2)^{1/2}$ *vs* E should give a straight line. For the allowed transition C is unity. Therefore it is concluded that the two spectra above are not those for allowed transitions. Konopinski and Uhlenbeck [Phys. Rev. *60*, 308 (1941)] have derived equations for C for first and second forbidden transitions. In general the calculation of those constants is made uncertain due to insufficient knowledge of the nuclear matrix elements. However, for a first forbidden transition with spin change of two, or for a second forbidden transition with a spin change of three there is only one matrix element involved in the constant, and its absolute value will not effect the spectrum shape. Therefore one can, in these cases, determine the degree of forbiddeness from the shape of the spectrum. For the *first forbidden* transitions with spin change of two

$$C = p^2 + q^2,$$

where p is the electron momentum and q the neutrino energy. Using this equation for C one can compute the corrected function and obtain a linear Kurie plot for a first forbidden spectrum. Figure 31 shows that when the data on Y^{91} are corrected in this manner that a linear plot is obtained. The maximum beta energy is 1.55 Mev. Langer and Price [Phys. Rev. *75*, 1109 (1949)] have shown in this manner that Y^{91} is a first forbidden transition.

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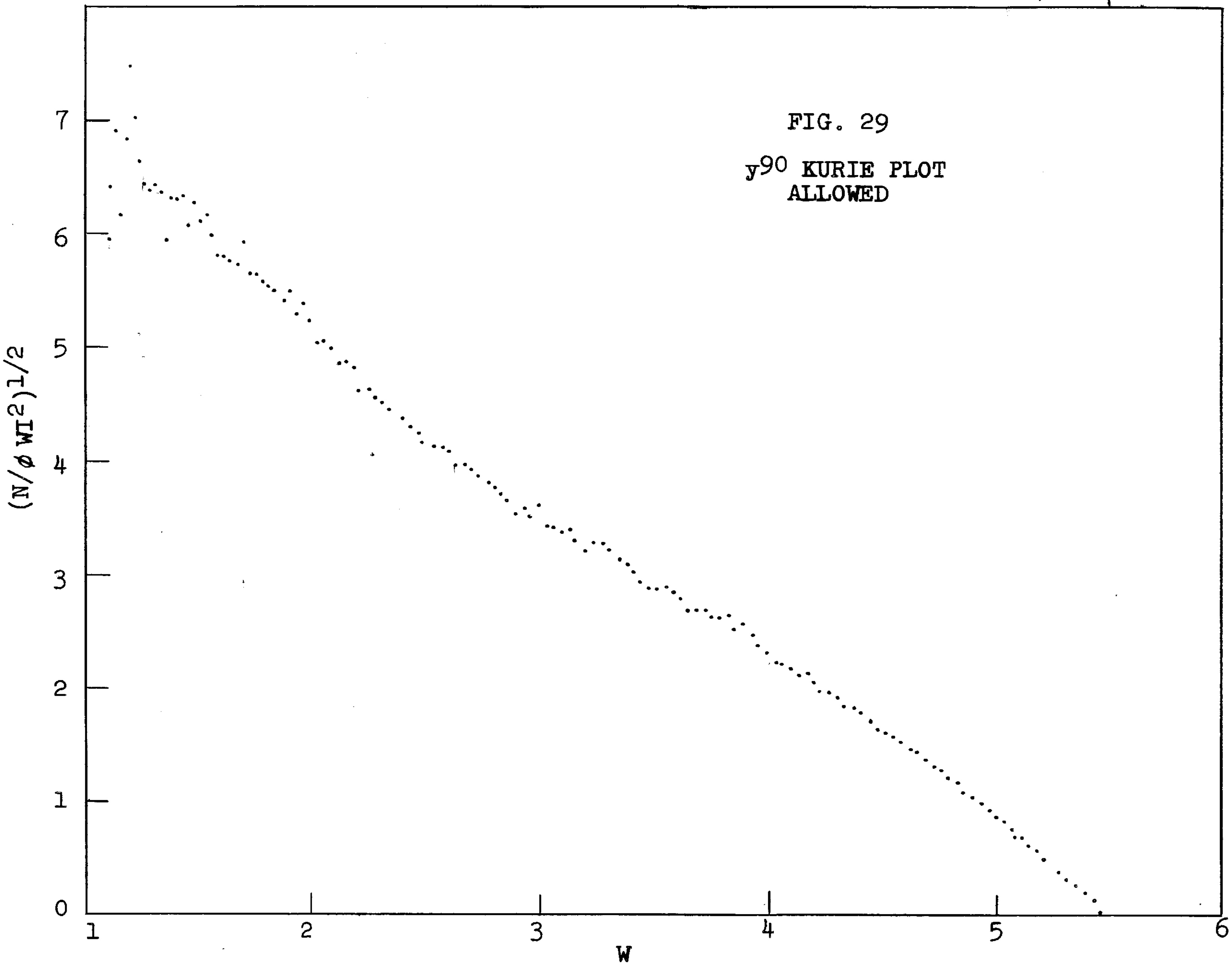

FIG. 29

Y^{90} KURIE PLOT
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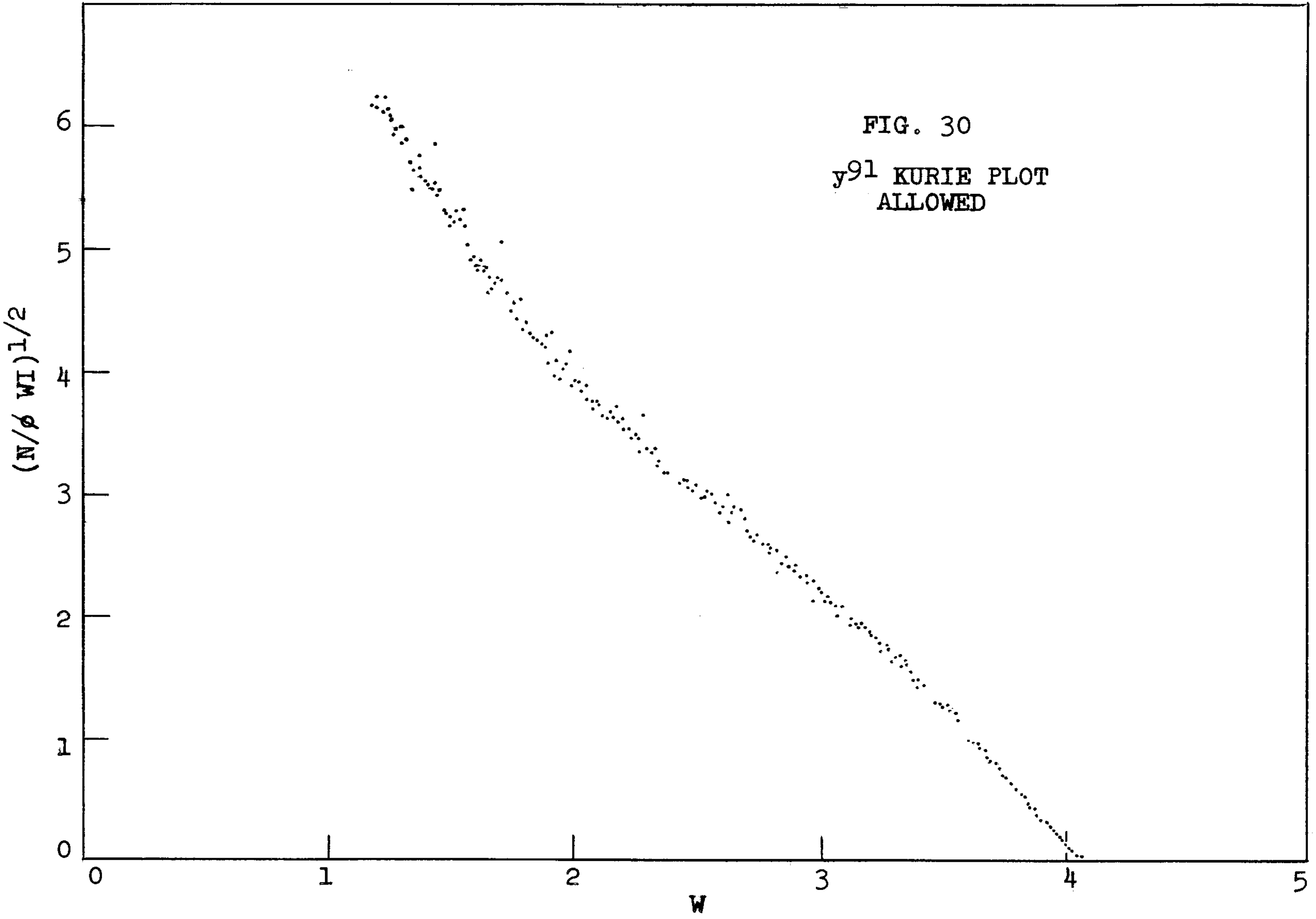

FIG. 30

y^{91} KURIE PLOT
ALLOWED

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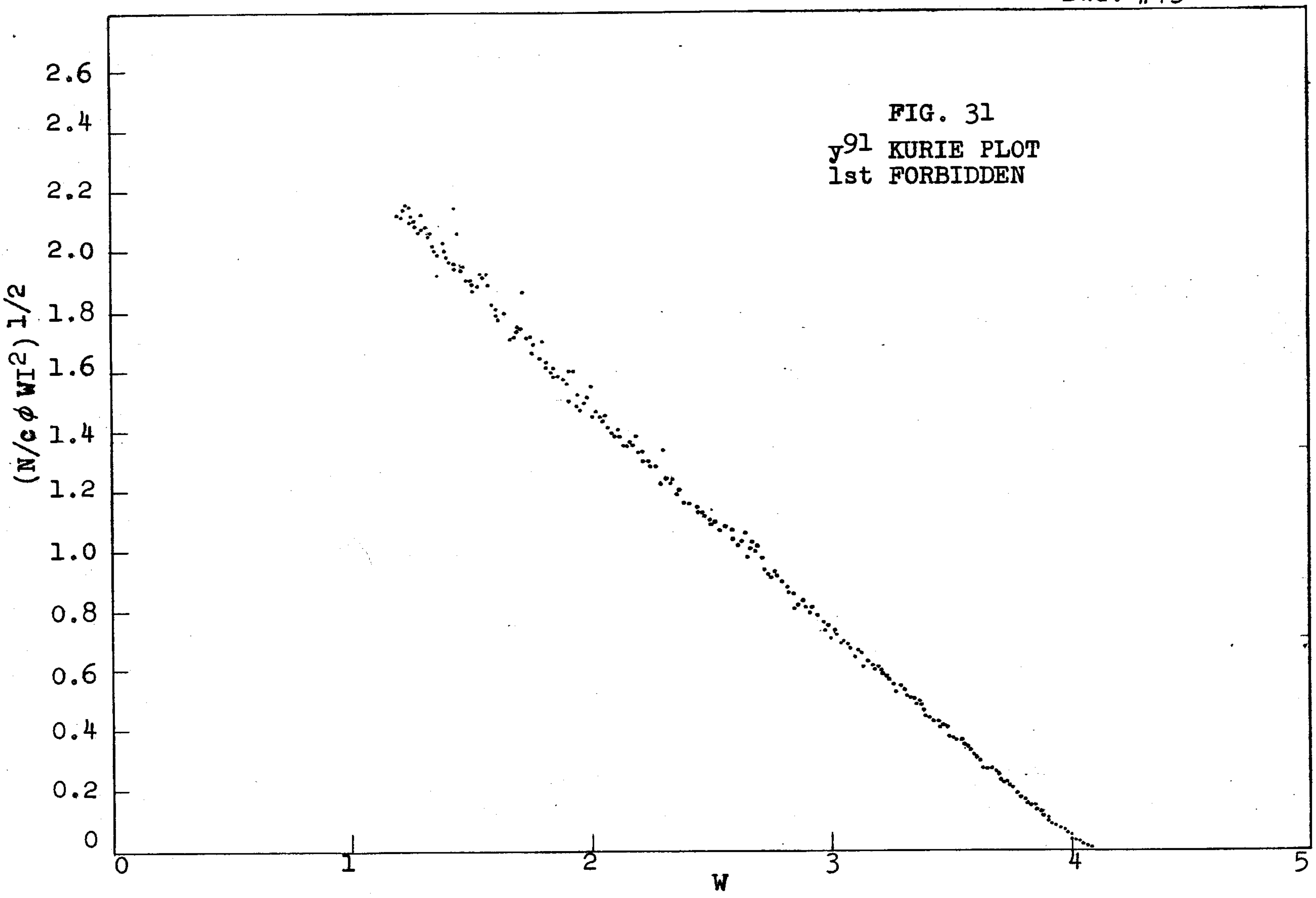

FIG. 31
Y^{91} KURIE PLOT
1st FORBIDDEN

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Although it is not known that the spin change in the decay of Y^{90} is two the data were computed in the same manner and are plotted in Fig. 32. Again a linear plot was obtained. The maximum energy is 2.28 Mev.

If the correction factors are computed for the second forbidden transition with a spin change of three and the corresponding Kurie plot is constructed a straight line is not obtained. Thus from the shapes of the spectra one concludes that beta disintegrations of Y^{90} and Y^{91} are first forbidden.

According to the Fermi theory, the reciprocal half-life of a radioactive nucleus is

$$\frac{1}{t} = \left[\frac{G^2}{2\pi^3 \ln 2}\right] \int_1^W CFpWq^2 dW$$

where G is the Fermi constant, C the above mentioned correction term to the Fermi function, p and W the electron's momentum and energy and q the neutrino energy. Therefore, if the electron energy distribution curve is known and if the constant C which contains the matrix elements can be computed, the half-life which corresponds to the maximum energy observed can be computed. This has been done both for Y^{90} and Y^{91}. The values obtained are uncertain because of lack of knowledge of the absolute value of the nuclear matrix elements. However, the order of magnitude of the matrix element is determined by the nuclear radius. In these calculations the radius function has been separated out of the matrix element and a value for the radius of 0.004 $A^{1/3}$ was used. G was taken to be 5×10^{-12}. In Table I are summarized the values of the product of the remaining part of the matrix element and the half-lives calculated for first and second forbidden transitions.

TABLE I

Calculated half-lives of Y^{90} and Y^{91}

	FIRST $\Delta j = 2$	SECOND $\Delta J = 3$	OBSERVED
Y^{90}	2.7 hrs.	3.8×10^4 hrs.	62 hrs.
Y^{91}	0.7 d.	3.8×10^4 d.	57 d.

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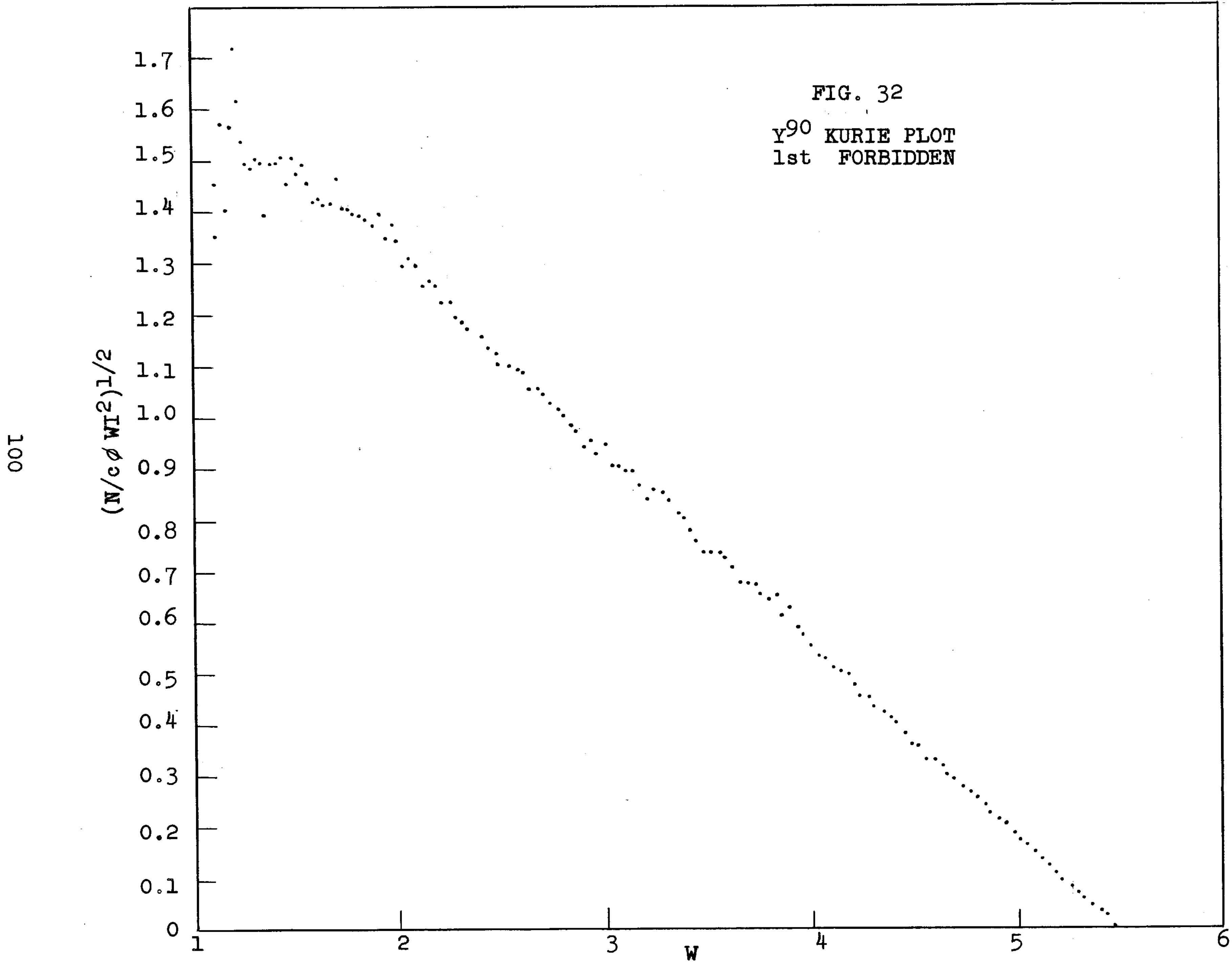

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Let us assume that the matrix elements are of the order unity and compare the calculated and observed half-lives. It appears that for Y^{90} the half-life obtained upon the assumption that the transition is first forbidden is in better agreement with the observed half-life than is the value obtained if the transition is assumed to be a second forbidden transition. This agrees with the conclusion from the spectrum shape. However for Y^{91} the observed half-life falls about midway between the two calculated half-lives so one can draw no conclusion.

Beta Disintegration Energy of Ho^{166}. Aluminum absorption curves of the activity of 27.2 hr Ho^{166} indicate the maximum beta energy to be about 2 Mev and also indicate the presence of a soft gamma ray. A thin source was prepared for the lens spectrometer and the spectrum was determined. A conversion line line at 64 Kev was observed. If these are L electrons, the corresponding energy of the gamma ray would be 73 Kev. The Kurie plot is a fairly straight line with an endpoint at 1.85 Mev. As this study was in progress Grant and Hill reported [Nature 163, 524 (1949)] their observation of this same isotope. They find the maximum beta energy to be 1.88 ± 0.02 Mev and the gamma ray energy to be 80.2 ± 0.7 Kev.

A Study of the 12 min Activity Produced in Nd. An attempt to detect a very short-lived beta emitter which might be the parent of the 12 min activity obtained by (n γ) on Nd has failed. It would appear that, if such a parent exists, it must have a half-life of less than 0.1 sec. Since it is not impossible that the 12 min activity is Nd and that the Pm daughter has a shorter half-life, it might be possible to make the assignment from the disintegration energy of the 12 min activity. The liquid drop model gives 2.36 Mev for Nd^{151} and 1.43 Mev for Pm^{151}. Coincidence counting has been done on the activity. The half-lives obtained from beta-gamma coincidences as well as from beta decay and gamma decay are in agreement. The best value appears to be 12 min. An aluminum absorption curve of the betas gives a maximum energy of 1.9 Mev. A Pb curve of the gammas indicates the presence of K X-rays and a 1 Mev gamma. However, the coincidence absorption curve indicates that the beta coincident with the X-rays and γ-rays has an energy of only 1.5 Mev. There are gamma-gamma coincidences and the lead absorption curve of these indicates that there are 1 Mev gammas coincident with about 50 Kev gammas or X-rays. These results are not inconsistent with the postulate that the 12 min activity is Nd and has a 1.5 Mev β and two gammas in coincidence and that the daughter activity has a 1.9 Mev beta and no gammas.

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In order to analyze the curves for the 12 min activity it was necessary to study the activities of the 1.6 hr activity of Nd^{149}. The coincidence study indicates that this isotope decays by 1.4 Mev beta decay followed by a 0.5 Mev gamma.

Study of Dy^{166}. The long-lived beta emitter in Dy mentioned in ORNL 336, p. 53, has been studied using the ion exchange separations technique. A sample of Dy which had been irradiated in the pile for five months was adsorbed on the column and eluted under conditions which are known to give excellent separation of the 27 hr Ho and 140 min Dy activities. The elution curve showed the presence of holmium activity and a high saddle between the holmium and dysprosium peaks. The dysprosium which was used was known to be extremely pure so it was suspected that the 27 hr holmium activity which was identified in the first peak from the column was formed during the irradiation by double neutron capture. This activity could form by either of two series of reactions:

$$(1)\quad Dy^{164} \xrightarrow{n\gamma} Dy^{165} \xrightarrow[140\ \text{min}]{\beta^-} Ho^{165} \xrightarrow{n\gamma} Ho^{166} \xrightarrow[27\ \text{hrs.}]{\beta^-} Er^{166}$$

$$(2)\quad Dy^{164} \xrightarrow{n\gamma} Dy^{165} \xrightarrow{n\gamma} Dy^{166} \xrightarrow[80\ \text{hrs.}]{\beta^-} Ho^{166} \xrightarrow[27\ \text{hrs.}]{\beta^-} Er^{166}$$

It was also observed that a sample of activity taken from the trailing edge of the Dy peak showed growth. Therefore, it seemed certain that at least part of the Ho activity observed had been formed according to Equation 2 This would also explain the high saddle between the holmium and dysprosium peaks since holmium would be forming in the column by decay of Dy^{166} and would "bleed out" ahead of the dysprosium peak. As a further check upon this hypothesis, the major part of the dysprosium peak was readsorbed on the column and a second separation of holmium and dysprosium was made. This separation gave a similar elution curve with the high saddle. Again the 27 hr holmium activity was identified and it was possible to obtain aluminum absorption curves of the tailing edge of the dysprosium peak before very much holmium had grown into the sample. In this way it has been established that Dy^{166} decays with a 0.4 Mev beta of half-life 80 hrs. (This is the same activity which was described in ORNL 336 as an 85 hr beta decay with 2 Mev energy.) In that sample the hard beta of the holmium daughter masked the soft parent beta because the

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measurements had not been made before an appreciable amount of holmium had grown into the sample.

From the ratio of 80 hr activity to 140 min activity in a sample of dysprosium which had undergone no chemical separation after irradiation, an approximate value of the neutron cross section of Dy^{165} was computed to be 3600 barns.

Study of $Dy^{(157\ \mathrm{or}\ 159)}$. After the 80 hr activity had decayed out of the above mentioned dysprosium samples, there was a residual activity with a half-life of 120 ± 20 days. This activity decays by K capture. In addition a preliminary study of the activity on the crystal spectrometer with P. R. Bell has shown that there is an unconverted gamma ray of 144 Kev. Absorption curves indicate the presence of soft electrons which may be Auger electrons.

PRODUCTION OF SPECTROCHEMICALLY PURE RARE EARTHS FOR RESEARCH PURPOSES

D. H. Harris and G. E. Boyd

The inventory of spectrochemically pure rare earth preparations has been added to as a result of Lu, Tb, Sm, Nd, Pr, Ce and La separations completed during the past quarter. At the present the amounts on hand are:

Sc_2O_3	0.150 g	Gd_2O_3	15.000 g
Y_2O_3	7.050	Tb_4O_7	0.801
La_2O_3	8.457	Dy_2O_3	1.399
CeO_2	7.851	Ho_2O_3	0.686
Pr_6O_{11}	6.395	Er_2O_3	6.262
Nd_2O_3	17.587	Tm_2O_3	0.649
Sm_2O_3	146.0*	Yb_2O_3	0.100
	2.338**	Lu_2O_3	0.131
Eu_2O_3	-----		

*Crystallized, contains 0.1% Eu

**By ion-exchange column.

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Currently a Ub-Lu and a Tb separation are in progress. The former is expected to yield between 0.5 and 1.0 gm of pure Lu_2O_3; the latter has given about 4-5 gm of pure Tb, but as yet the spectrochemical analysis of this material has not been completed.

During the quarter now elapsed 31 samples of different spectrochemically pure rare earths were shipped to seven AEC research groups.

COUNTING YIELDS OF LOW ENERGY BETA EMITTERS

J. C. Griess, A. R. Brosi, H. Zeldes

Several radioactive isotopes have recently been discovered at ORNL which have long half-lives and very soft beta radiations. The radiations from these isotopes have been detected in a slide chamber proportional counter in which the source can be placed in the active region of the counter. The counting yield (i.e., the fraction of the beta disintegrations counted) must be known in order to determine the decay constants of these long lived activities. The purpose of this work was to determine the counting yields of essentially weightless samples, mounted on "infinitely thick" platinum, as a function of the maximum energy of the beta radiation. Counting yields were obtained by dividing the beta counting rate observed in the proportional counter by the absolute disintegration rate determined from coincidence counting rates.

The soft beta emitters chosen were Ru^{106}, Cb^{95} and Co^{60} with maximum beta energies of 0.03, 0.147 and 0.31 Mev, respectively. Co^{60} and Cb^{95} have well known decay schemes with a single beta ray followed by gamma emission. Ru^{106} has a Rh daughter which decays by beta and gamma emission. It is possible to determine the absolute disintegration rates of all of these isotopes by coincidence methods.

The Co^{60} sources were prepared by electroplating pile bombarded cobalt onto platinum discs. Self absorption was shown to be negligible by the agreement in counting yields obtained with two sources which differed by a factor of five in the mass of cobalt per square centimeter. The mass of the most active source amounted to only a few micrograms per square centimeter.

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The Cb^{95} sources were prepared by electrolytic decomposition of an oxalic acid solution of carrier-free Cb^{95} activity. On reduction of the oxalic acid concentration the Cb^{95} was adsorbed on the cell walls and hence on a platinum disc at the bottom of the cell.

The Ru^{106} sources were prepared by electroplating from a Ru^{106} tracer solution by the method described in ORNL 336. The mass of ruthenium in the samples was of the order of 0.1 micrograms/cm^2. By using sources with different masses of ruthenium, self absorption was shown to be negligible.

Although the voltage plateaus were slightly different with the different radiations, the plateaus in all cases extended through 1750 volts. The counting yields at this voltage versus maximum beta energy are given in Table II. Agreement between different sources of the same radiation was within the counting errors of about 2%. In using these data to determine disintegration rates of other soft beta emitters, larger and uncertain errors could be expected because of different energy distributions and because of errors in interpolation between the energies given in the table.

TABLE II

Counting yields of low energy beta emitters

BETA EMITTERS	MAXIMUM ENERGY	COUNTING YIELD
Ru^{106}	30 Kev	53.5%
Cb^{95}	147 Kev	62.1%
Co^{60}	310 Kev	68.8%

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SUMMARY

A new procedure for the preparation of formaldehyde-C^{14} has been developed. Methanol-C^{14} is converted to methyl-C^{14} acetate with acetyl chloride, the ester is chlorinated in the methyl group, and the resulting chloromethyl-C^{14} acetate is hydrolyzed to formaldehyde-C^{14} in 60% yields based on methanol-C^{14}. Approximately 17 millicuries of high specific activity formaldehyde-C^{14} has been prepared by this procedure.

A stock of approximately 300 millicuries of carboxyl-C^{14} sodium acetate has been prepared according to the procedure described previously(1).

A new method for the preparation of acetic acid-2-C^{14} has been developed, but has not yet been applied to the production of active material. Methanol-C^{14} is added to sulfur trioxide to give methyl sulfate esters. Treating these with sodium cyanide at elevated temperatures gives acetonitrile which yields sodium acetate-2-C^{14} on alkaline hydrolysis. Yields ranging to 80% based on methanol have been obtained with inactive material.

An apparatus has been designed and built for the large-scale production of sodium formate-C^{14} following procedures previously described(2). The average radiochemical yield of sodium formate-C^{14} from barium carbonate-C^{14} was 66% based on unrecovered carbonate. Using this apparatus, a stock of 129 millicuries sodium formate-C^{14} of high specific activity has been accumulated.

The synthesis of ring-labeled benzoic acid and its intermediates according to procedures tentatively put forth earlier(3) has begun employing active materials.

A total of about 140 millicuries of high-activity methanol-C^{14} has been produced by the lithium aluminum hydride reduction of $C^{14}O_2$.

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(1) ORNL-229, Progress Report, September, October, November, 1948, pp. 47-8.
ORNL-336, Progress Report, December, 1948, January, February, 1949, pp. 64-5.

(2) ORNL-336, Progress Report, December, 1948, January, February, 1949, p. 63.

(3) Ibid., pp. 68-73.

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THE SYNTHESIS OF LOW MOLECULAR WEIGHT INTERMEDIATES CONTAINING C^{14}

1. *Formaldehyde-C^{14}. (A. R. Jones and W. J. Skraba).* (a) **Discussion:** The preparation of this intermediate has been accomplished by an adaptation of the method of Henry(4) and of Michael(5) to the vacuum line. According to this procedure, methyl acetate is chlorinated at room temperature or below to chloromethyl acetate. This compound yields formaldehyde on hydrolysis. The yields average about 60% of aqueous product contaminated with hydrogen chloride and acetic acid. The acids are neutralized, and the formaldehyde-water mixture is distilled off.

In efforts to improve the yields, methyl trichloroacetate, methyl tosylate, methyl benzoate, and methyl chlorocarbonate were substituted for methyl acetate in the chlorination and hydrolysis. The yields of formaldehyde were uniformly poor.

The preparation of hexamethylenetetramine from the hydrolysis solution was unsatisfactory.

(b) **Experimental:** (1) **Methyl-C^{14} Acetate** - Methanol-C^{14}, 10.4 mmoles (2.05 microcuries/mmole) and acetyl chloride, 10.4 mmoles, (b.p., 50° C) were introduced to a vacuum line, and distilled to the liquid nitrogen-cooled nipple of a one-liter reaction bulb. The vessel was closed from the manifold, and the reagents were warmed to 40-50° C for forty-five minutes. The bulk was then cooled to -80° C and evacuated to 10^{-4} mm to remove a part of the hydrogen chloride evolved during the reaction.

(2) **Chloromethyl-C^{14} Acetate** - Commercial chlorine gas was purified by freezing with liquid nitrogen and pumping off non-condensible contaminants. A 1400-ml aliquot of chlorine at 27° C and 12.9 cm mercury pressure (9.6 mmoles) was added to the product of the above reaction frozen down in liquid nitrogen. (The mercury in the manometer used to determine the chlorine pressure was protected from the action of the chlorine by a layer of sulfuric acid.) The bulb was isolated from the manifold, and the frozen reactants were allowed to warm to room temperature. Disappearance of the chlorine color began at low temperatures. The contents of the bulb were recondensed and allowed to return

(4) L. Henry, Ber., 6, 739 (1873).

(5) A. Michael, Am. Chem. J., 1, 418 (1879).

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to room temperature several times to insure thorough mixing. When all traces of color had disappeared, the bulb was cooled to -80° C and evacuated to 10^{-4} mm mercury pressure to remove part of the hydrogen chloride.

(3) **Formaldehyde-C^{14}.** The crude chloromethyl acetate was distilled into a 24-ml bulb equipped with a 4-mm straight-bore stopcock and containing 3 ml of distilled water. The spring-loaded stopcock was closed, and the bulb was immersed in boiling water for thirty minutes. The cooled solution was transferred to a small pear-shaped flask, made slightly basic with potassium hydroxide pellets, and then slightly acidic with acetic acid. To the flask was added 5 ml of commercial formalin solution containing approximately 60 mmoles of formaldehyde. The mixture was distilled to dryness at normal pressure. The distillate weighed 9.027 gm.

From a 75 λ aliquot weighing 78 mg was obtained 159 mg of the dimedon derivative of formaldehyde, indicating a 65.5% yield based on the initial methanol. The activity of 25.5 mg sample was 0.018 microcuries determined by dry combustion and ion current measurement on the resulting $C^{14}O_2$ by means of a dynamic condenser electrometer. The specific activity of the formaldehyde was 2.07 microcuries/mmoles as compared with 2.05 microcuries/mmole for the methanol. The cause of the discrepancy here is not known at present.

By the above procedures, 17 millicuries of formaldehyde-C^{14} of 0.210 millicuries/mmole specific activity has been produced.

3. Acetic Acid-1-C^{14} (D. N. Hess). Approximately 300 millicuries of acetic acid-1-C^{14} was prepared according to the procedure previously described.

4. Acetic Acid-2-C^{14}. (a) **Discussion:** Methanol reacts with sulfur trioxide to give mixtures of methyl sulfate and methyl hydrogen sulfate(6), which on treatment with sodium cyanide yield acetonitrile(7). The acetonitrile may be hydrolyzed in the presence of either alkali or acid to acetic acid. With methanol-C^{14}, acetic acid-2-C^{14} would be the product. The series of reactions with inactive materials has resulted in yields of about eighty per cent based on methanol.

A similar scheme employing phosphorus pentoxide in place of sulfur trioxide was not successful due to the formation of considerable methyl ether.

(b) **Experimental:** (1) **Methyl Sulfate and Methyl Hydrogen Sulfate** - Sulfur trioxide, prepared by heating a mixture of fuming sulfuric acid and phosphorus pentoxide under vacuum, was distilled through two traps containing phos-

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(6) Guyot and Simon, Compt. rend., 169, 655 (1919).

(7) Dumas et al, Compt. rend., 25, 473.

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phorus pentoxide into a small vessel into which was then distilled an equivalent quantity of methanol (about 10 mmoles). The liquid nitrogen bath was replaced by one at a temperature of 0° C(8). The reaction was allowed to proceed with stirring (magnetic bar) for thirty minutes. At the end of this time, the mixture was frozen with liquid nitrogen and the flask was removed from the line. A combination condenser and dropping funnel was fitted to the flask; the apparatus was closed from the air, and the flask was again immersed in liquid nitrogen. A two-fold excess of 10-molar sodium cyanide solution was added; the liquid nitrogen bath was replaced by a 0° C bath, and stirring was begun when the mixture became fluid. After thirty minutes, the flask was returned to the vacuum line, frozen, evacuated, and the water and acetonitrile were distilled to another flask. A nine-fold excess of 10-molar potassium hydroxide solution was added, and the mixture was refluxed for fifteen hours. The major part of the water was removed by distillation at atmospheric pressure, and the last traces were removed by heating under high vacuum. Acetic acid was obtained by adding 100% phosphoric acid to the dry residue, and distilling the product to a liquid nitrogen-cooled trap under high vacuum. The distillation required about twelve hours. The acetic acid, obtained in up to eighty per cent yields, had the following constants: b.p. 115°, n_D^{23} 1.3708; literature values: b.p. 116°, n_D^{23} 1.3705.

5. *Formic Acid. (J. G. Burr and H. E. Heller).* (a) **Discussion:** Information has been obtained on the mechanism of the reaction between carbon dioxide and lithium borohydride to yield formic acid. Complex reactions of an obscure nature prevent a complete elucidation of the mechanism. The reaction has been used in the high-level production of sodium formate-C^{14}. The method is superior to others(9) in that it does not require the use of elevated temperatures or pressures.

Methanol-C^{14} in 13% yields was identified among the products of the tracer runs, but formaldehyde could not be detected. Elevation of the reaction temperature from 0° to 80° C did not increase the yield, but reduced the absorption of carbon dioxide. At -80° C the reaction did not take place. Diethyl carbitol as solvent increased the absorption of carbon dioxide, but lowered the yield of formic acid. The reaction did not take place in tripropylamine solution. During the reaction, a variable amount of boron was converted to diborane which

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(8) The reaction becomes violent at temperatures much above 0°C.

(9) Calvin, Heidelberger, Reid, Tolbert, and Yankwich, "Isotopic Carbon", John Wiley and Sons, Inc., New York (1949), p. 64.

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appeared in the barium hydroxide traps as boric acid, and a solid precipitated which, when isolated in an inert atmosphere, contained 0.73 mols of boron per mol of formate, and which evolved hydrogen when moistened.

The methanol formed was not produced by the action of lithium borohydride on formate since lithium formate was not reduced by lithium borohydride alone or in the presence of methanol. Although sodium trimethoxyborohydride will reduce carbon dioxide to formic acid(10), the corresponding lithium compound could not be an intermediate here since a solution of lithium borohydride containing two mols of methanol per mol of borohydride absorbed carbon dioxide very poorly and converted it to formate in very poor yield.

The reduction of carbon dioxide to formate with the simultaneous production of diborane probably occurs by the process represented by equation (1), the production of methanol by the competitive process represented by equation (2). This is analogous to the reduction of carbon dioxide to methanol by lithium aluminum hydride(11). However, the variable ratio of diborane to formate, and the anomalous composition of the solid formed in this reaction make it evident that complex secondary processes must take place.

$$(1) \quad LiBH_4 + CO_2 \longrightarrow LiOOCH + \tfrac{1}{2}B_2H_6$$

$$(2) \quad 3LiBH_4 + 4CO_2 \longrightarrow LiB(OCH_3)_4 + 2LiBO_2$$

During exploratory and tracer runs, simple apparatus such as flasks, burettes, and stillheads found in any laboratory sufficed to carry out the reactions. However, for high-level work the apparatus shown in Fig. 33 was devised so that all operations might be carried out without exposing the active material to the external atmosphere.

(b) **Experimental:** (1) **Tracer Experiments** - After dissolving lithium borohydride(12) in ethyl ether, and decanting from the considerable solid residue, the solution was stored in a closed system, and assayed by evaporating a sample under water pump vacuum at 100°, and measuring the evolved hydrogen from dilute acid decomposition of the residue.

(2) **Sodium Formate-C^{14}** - In a typical run, carbon dioxide obtained from 10 mmoles of barium carbonate (containing 51 microcuries of activity)(13) was

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(10) Irving Sheft, M. S. Dissertation, The University of Chicago, March, 1944.

(11) Nystrom, Yanko, and Brown, J. Am. Chem. Soc., 70, 441 (1948).

(12) Lithium borohydride must be handled in a dry box, preferably in an inert atmosphere, as some samples of the solid are spontaneously inflammable in moist air.

(13) Radioactivities were determined by ion current measurements of CO_2 or volatile organic vapors using a dynamic condenser electrometer.

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Key to Figure 33

A. Nitrogen tank.

B. Pressure-reducing valve.

C. Pressure reservoir for actuating burettes.

D. Stopcock with notches filed in the core for fine adjustment of gas flow through the system.

E. Flowmeter

F. Mercury-filled pressure release for burette system.

G. CO_2 generator.

H. Trap for water vapor.

I. Three-way stopcock.

J K .... J_1K_1. Pressure-actuated burettes for adding reagents to the reaction system without exposing the mixtures to the air.

L. Reaction vessel.

M. Tip of gas-introduction line.

N. Magnetically operated tungsten wire plunger for clearing M of precipitated solids.

O_1, O_2. Internal condensers.

P. Three-way stopcock.

Q. Reaction vessel.

R. Pressure manifold for burettes.

S. Outlet manifold for burettes.

T_1 .... T_{10}. Stopcocks for controlling filling and emptying of the burettes.

U. Three-way stopcock connecting outlet mainfold to the air or to vacuum.

V. Three-way stopcock connecting the entire reaction system to the air or to high vacuum.

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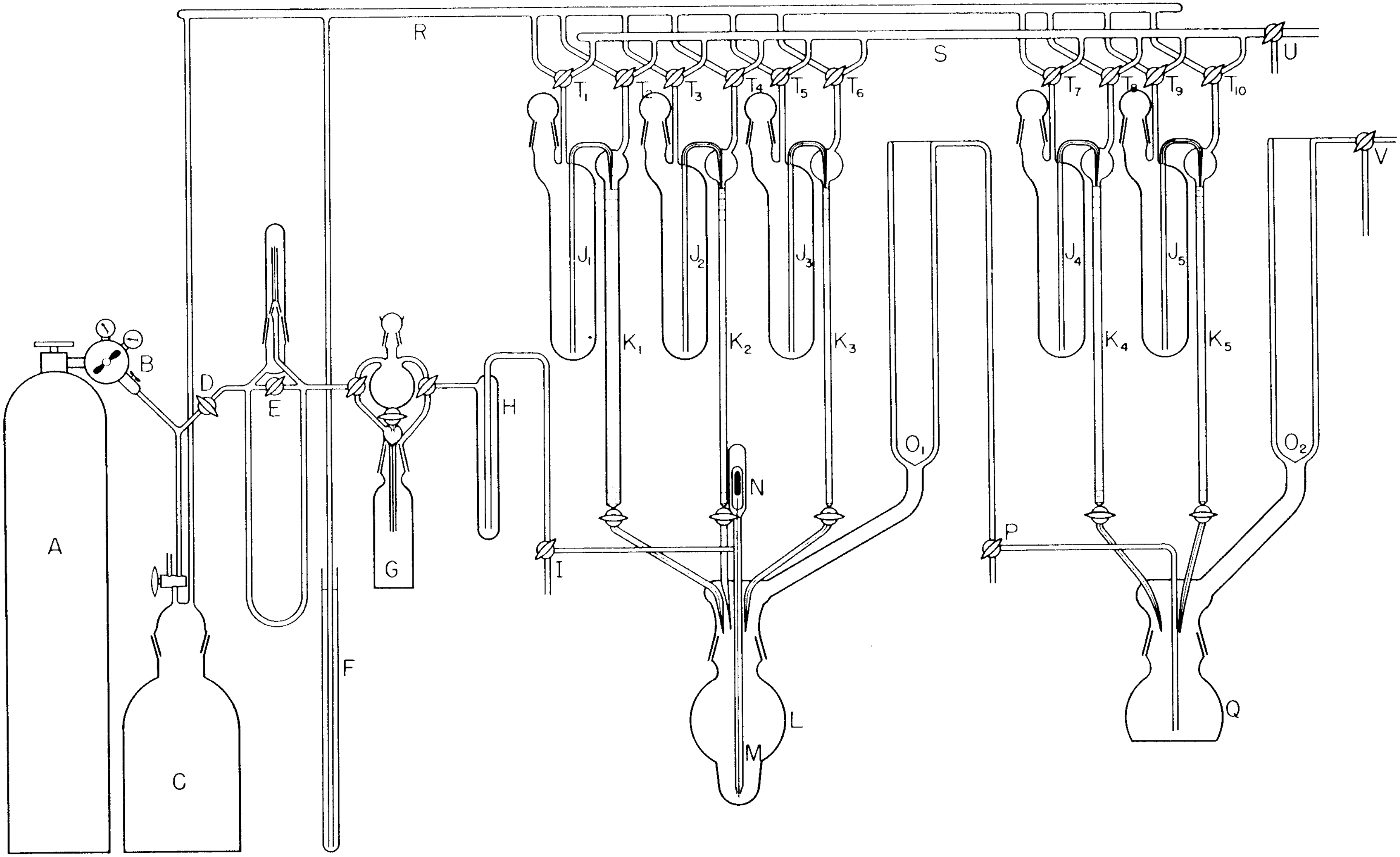

FIG. 33

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dried by passage through a trap at -80° and a second trap filled with Drierite, then swept by nitrogen into 27 ml of 0.037 *M* lithium borohydride-ether solution (10 mmoles) maintained at 0° C. Passage of the exit gases through saturated barium hydroxide led to the recovery of 0.2154 g (1.09 mmoles) of isotopic barium carbonate containing 5.6 microcuries of activity. During the reaction, volatilized ether was returned to the solution by a cold finger filled with dry ice (Fig. 33). A heavy powdery precipitate formed in the reaction solution. The reaction solution was hydrolyzed with 6 ml of water, and the ether was then removed in a strong stream of nitrogen. This ether contained 2-3% of the initial radioactivity.

During exploratory runs, the aqueous solution obtained at this point was subjected to qualitative tests. Formic acid was identified as the S-benzylthiuronium salt, and by the mercuric chloride reaction; methanol was detected by the Eegrine test(14); formaldehyde was shown absent by the Eegrine test and by the dimedon test. The formate content was also determined by boiling the aqueous solution to remove volatile organic substances, and oxidizing with alkaline permanganate(15).

In the experiments with isotopic carbon dioxide, the aqueous solution obtained was acidified with 1.5 ml of 85% phosphoric acid. High vacuum distillation gave a product containing, by titration with NaOH, 6.3 mmoles (71%) of formic acid; the phosphomolybdate test revealed the presence of a trace of phosphate, and turmeric proved the absence of borate. The radiochemical yield was determined by adding 0.50 g of inactive sodium formate to an aliquot of the neutralized distillate, and preparing the S-benzylthiouronium salt. Assay of this derivative gave a radiochemical yield for sodium formate-C^{14} of 6.1 mmoles, (69% of CO$_2$ reacted). The remaining formate solution was distilled to dryness in high vacuum at room temperature.

To the distillate, 3.00 ml (74.2 mmoles) of inactive methanol was added, and the solution was very slowly distilled through a Widmer column (an exploratory dead run under identical conditions gave methanol with a refractive index at 28° of 1.3247). Two small samples of methanol were withdrawn from the column. Radiochemical assay of these samples proved the presence of 1.1 mmoles of methanol-C^{14} in the distillate (13% of CO$_2$) reacted.

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(14) E. Eegrine, Microchem. Acta. 2, 329 (1937).

(15) Newer Methods of Volumetric Analysis, 2nd Edit., W. Bottger, Editor, Van Nostrand Co., New York (1938), p. 58.

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(3) **Formation of Diborane** - The alkaline hydrolysis solution from the reaction of 5.0 mmoles of inactive carbon dioxide with 4.9 mmoles of lithium borohydride was evaporated carefully to dryness (overheating at this point caused extensive conversion to oxalate), and the residue was dissolved in water. The solution was made strongly acid, boiled, and then titrated in the presence of glycerine for boric acid. A total of 3.3 mmoles of boric acid was found. The formate produced in this reaction was 2.2 mmoles as determined by permanganate titration. The solution in the carbon absorption traps at the end of the reaction train (Fig. 33) was similarly found to contain 1.6 mmoles of boric acid. The amount of boric acid in the bubblers was always less than the amount of formate produced in the reaction, but there was no simple relationship. From a dry ice-cooled trap containing anhydrous ethereal trimethylamine inserted in the system before the barium hydroxide bubblers, a solid compound could be recovered which gave a white crystalline sublimate melting at 92-95° (Lit(16) for trimethylamine borine: 94-95°).

(4) **Apparatus and Procedure for High-Level Production of Sodium Formate-C^{14}** -

The apparatus is shown in Fig. 33 (not to scale).

A magnetic stirring-bar was placed in the lower vessel of G and the required amount of BaCO$_3$ was weighed in. The solid was covered with water, a drop of octyl alcohol was added to prevent foaming during the decomposition, and the vessel was placed in position on the generator. The upper vessel of G was filled with 30% HClO$_4$ and capped. A dry-ice filled Dewar was placed around H, and two Ba(OH)$_2$ bubblers filled with 100 ml of half-saturated Ba(OH)$_2$ each were connected in series to the external outlet of P. Reservoir C was filled with nitrogen from A to provide pressure to actuate the system of burettes $J_1K_1 \ldots J_5K_5$; the stopcocks on G were adjusted so that both chambers of G would be washed with gas, and the entire system from G through H, I, L, internal condenser O$_1$, P, and the Ba(OH)$_2$ bubblers was rinsed with nitrogen for thirty minutes.

The gas flow was reduced to about 10 cc/min, LiBH$_4$-ether reagent was added from burette J_1K_1, O$_1$ was filled with dry ice, and the stopcock at the bottom of the upper chamber of G was adjusted to give two drops of HClO$_4$ per minute to the lower chamber of G. The gas flow through G was adjusted to pass through the lower chamber only, and vessel, V, was immersed in an ice-water

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(16) Burg and Schlesinger, J. Am. Chem. Soc. 59, 780 (1937).

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bath. The CO_2-generation and subsequent sweeping required about an hour and a half for a 10-mmole run. After about the first half hour CO_2 began to show up in the first $Ba(OH)_2$ bubbler as precipitated $BaCO_3$, but none was found in the second bubbler until after the addition of a few ml of water from burette J_2K_2 to decompose the reaction mixture in L. From time to time during the reduction and decomposition, it was necessary to clear tip M of precipitated material by agitating plunger N with a small magnet. When the violent reaction resulting from addition of water had subsided, the dry-ice remaining in O_4 was removed by a stream of air, the $Ba(OH)_2$ bubblers were disconnected from p and replaced by a hose leading to the main vent of the California hood in which the apparatus was built, and the ether was evaporated from the mixture by increasing the gas flow through the system to several hundred cc/min.

When the ether had evaporated, concentrated H_3PO_4 was added from burette J_3K_3 causing a further violent evolution of gas. When this had subsided, stopcock I was closed to vessel L, L and Q were connected through P; L was frozen down in liquid nitrogen, and stopcock V was opened to the high vacuum system; Q was immersed in liquid nitrogen, and when a good vacuum was obtained, L was allowed to warm so that distillation of the mixture of water and formic acid to Q occurred. In the final stages of the distillation, L was warmed very strongly with a smoky flame to drive over the last traces of acid.

When the distillation was complete, Q was allowed to warm and the system was open to the air. Q was momentarily removed and a drop of phenolphthalein indicator was added. The formic acid was then titrated with 5 *N* NaOH from burette J_4K_4. The slightly basic titration mixture was set aside for combination with the products from other runs.

The results obtained with this apparatus are summarized in Table 1. A total of 11.8962 g of isotopic barium carbonate, containing an estimated 203 millicuries of C^{14}, was processed as above in five runs. From these runs, the recovered barium carbonate weighed 1.9469 g (9.84 mmoles, 16.3%), and contained an estimated 32 millicuries of C^{14}. By titration, the total amount of formic acid produced was 33.4 mmoles (66% based on the reacted carbon dioxide). The neutralized formate solutions (containing a slight excess of alkali) were combined and vacuum distilled almost to dryness. The residue was taken up in distilled water, centrifuged, and made up to 100.0 ml. From this solution, two 100 λ samples were taken, and each pipetted into a solution of 2.000 g (29.4 mmoles) of sodium formate in 10 ml of water. The S-benzylthiuronium

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TABLE I

Summary of data on reduction of CO_2 to formic acid

RUN	$BaCO_3$ DECOMPOSED (mmoles)	CO_2 REDUCED TO ACID(a)		CO_2 RECOVERED(b)		CO_2 LOST	
		mmoles	percent	mmoles	percent	mmoles	percent
1	9.42(c,d)	---	---	---	---	---	---
2	9.51(d)	4.34	45.7	3.79	39.9	1.36	14.4
3	10.00(d)	5.47	54.7	3.64	36.4	0.89	8.9
4	,,(d)	5.94	59.4	3.06	30.6	1.00	10.0
5	,,(d)	5.72	57.2	1.79	17.9	2.49	24.9
6	10.87	4.18	38.4	1.51	13.9	5.18	52.3(e)
7	10.00	5.84	58.4	2.87	28.7	1.29	12.9
8	12.81	7.96	62.2	1.33	10.4	3.52	27.4
9	15.82	9.55	60.3	2.36	14.9	3.91	24.8
10	10.00	5.72	57.2	1.77	17.7	2.51	25.1

(a) Determined by titration with standard NaOH solution.

(b) Determined by weighing the $BaCO_3$ precipitated in the after bubblers.

(c) Bubble tip M (Fig. 33) plugged during this run. As a result of this, the plunger N was added to the apparatus to allow clearing of the plugged tip without opening the apparatus.

(d) These runs were testing experiments for the apparatus, and were carried out with inactive $BaCO_3$.

(e) The $BaCO_3$ used in this run foamed badly on contact with the $HClO_4$, and much CO_2 was lost when the apparatus was dismantled for cleaning.

[redacted]

salts were then prepared and recrystallized from ethanol. Duplicate assays of each sample of the salts showed an average specific activity of 0.0206 microcuries per mg. This corresponds to a total yield of 129 ± 2 millicuries of sodium formate (75% based on reacted carbon dioxide activity). Crystallization of the derivatives was so carried out as to produce a considerable fractionation should more than one acidic species be present; however, assay of the crude derivative led to the same result, within experimental error, as assay of the recrystallized salt. If radioactive species other than formate were present in the solution, direct assay of the solution should give a higher value than assay through a formate derivative; both types of assay, however, gave the same value within experimental error.

5. *Production of* $C^{14}H_3OH$ *(R. G. Mansfield).* A total of 139.9 millicuries of methanol was produced by $LiAlH_4$ reduction of CO_2.

THE SYNTHESIS OF HIGH MOLECULAR WEIGHT INTERMEDIATES CONTAINING C^{14} RING-LABELED BENZOIC ACID AND INTERMEDIATES

C. J. Collins

Following the procedure outlined previously(17), the snythesis of vitamin K labeled in the 8-position with C^{14} has been carried through to 2-methylnaphthalene-8-C^{14}. The carbonation of γ-(p-tolyl)-propylmagnesium bromide has been effected using 30 mmoles of carbon dioxide containing 16.2 millicuries of $C^{14}O_2$. The efficiency of this reaction was 85.5% based on carbon dioxide unrecovered. The product consisted of 2.62 grams of γ-(p-tolyl)-butyric acid containing 7.85 millicuries of C^{14}. A 1.34 gram (4.0 millicuries) quantity of this acid was converted to 2-methylnaphthalene-C^{14}. The product weighed 0.57 grams, representing a 54% chemical yield.

The apparatus for carbonation of the Grignard reagent shown in Fig. 34 is a modification of the one shown previously(18).

(17) ORNL 336, Progress Report, Dec., 1948, January, February, 1949, pp. 68-73.

(18) Ibid., Fig. 2, p. 71.

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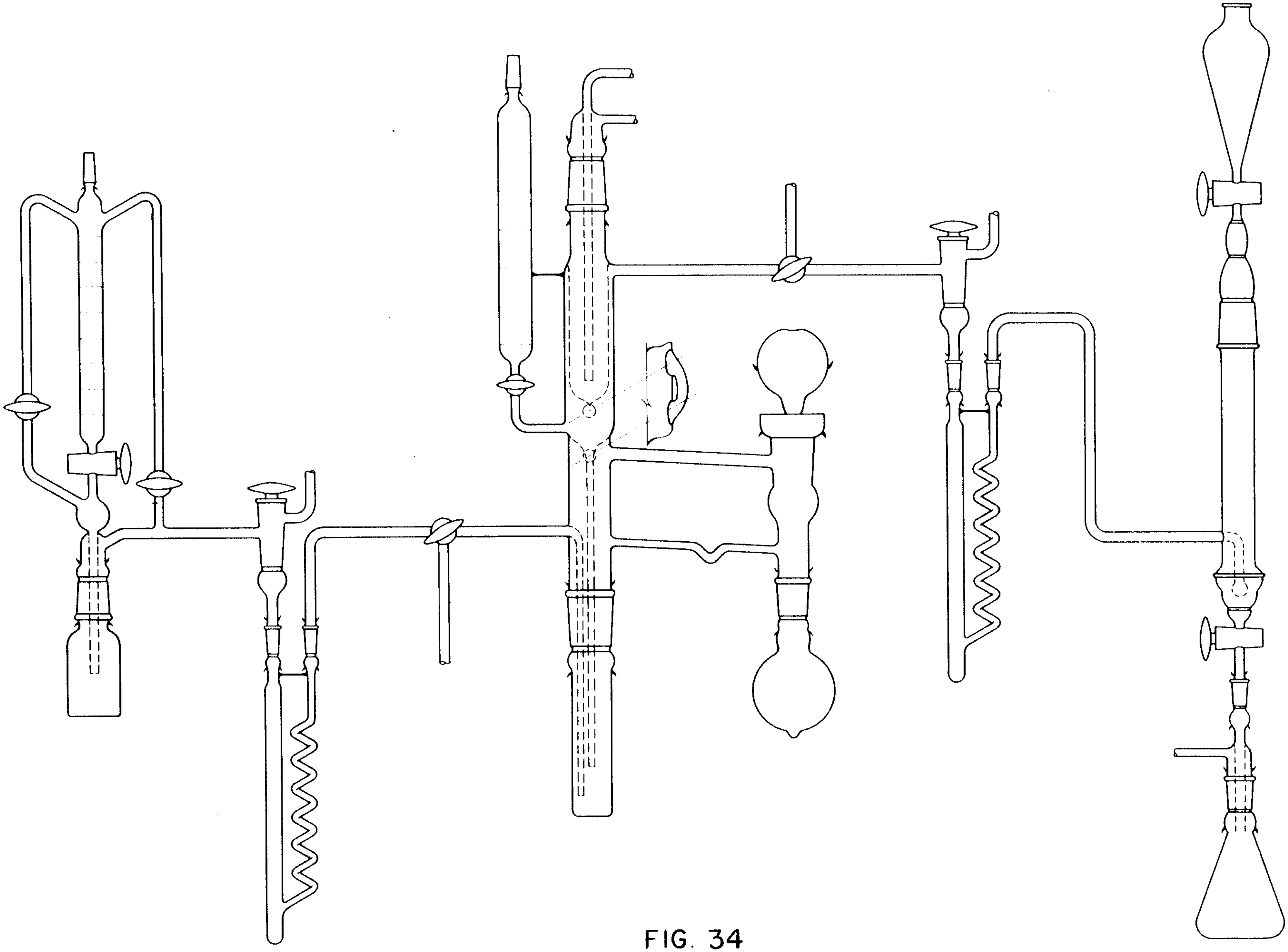

FIG. 34
GRIGNARD CARBONATION APPARATUS

[redacted]

CHEMISTRY OF SEPARATIONS PROCESSES

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[redacted]

I. VOLATILITY STUDIES

A. Agron, E. G. Bohlmann

Equipment is being set up to study the properties of a number of metallic fluorides. It is anticipated that a number of different structural materials will be tried for the construction of laboratory-scale vacuum lines for this study.

II. SOLVENT-EXTRACTION PRINCIPLES AND APPLICATIONS

STUDY OF THORIUM HYDROLYSIS BY TTA-BENZENE EXTRACTION

W. C. Waggener, R. W. Stoughton

The hydrogen ion dependence of the expression $(R)_b^a\,[(HT)/(H^+)]^4$ at a constant ionic strength of 0.5 is being studied in the *p*H range 0.3 - 3.7 using Th^{234} tracer in the presence of about 10^{-7} *M* natural thorium. [$(R)_b^a$ represents the distribution ratio of thorium between aqueous and benzene phases, and $(HT)/(H^+)$ represents the ratio of activities of TTA and hydrogen ion in benzene and aqueous phases respectively.] This expression should remain constant with increasing *p*H until the fraction of Th(IV) hydrolyzed becomes appreciable.

It was desirable for counting the phases to maintain the ratio $(R)_b^a$ near unity, necessitating dilutions of the benzene phase from 10^{-1} to 10^{-4} *M* TTA with decreasing acidities of aqueous phase. Thorium was introduced initially into 0.25 *M* benzene-TTA, and aliquots taken for dilutions over the range.

Preliminary results indicated that the expression $(R)_b^a\,[(HT)/(H^+)]^4$ begins to increase rapidly between a *p*H of 1 and 2. This agrees with recent work of E. Zebroski and W. H. Alter(1) using a similar TTA extraction method, but indicates a much larger value for the first hydrolysis constant than the value of 2.5×10^{-4} obtained by John Casper(2) by method of direct titration.

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(1) E. Zebroski, W. H. Alter, KAPL-134,3; 182,10 (1949).

(2) John Casper, Dissertation, Johns Hopkins (1941).

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However, results by the extraction method appear questionable in view of a tendency observed for thorium activity in benzene TTA to adsorb or precipitate from the solution with increasing dilution.

Disparity between calculated and observed specific activity for dilutions of 0.25 *M* benzene TTA ranged from 2% at 100-fold (2.5×10^{-3} *M*) to 13% to 94% at 2000-fold dilution (1.25×10^{-4} *M*). The activity absorbed was partially elutable with benzene (27% in a single experiment), and entirely so with concentrated nitric acid. Material balances calculated after elution with acid were good.

Studies still in progress indicate that this disparity increases with (1) increasing time, (2) increasing relative surface area, and (3) decreasing TTA concentration, but is essentially independent of the concentration of natural thorium between 10^{-6} *M* and 10^{-9} *M*.

Reducing the concentration of water from its solubility in benzene (about 0.03 *M*) to 10^{-5} *M* had no recognizable effect.

It does not seem likely that ThT_4 is the adsorbing species. Present work is aimed to establish whether adsorption of thorium is due to hydrolysis of ThT_4 or its reaction with an unknown impurity present either in the TTA or benzene.

SEPARATION OF Hf AND Zr

J. P. McBride, R. W. Stoughton

1. Introduction. The extraction of Hf and Zr with a benzene-TTA (thenoyl trifluoroacetone) solution from an aqueous acidic solution containing a non-complexing anion may be represented by an equation of the form

$$M(OH)^{+n}_{4-n} \text{ to } m\,HT_B \rightleftarrows MT_{m_B} + nH^+_A + (4-n)\,H_2O$$

where HT represents TTA and the subscripts indicate the phases in which the various species appear (i.e., A-aqueous; B-benzene). Corresponding to the above equation the following equilibrium constant is formulated:

$$K = \frac{(MT_m)_B\,(H^+)^n}{[M(OH)^n_{4-n}]\,(HT)_B^m} \qquad (1)$$

[redacted]

[redacted]

where (H^+) and (HT) are the hydrogen ion and TTA activities and where $[M(OH)_{4-m}^{n}]$ represents the activity of the aqueous metallic species (assuming a single species), n its charge, and m the number of T anions associated with each M species in the benzene phase. When the activity coefficients of MT_m and $M(OH)_{4-m}^{n}$ remain constant the expression becomes:

$$K = \frac{DR_{(B/A)}\,(H^+)^n}{(HT)_B^m} \qquad (2)$$

where $DR_{(B/A)}$ refers to the distribution ratio of the metal ion, (organic over aqueous). If more than one species were present in either phase, the above equation would, of course, have to be modified.

Data have been reported which indicate that the extraction of Zr from 2 *M* $HClO_4$ may be represented by the equation

$$M(OH)_A^{+3} + 4\,HT_B \leftrightarrows MT_{4B} + 3H_A^+ + H_2O$$ (3)

Work at this laboratory indicates that the same equation also holds to a close approximation for the extraction of Hf from 0.5 *M* HNO_3. (4)

A recent report from Knolls laboratory postulates a third power acid dependence but a second power TTA dependence for Hf extraction from dilute HNO_3 (up to 1 *M*) which increases to approximately fourth power as the acidity of the aqueous phase increases. (5)

The experiments reported below have been done to determine the acid and TTA dependence for the extraction of Hf from HCl solutions.

2. ***Experimental.*** The TTA solutions were prepared with thiophene-free benzene using a TTA sample of better than 99.5% purity, obtained from M. Calvin of the University of California.

A stock solution of Hf tracer in 10 *M* HCl was prepared by dissolving 47.8 mg of pile-irradiated hafnium, as hafnium oxychloride, in concentrated HCl and diluting to a final volume of 25 ml.

The experiments on acid dependence were performed by equilibrating aliquots of a 0.0200 *M* TTA solution containing Hf tracer with equal volumes of acid solutions prepared by diluting concentrated acid to the required strength. In the first series NaCl was added to give a constant ionic strength of 4.0, while the second series was run at varying ionic strength, without adding NaCl. The 0.0200 *M* TTA solution was made by equilibrating a 0.0205 *M* TTA solution with an equal volume of 0.5 *M* HCl containing 50 microliters of the stock

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(3) R. E. Connick, W. H. McVey, UCRL 101, March 1948.

(4) J. P. McBride, ORNL 303.

(5) B. E. Dearing, J. F. Flagg, D. C. McCarty, KAPL-180.

[redacted]

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Hf tracer solution. On the basis of $DR_{(B/A)}$ of 40 for TTA the resulting TTA-benzene solution should have been 0.0200 *M*.

The experiments on TTA dependence for the extraction of Hf from 0.5, 1.0, and 3.0 *M* HCl were run using aliquots of a stock 0.015 *M* TTA benzene solution containing Hf tracer, diluting to the required TTA molarity with dilute TTA-benzene solutions and equilibrating with equal volumes of acid solutions of the required strength. The 0.015 *M* TTA solution containing tracer was prepared as above by equilibrating 12.5 ml of a 0.01537 *M* TTA-benzene solution with an equal volume of 0.5 *M* HCl containing 250 microliters of the stock tracer solution. The solution was diluted with benzene or a 0.0825 *M* TTA-benzene solution to give the required TTA molarities.

All equilibrations were made at room temperature, 25°-31° C, and for approximately 2½ hours. Hf analyses were made by mounting samples of each phase on glass plates in the usual manner and counting without inserting an absorber between the plate and the G-M tube. The ratio of the activity in the benzene phase to that in the aqueous is, of course, equal to the distribution ratio. Where the presence of NaCl would interfere with the Hf counting in the aqueous phase an aliquot of the phase was extracted with an equal volume of benzene containing a large excess of TTA over that estimated for complete extraction and an aliquot of the resulting benzene phase counted.

3. *Dependence of Hf Extraction on HCl Molarity at Constant TTA Concentration.* As indicated in the introduction the distribution ratios (benzene over aqueous) for the extraction of a metal ion may be represented by

$$DR_{(B/A)} = \frac{K(HT)_B{}^n}{(H^+)^n} \qquad (3)$$

assuming a single species in each phase and that the activity coefficients remain constant; *m* and *n* have the aforementioned significance. Taking the log of both sides one obtains

$$\log DR_{(B/A)} = \log K + m \log (HT)_B - n \log (H^+).$$

Hence if one obtains the $DR_{(B/A)}$ at constant TTA concentration as a function of acid concentration a plot of log $DR_{(B/A)}$ *vs* log (H^+) should give a straight line with a slope *n* equal to the charge on the aqueous metallic species.

Figure 35 illustrates the data obtained on equilibrating aliquots of a

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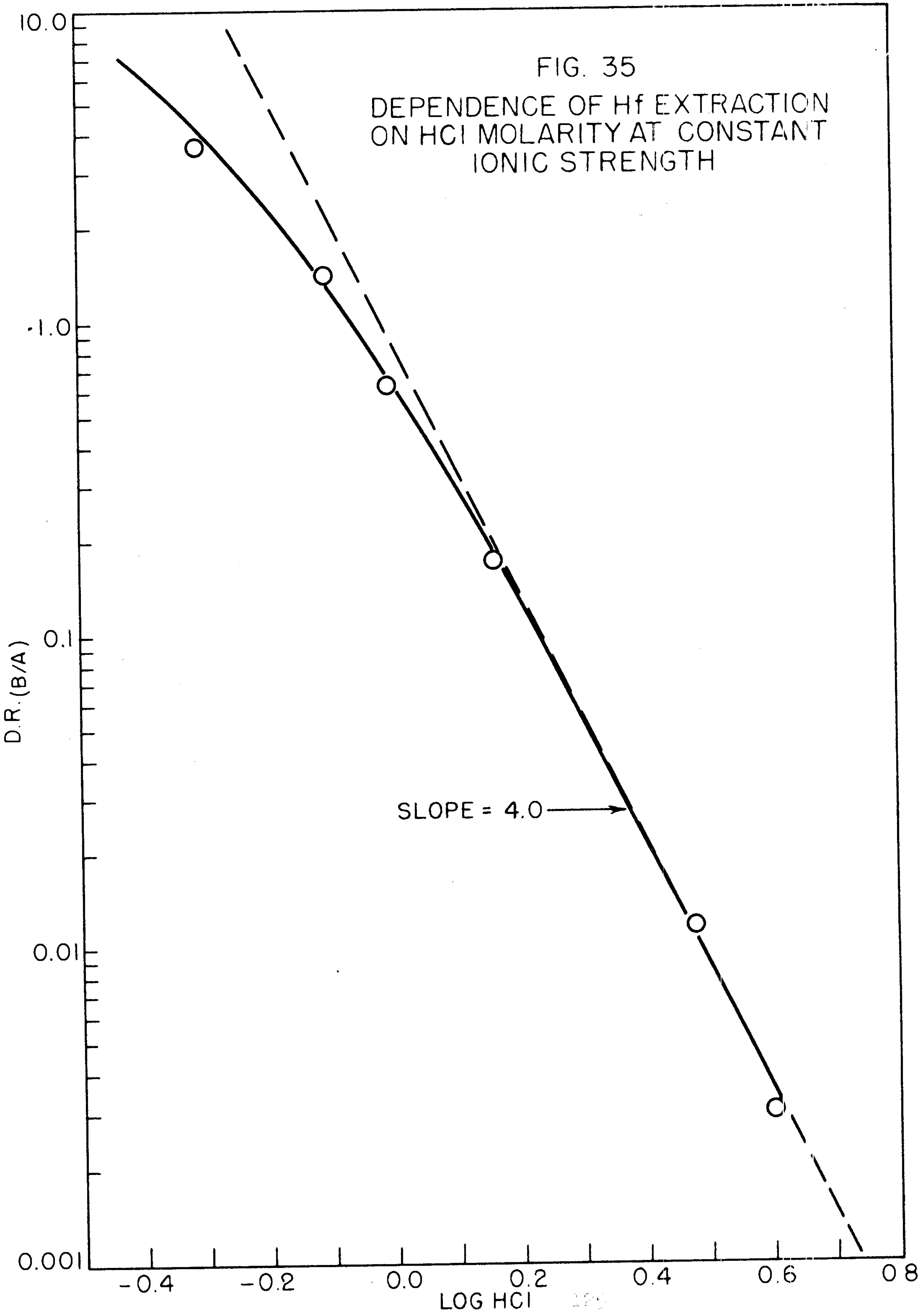

FIG. 35

DEPENDENCE OF Hf EXTRACTION ON HCl MOLARITY AT CONSTANT IONIC STRENGTH

[redacted]

0.0200 *M* TTA-benzene solution with equal volumes of 0.5 to 4.0 *M* HCl solutions maintained at constant ionic strength of 4.0 by the addition of NaCl. The log $DR_{(B/A)}$ is plotted against log *M* HCl. It is assumed that at constant ionic strength the H^+ molarity is nearly proportional to the hydrogen ion activity and that any changes in the hydrogen ion activity coefficient which does occur on going from a pure HCl solution to a predominantly NaCl solution are such as to make the absolute value of the apparent slope a maximum.

The data are best represented by a limiting slope of four, for the more concentrated solutions, which becomes less than three for the more dilute solutions.

Figure 36 illustrates a similar series of experiments in which the $DR_{(B/A)}$ is studied as a function of acid concentration with nothing else present at macro concentrations. It is to be expected that under these conditions the hydrogen ion activity coefficient increases rapidly as one goes to the more concentrated solutions. The plot of log $DR_{(B/A)}$ *vs* log HCl molarity is found to be represented rather closely by a straight line with a slope of 3.53. The broken line demonstrates a plot of the log $DR_{(B/A)}$ *vs* the log of the approximate "effective" hydrogen ion activity.(4) The line shows a somewhat lower acid dependence, i.e., 2.75. The effective hydrogen ion activity is obtained by multiplying the molarity by a semi-empirical activity coefficient obtained as follows:

It is assumed, as in ORNL 303, that the hydrogen ion activity coefficient up to 1.5 *M* acid is best represented by the geometric mean of the $\gamma_{\pm\,HCl}$ and an activity coefficient estimated by the McInnes hypothesis $[\gamma_{H^+(M)}]$.(6) The McInnes hypothesis states that the activity coefficient of a univalent ion is the same in all univalent salt solutions of the same ionic strength and that since K^+ and Cl^- have nearly equal radii and mobilities

$$\gamma_{\pm\,KCl} \cong \gamma_{K^+} \cong \gamma_{Cl^-}$$

Given a value for γ_{Cl^-} the individual activity coefficient of other ions may be calculated for solutions of the same ionic strength as illustrated below for the hydrogen ion in HCl solution

$$\frac{(\gamma_{\pm\,HCl})^2}{\gamma_{\pm\,KCl}} \cong \gamma_{H^+(M)}$$

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(6) D. A. McInnes, J. Amer. Chem. Soc. 41, 1086-92 (1919).

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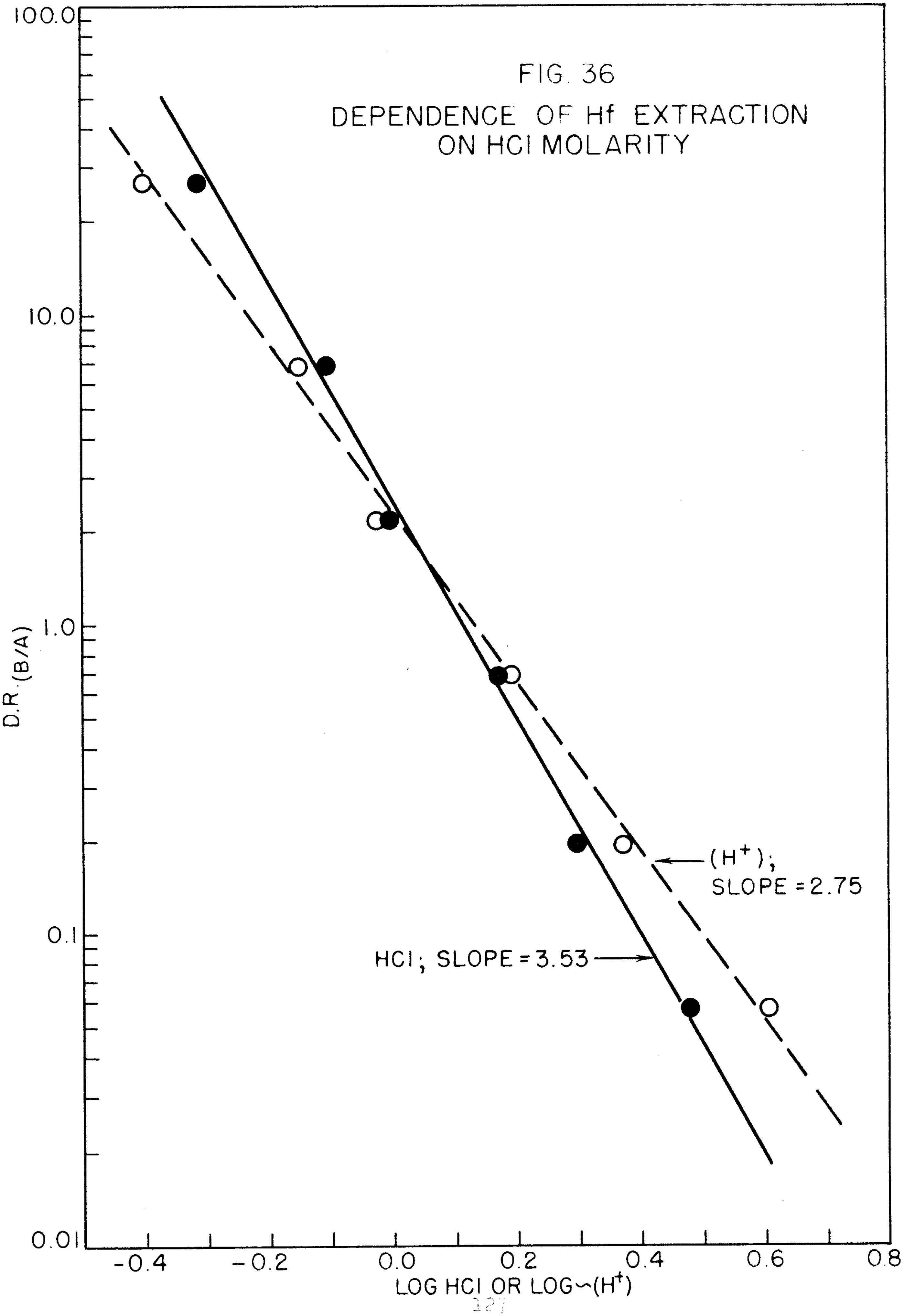

FIG. 36

DEPENDENCE OF Hf EXTRACTION ON HCl MOLARITY

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It is here assumed that the true γ_{H^+} may then be approximated by the expression

$$\gamma_{H^+} = (\gamma_{\pm HCl}\,\gamma_{H^+(M)})^{\frac{1}{2}}$$

Given γ_{H^+}, a molar activity coefficient fc_{H^+} may be calculated from

$$fc_{H^+} = m\,\gamma_{H^+}/M$$

where m and M are the molality and corresponding molarity.

In the case of Hf extraction from HNO_3, the hydrogen ion activity coefficients seemed to be well approximated by such calculations up to 1.5 M HNO_3. For the more concentrated solutions it was possible to make an empirical correction for changes in the activity coefficients of all aqueous species involved in the TTA extraction in terms of an "effective" hydrogen ion activity coefficient $(fc_{H^+}{}')$. Since the activity coefficients calculated for the HCl solution were nearly the same as those calculated for the HNO_3 solutions it was felt that the effective hydrogen ion activity coefficients in the extraction of Hf from the more concentrated HCl solutions could be best approximated by the use of the "effective" activity coefficients obtained in ORNL 303 and given in the last column of Table I.

4. *Dependence of Hf Extraction on TTA Activity.* Figure 37 illustrates the data obtained for Hf extractions from 0.5, 1.0, and 3.0 M HCl as a function of TTA concentration. Log $DR_{(B/A)}$ is plotted against log TTA activity. The TTA activities were obtained by the use of the activity coefficients of King and Reas$^{(7)}$ after correcting the TTA concentration for solubility in the aqueous phase, assuming a distribution ratio (benzene over aqueous) of 40.

The data for all acid concentrations show a slope of 3 at the higher TTA concentrations. At the lower TTA concentration the TTA dependence at 0.5 and 1.0 M HCl seems to be between 1 and 2. The data for the 3 M HCl solutions do not go low enough in TTA to show the lower TTA dependence.

The dotted line in Fig. 37 illustrate the data obtained for 0.5, 1.0, and 3.0 M HNO_3 over the same range of TTA concentrations and reported in ORNL-303. The distribution data are quite similar at the higher TTA concentrations with a small difference in TTA dependence, i.e., 3.7 in extraction from media HNO_3 compared with 3.0 in HCl media. However, the hydrochloric acid system shows a striking increase in distribution ratios at the lower concentrations.

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(7) E. L. King, W. H. Reas, BC-69.

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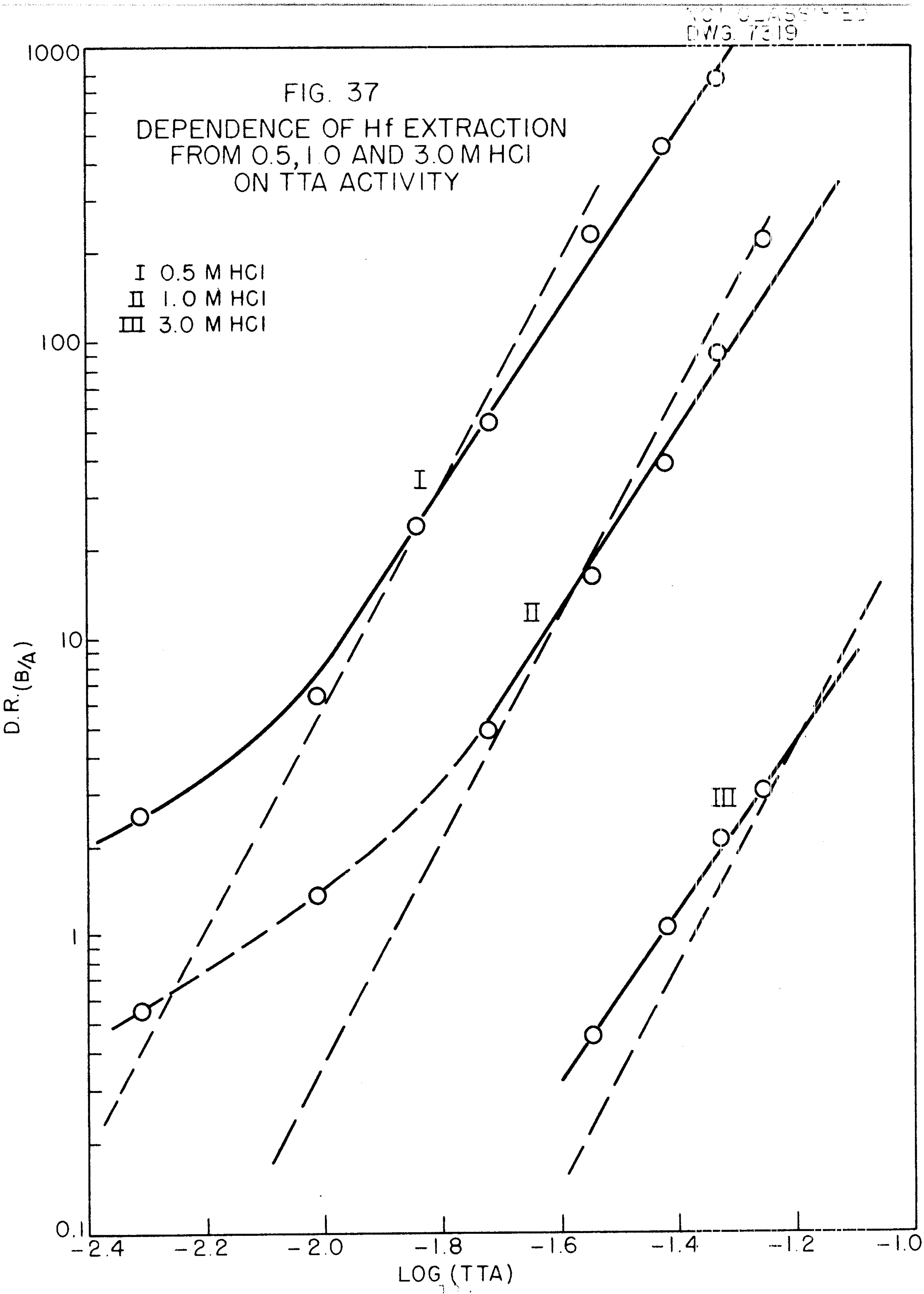

FIG. 37

DEPENDENCE OF Hf EXTRACTION FROM 0.5, 1.0 AND 3.0 M HCl ON TTA ACTIVITY

[redacted]

TABLE I

Effective hydrogen ion activity coefficients for TTA-Hf-HCl extractions

	HNO_3			HCl			
m	$(\gamma_{\pm HNO_3}\gamma_{H^+})^{1/2}$	MOLARITY	fc_{H^+}	$(\gamma_{\pm HCl}\gamma_{H^+})^{1/2}$	MOLARITY	fc_{H^+}	fc'_{H^+}
0.5	0.814	0.492	0.827	0.812	0.494	0.824	0.824
1.0	0.933	0.970	0.962	0.930	0.981	0.951	0.951
2.0	1.240	1.876	1.322	1.336	1.924	1.389	(1.206)
3.0	1.765	2.749	1.926	1.990	2.829	2.110	(1.365)
4.0	2.67	3.564	2.997	3.07	3.706	3.310	(1.460)

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5. *Discussion.* Examination of the Hf distribution data obtained with the HCl and HNO_3 system leads one to conclude that:

(1) the extracted species are not identical in the two cases;

(2) more than one species, one or more of which may contain Cl, are extracted from HCl solution;

(3) the acid dependence over the range, 0.5 to 3.5 *M*, is close to 3 in both cases, and

(4) the TTA dependence at higher TTA concentrations is 3.0 in the case of HCl and 3.7 in the case of HNO_3.

Efforts to obtain direct chemical evidence for an extractable Cl complex are as yet inconclusive. Trace Cl^{38} has been obtained for this purpose. It can be stated that there is no detectable extraction of Hf or Cl into benzene in the absence of TTA. In two experiments in which dead macro Hf was extracted with TTA from 0.77 *M* HCl containing tracer Cl^{38}, a chlorine concentration of 10^{-4} *M* was detected in the organic phase. The approximate Hf concentration found in a similar run in which tracer Hf but no Cl^{38} was used was about 10^{-3} *M*. Work will be continued to establish definitely the existence of a chloride extractable species and to determine the formula.

During the course of the chloride work several experiments were run at the lower TTA concentrations in which stock tracer was added directly to 0.73 *M* HCl and extracted. The TTA dependence over the region 0.004 to 0.015 *M* was found to be 2.26, but the distribution ratios were lower by a factor of 10, indicating that much of the Hf in the 10 *M* HCl stock solution was not in the monomeric state. As in the case of the HNO_3 systems, it is felt that the distribution data obtained when the tracer is initially in the benzene phase more correctly represent the true distribution data for monomeric Hf.

III. ION-EXCHANGE

SEPARATION OF ANIONS OF THE FIFTH, SIXTH AND SEVENTH GROUPS

R. W. Atteberry and G. E. Boyd

The recent availability of high capacity, fast, strong base synthetic organic exchangers has enormously enlarged the potentialities of the ion exchange separations technique, and, in view of this and other developments, it

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may be asserted that it is now possible to separate every element of the periodic table giving an ion in solution from every other such element. The work during the past quarter has been devoted to a systematic demonstration of these possibilities for the anions formed by the fifth, sixth and seventh groups of the periodic table. An account of a preliminary study of the separation of the halides, Cl^-, Br^-, and I^- can be given.

Firstly, measurements were made of the equilibrium distributions of these halide ions in NaOH solutions of varying concentrations in order to determine the extent of the differences of their "exchange potentials". Three new commercially procurable anion exchangers, Amberlite IRA-400 (8) and Dowex A-1 and A-2 (9) were employed. The exchanging groups in these materials are reported to be quaternary amine groups and this has been borne out by *p*H titrations made on the "OH" or hydroxyl forms which show them to act like strong bases. A comparison of the selectivity of each of these exchangers, using the hydroxide-chloride equilibrium distribution measurements showed the IRA-400 and A-1 to be quite similar, whereas the A-2 showed an appreciably lower affinity for Cl^-. A comparison of the "exchange potentials" of Cl^-, Br^- and I^- in NaOH solutions with IRA-400 and in Na_2CO_3 solutions with A-1 has revealed the sequence to be $I^- > Br^- > Cl^-$. The potential of I^- ion was quite high as illustrated by K_d values of 980 and 460 in 1 *N* NaOH and 1 *N* Na_2CO_3, respectively.

The ratios of the K_d values in 1 *N* Na_2CO_3 for Dowex A-1 were: $Cl^- : Br^- : I^- = 22 : 68 : 460$, or, $1 : 3.1 : 20.9$. Accordingly, the chromatographic separation of these halides should be achievable readily using a 1 *N* Na_2CO_3 elutriant. Two ion-exchange columns, each approximately 1 cm² × 10 cm of 200-300 mesh IRA-400 and A-1, respectively, were set up, and break-through curves for the uptake of 37 m Cl^{38} from 1 *M* Na_2CO_3 were measured. The concentration history of chlorine activity issuing from the column (i.e., C/C_0 against time of flow or volume) gave a typical "S" shape curve, although there was some asymmetry about the mid-point. An estimate of the number of theoretical plates using the formula:

$$p \approx 2\left(\frac{F_{\text{mid.}}}{W}\right)^2 = 2\left[\frac{F_{c/c} = 0.5}{F_{c/c} = 0.5 - F_{c/c} = .078}\right]^2$$

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(8) Resinous Products Division, Rohm and Haas Company, Philadelphia, Pa.

(9) Dow Chemical Company, Midland, Mich.

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gave 250 for the IRA-400 column and 230 for the A-1 column. A value of K_d of 15 computed from the number of "free volumes" at the mid-point of the breakthrough curve agreed satisfactorily with the value of 18 observed in shaking experiments. Next, a 1 cm^2 × 15.5 cm 170/200 mesh Dowex A-1 bed was prepared in the carbonate form by washing with 6 *l* of 1 *M* Na_2CO_3 and 3 *l* of distilled H_2O. The top two cm of exchanger was removed from this bed, equilibrated with a tracer mixture containing 37 m Cl^{38}, 34 h Br^{83} and 8 d I^{131}, and then placed back on top of the bed. The elution was conducted using 1 *M* Na_2CO_3. A reasonably good chromatographic separation of the Cl^-, Br^- and I^- was obtained, the peaks coming out at 12.3, 45.2 and 567 "free column volumes", respectively, with a 100-fold decrease in each activity between successive peaks and troughs. Finally, a separation of Cl^- and Br^- was conducted by means of a frontal analysis. Here, a mixture of 38 m Cl^{38} and 34 h Br^{83} in 1 *M* Na_2CO_3 was poured continuously through the anion exchanger. The step-wise character of the concentration or activity history of the effluent indicated a good separation.

IV. FISSION PRODUCT SEPARATIONS

RaLa PROCESS

W. H. Baldwin, C. E. Higgins

As a result of renewed interest in the RaLa process, research has been initiated in the Technical and Chemistry Divisions, which is directed toward two objectives, (1) improvement in the quality and yield of the product from the existing process, and (2) a longer range development of a more efficient process which will consistently give a quantitative yield of satisfactory product in a safer manner than is now possible. Current research in the Chemistry Division is concerned with elucidation of details of the chemical steps of the present process. This knowledge is considered to be essential for the proposed 5-10 fold increase in scale of the process. Although much of the chemistry of this process has been summarized in MonN-330, many phases of the process were not studied in the relatively brief period in which the process was developed.

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1. *Summary.* The distribution of fission products in the lead sulfate carrying out carbonate metathesis steps of the RaLa process was investigated in laboratory experiments. Relatively small amounts of activity (0.03% of gross beta and gross gamma) were observed in the off gases. At the completion of the metathesis step the product was contaminated with relatively large amounts of the original Sr beta activity (73% and 39% in two experiments) and total rare earth activity (41% and 26%). After separation of the activities on an ion-exchange column, recognizable quantities of Y, Nd, Pr and Ce were detected.

A change in the order of the purification steps, from two nitrate and two chloride precipitations to one nitrate, two chloride and one nitrate precipitations was shown to be operable and to give good separation from contaminating Fe, Ni, Cr and Pb.

2. *Fission Products Carried through Sulfate Precipitation and Carbonate Metathesis.* Concern over the handling of large quantities of radioactive uranium slugs after a short cooling time (irradiated uranium to supply 10,000 to 20,000 curies of barium after cooling for less than one day) lead to inquiry into the identity of the fission products which would accompany the product through the sulfate precipitation and the metathesis steps. Two laboratory experiments were made to study the distribution of fission products.

(a) **Experimental Conditions.** The sulfate precipitation was made in such a manner that the slurry containing the lead sulfate was of the following composition; 0.93 M UNH plus sufficient "dissolver solution" from Bldg. 706-D to provide tracer fission product activities, 0.5 M HNO_3, 3.4 M H_2SO_4 and 0.3 g Pb(II)/l as nitrate. The solution, containing all substances except H_2SO_4, was heated to 90° C after which the necessary volume of 18 M H_2SO_4 was added dropwise over a 30 minute period. Heating was continued at 90° C for one hour; then the slurry was allowed to cool and settle. The cake was first washed with 3 M H_2SO_4 [150 ml/g Pb(II)], then four times with distilled water [150 ml/g Pb(II)].

The sulfate cake was converted to the carbonate by heating at 90° C for 15 min. with 4 M K_2CO_3 [24 ml/g Pb(II) used in the sulfate precipitation], diluting with distilled water to 0.5 M K_2CO_3, heating for 30 minutes longer, cooling, settling and decanting the supernatant. The metathesis step was repeated and the cake was dissolved in 0.5 M HNO_3 and diluted to a convenient volume for analysis.

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Test Run "A" was made on a 50 ml scale during the sulfate precipitation using as tracer on ml of "dissolver solution" 1MA from 706-D, Run 30. During the sulfate precipitation the gases above the vessel were sucked through 10 ml of 1 : 1 mixture of ethanol and water which was 2 *M* in NaOH. This solution will be referred to as the "off gases".

Test Run "B" was made on a one liter scale containing one ml of dissolver solution which was obtained from a later dissolving. The only departure from the general conditions was the use of aerosol (1 g/l) in the first water wash of the sulfate cake.

Radiochemical analyses of solutions from Runs "A" and "B" are summarized in Table II. The product from Run "B" was examined further, employing ion-exchange to fractionate the contaminating fission product activities.

The solution (50 ml at *p*H 1) was passed through an IR-100 resin packed column (70 mm high 12 mm i.d.) to absorb the activity. The bed was then washed with 0.1 *M* HCl. The activity passing through the column was labeled "not absorbed" and when examined radiochemically six weeks later was found to contain Ba-La, and Sr-Y (Table III).

The resin was washed with 3 *M* HCl; the eluate was evaporated just to dryness, taken up in several 0.1 ml portions of 0.1 *M* HCl, transferred to the top of a resin column (6 mm i.d. 110 cm, packed with 200-300 mesh Dowex 50) and washed with citric acid buffered as shown in Table III.

The elements Y, Nd, Pr and Ce were separated from the column. Judging from these results (Table III) it is to be expected that the Ce with long-lived isotopes might be an undesirable contaminant of the product (L. B. Emlet to C. N. Rucker, April 19, 1949 "Report on the Los Alamos RaLa Meeting April 13 and 14, 1949").

The inability of the column to separate La, Ba and Sr may be associated with the presence of weighable quantities of Pb in the solution which was passed through the column.

3. *Purification of the Electrolyzed Product.* It was requested by the Operations Division that modifications in the purification steps be tested on a laboratory scale before inclusion in a regular plant run. Concentration of the product from electrolysis by the precipitation of $BaCO_3$ was tested as a replacement for the evaporation step currently employed. The order of the product precipitation steps was changed to permit the final evaporation and shipping of barium nitrate (the new order of treatment included one nitrate, two chloride,

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TABLE II

Distribution of fission product activities after lead sulfate precipitation and metathesis steps

	RUN A				RUN B PRODUCT
	SULFATE* (Percent Waste)	OFF GASES* (Percent)	METATHESIS* (Percent Waste)	PRODUCT* (Percent)	Percent of That in Starting Solution
Gross beta	64	0.03	3	33	27
Gross gamma	39.5	0.03	0.5	60	55
Ru beta	61	0.01	39	0.03	0.03
Zr gamma	99	< 0.001	0.4	0.5	5.8
Cb gamma	100	- - - -	< 0.01	< 0.01	0.5
Ce beta	- - -	- - -	- - -	- - -	19
Pu alpha	99.9	- - -	- - -	0.1	< 0.8
Sr beta	22	- - -	5	73	39
Total rare earth beta	57	- - -	2	41	26
I beta	90	1	9	0.01	1.2
Ba beta	18	0.001	1	81	93

*percentage based on the sum of the four solutions since the starting solution was not sampled.

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TABLE III

Fractionation by ion-exchange of F.P.'s associated with the product from run B

Column: 6 mm diameter was filled to a
height of 110 cm with Dowex 50
resin 200-300 mesh

SAMPLE NUMBER	CITRATE			TOTAL c/min APP. 10% GEOM.	COUNTED	ELEMENT
	M	pH	ml			
1	0.24	2.86	171	---	---	---
2	0.24	3.0	105	---	---	---
3	0.24	3.0	120	1.2×10^5	3/15/49	Y
4	0.24	3.0	71	---	---	---
5	0.24	3.0	54	1.2×10^5	3/18/49	Nd
6	0.24	3.0	77	---	---	---
7	0.24	3.2	22	---	---	---
8	0.24	3.2	129	3.6×10^5	3/18/49	Pr
9	0.24	3.2	60	---	---	---
10	0.24	3.2	157	1.48×10^7	3/18/49	Ce
11	0.24	3.2	420	---	---	---
12	0.5	7.5	265	5×10^7	3/24/49	Ba-La*
Not Absorbed						Sr-Y* Ba-La* Sr-Y*

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* Determined radiochemically.

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and finally one nitrate precipitation instead of two nitrate and two chloride precipitations which have long been used in the 706-D operation.)

(a) **Experimental Conditions.** To one liter of solution containing 300 mg Ba(II) (plus tracer), 100 mg Pb(II), 100 mg Fe(III), 100 mg Cr(II) and 100 mg Ni(II) was added 145 ml of 4.8 *M* K_2CO_3. The mixture was agitated at room temperature and then filtered through a sintered glass funnel 90 mm in diameter and with a medium porosity. This particular funnel came from the supply which is used in the 706-D operation.

The precipitate was gelatinous and brown in color. Filtration required over 90 minutes. This was considered to be slower than desired for production.

The precipitate was dissolved from the funnel with 500 ml of 1 *M* HNO_3 and barium nitrate was precipitated by the addition of 2500 ml of 23 *M* HNO_3. After standing for three hours at room temperature the product was separated on the same funnel which had been used before. The precipitate, dissolved in 50 ml distilled water, was treated with 500 ml of an HCl-ether mixture (five volumes of 12 *M* HCl and one volume diethyl ether), agitated for 5 minutes and filtered on the same funnel. A second precipitation of barium chloride was made in the same manner as the first. The second barium nitrate precipitation was made by dissolving the barium chloride in 50 ml distilled water and adding 250 ml of 23 *M* HNO_3, allowing to stand three hours and filtering as before. The precipitate was dissolved in 50 ml distilled water for convenience in analysis.

(b) **Discussion of Results.** The analytical summary (Table IV) indicates a relatively high loss of barium in the carbonate waste and in the second chloride waste. Because of the slow rate of filtration and loss of product the carbonate precipitation step seems less desirable than concentration by evaporation at this time. No explanation is presently available for the higher loss of product in the second chloride waste solution.

Decontamination from the inactive elements Fe, Cr, Ni and Pb was sufficient to meet specifications. No indication was observed that the processes would not work well in the order named and has subsequently been used successfully in the plant.

SEPARATION OF FISSION PRODUCT RARE EARTHS

C. E. Higgins and W. H. Baldwin

1. Introduction and Summary. The more efficient separation of fission product activities attained by operating ion-exchange columns at elevated

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TABLE IV

Purification of the product by carbonate, nitrate and chloride precipitation

SOLUTION	RADIOCHEMICAL Ba (Percent)	Fe (mg)	Ni (mg)	Cr (mg)	Pb (mg)
Starting solution	100	100	100	100	100
Carbonate Waste	12.5				
First Nitrate Waste	0.7				
First Chloride Waste	4.3				
Second Chloride Waste	10.7				
Second Nitrate Waste	0.3				
Nitrate Product	66.6	0.8	Not detectable	Not detectable	1.85

Material Balance 95.1

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temperatures has been repeatedly demonstrated in the laboratory. However, there is reason to believe that the remote operation of columns (which would be required for the separation of very high levels of fission activities) at temperatures near the boiling point of water would be difficult. For example, troubles in operation resulting from bubbles formed in the bed by radiation decomposition of solutions have been experienced in the laboratory. Therefore, ion-exchange characteristics at temperatures between 25° and 100° C have been investigated. Distribution data have been obtained for Eu and Y between resin and citrate buffer solution at 75° C which are slightly better than those obtained at 50° C.

Because the specific separation of Eu and Sm from fission product mixtures is hampered by the presence of Y, methods are being sought for the separation of Y, Eu and Sm as rapidly as possible. A rapid separation is desired to permit investigation of the short-lived Eu and Sm radioisotopes. Tests have been made which show that a preliminary separation of Eu and Y prior to separation by ion-exchange can be effected by a $BaSO_4$ precipitation from a solution of $MgSO_4 \cdot 7H_2O$. The Eu:Y ratio is improved by a factor of 10 for Eu(III) and 13 for Eu(II).

2. *Distribution Data.* Distribution coefficients between unscreened Dowex 50 resin and 0.238 *M* citrate at a temperature of 75° C were obtained for Eu and Y and are tabulated in Tables V and VI with a plot in Fig. 38. The curves essentially parallel those obtained at 50° C with K_D being greater at 75° C than at 50° C for any given *p*H. The curves are somewhat more divergent at 75° C than at 50° C at the low and middle *p*H's but results are no better at the higher *p*H's.

3. *Preliminary Separation by $BaSO_4$ Precipitation.* From the literature it was found that McCoy [J.A.C.S. 58, 2279 (1936)] had separated Eu from other rare earths by reducing to Eu(II) with zinc dust and precipitating with $BaSO_4$ by adding $BaCl_2$ to the hot $MgSO_4$ solution containing the Eu(II) and rare earths, converting sulfates to chlorides and further purifying by repeated passage through a Jones reductor and precipitation of the sulfate.

It was hoped that a sizable increase in the Eu to Y ratio could be accomplished by a $BaSO_4$ precipitation prior to a column separation of these two isotopes. Tests to find conditions for carrying of Eu and non-carrying of Y were conducted as follows: one ml sample of each tracer were added to one ml

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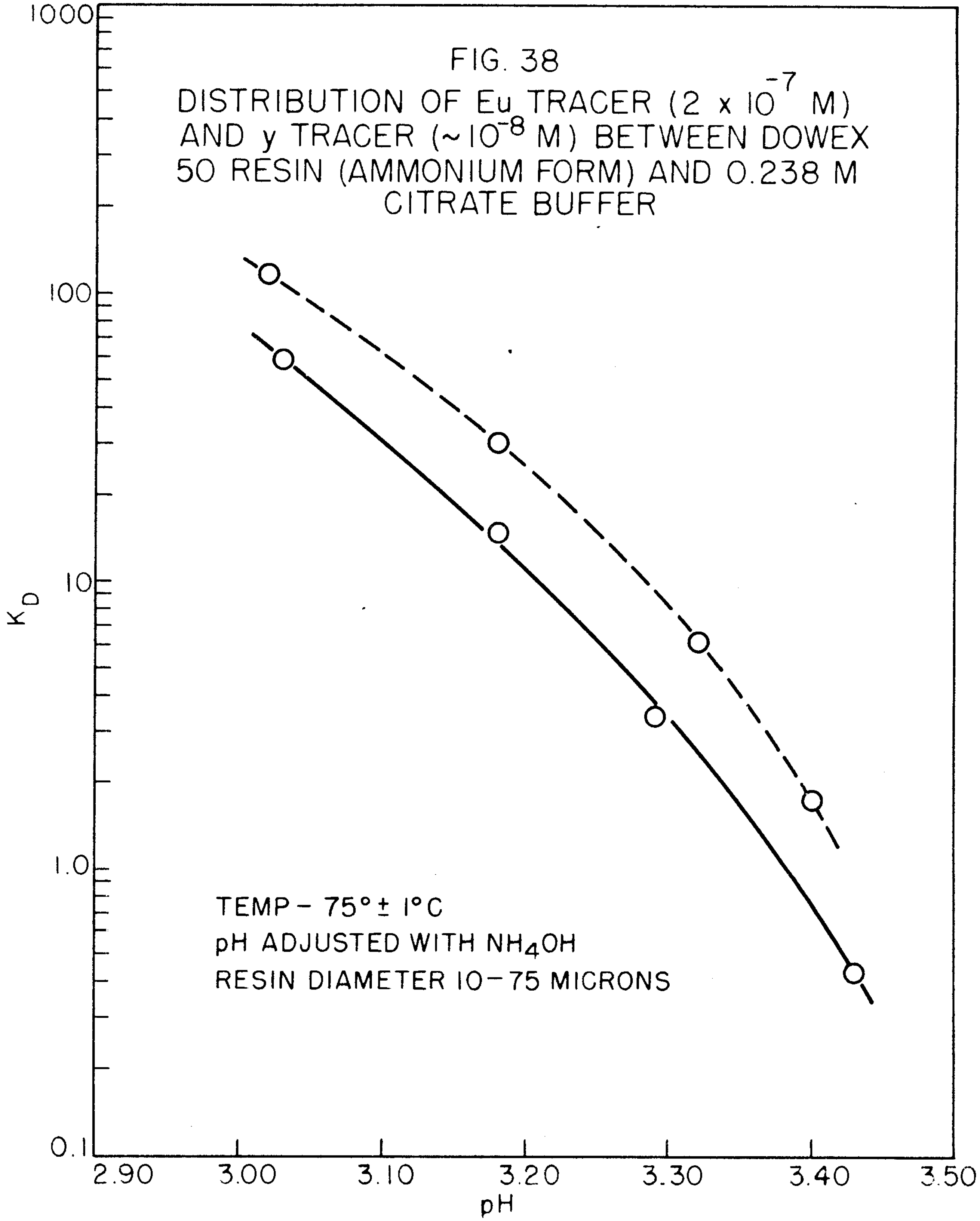

FIG. 38

DISTRIBUTION OF Eu TRACER (2×10^{-7} M) AND y TRACER ($\sim 10^{-8}$ M) BETWEEN DOWEX 50 RESIN (AMMONIUM FORM) AND 0.238 M CITRATE BUFFER

TEMP – 75° ± 1°C
pH ADJUSTED WITH NH_4OH
RESIN DIAMETER 10–75 MICRONS

TABLE V

Eu distribution coefficients at 75 ± 1° C*

Solution: 15 ml 0.238 *M* citrate, 2 x 10^{-7} *M* Eu, *p*H as tabulated, NH_4OH used to adjust *p*H**
Resin: Dowex 50, ammonium form, 10-75 microns, oven dried.

*p*H	3.02		3.18		3.32		3.40	
Weight resin (grams)	0.1577	0.1615	0.6387	0.5993	2.8114	2.9993	4.7046	4.9255
Original buffer *p*H	3.04	3.04	3.17	3.17	3.33	3.33	3.50	3.50
*p*H after first equilibration	3.03	3.02	3.18	3.18	3.33	3.32	3.42	3.41
*p*H after second equilibration	3.01	3.02	3.21	3.17	3.34	3.31	3.40	3.38
K_D—First equilibration	110	140	29.1	34.7	5.97	5.79	1.60	1.60
K_D—Second equilibration	108	116	26.0	34.1	5.84	5.37	1.40	1.46
K_D—Resin strip	101	123	27.7	35.3	7.42	6.50	2.06	2.26
Average	106	126	27.6	34.7	6.41	5.89	1.69	1.77
Percent material balance	97	96	103	102	114	111	114	118
Average Eu K_D	116		31.2		6.15		1.73	

* Distribution Coefficient $= \dfrac{\text{cts in resin/mass of resin}}{\text{cts in solution/volume of solution}}$

** Beta Activity in Buffer (Original) = 18,200 c/m/ml at 10% geometry and no absorber

TABLE VI

Y distribution coefficients at 75 ± 1° C*

Solution: 15 ml 0.238 *M* citrate, ~ 10^{-8} *M* Y**, *p*H as tabulated, NH4OH used to adjust *p*H

Resin: Dowex 50, ammonium form, 10-75 microns, oven dried

*p*H	3.03		3.18		3.29		3.43	
Weight resin (grams)	0.1592	0.1727	0.8151	0.7268	3.0101	3.5606	5.0225	4.8549
Original buffer *p*H	3.03	3.03	3.18	3.18	3.33	3.33	3.54	3.54
*p*H after first equilibration	3.03	3.03	3.17	3.17	3.30	3.27	3.43	3.43
*p*H after second equilibration	3.05	3.02	3.18	3.19	3.30	3.28	3.44	3.43
K_D--First equilibration	63.0	56.8	15.9	15.6	2.90	3.20	0.030	0.232
K_D--Second equilibration	63.2	56.9	15.2	14.9	2.72	3.60	0.142	0.325
K_D--Resin strip	58.0	55.1	13.8	14.0	3.60	4.37	0.768	1.096
Average	61.4	56.3	15.0	14.8	3.07	3.72	0.313	0.551
Percent material balance	97	99	96	98	111	109	120	122
Average Y K_D	58.8		14.9		3.40		0.432	

$$* \text{ Distribution Coefficient } = \frac{\text{cts in resin/mass of resin}}{\text{cts in solution/volume of solution}}$$

** Beta Activity in Buffer (Original) = 28,400 c/m/ml at 10% geometry with no absorber

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quantities of various concentrations of $MgSO_4 \cdot 7H_2O$ and the mixtures were heated to boiling. One ml $BaCl_2$ [1 mg Ba(II)/ml] was then added and again heated to boiling. The sample was then centrifuged, the supernatant decanted, and the activity in the $BaSO_4$ determined. Results are tabulated in Table VII. The same ratios and general procedure were used in testing under reducing conditions, except that the 2 ml tracer-$MgSO_4 \cdot 7H_2O$ solutions were made 1 *N* in H_2SO_4 and were heated on the water bath at 100° C for an hour with ~0.5 g amalgamated zinc with addition of water to keep the volume constant before addition of $BaCl_2$. These results are tabulated in Table VIII. The concentration of the $MgSO_4 \cdot 7H_2O$ solution affects both the amount of activity carried by the $BaSO_4$ and the final ratios of Eu to Y. At the lower concentrations, over 80% of the Eu was carried and approximately 20% of the Y was also carried, changing the Eu to Y ratio by a factor of four. At the higher concentrations of $MgSO_4 \cdot 7H_2O$ it was found that less activity was carried, but the ratio was improved, the best ratio being found to be approximately 13 where a 400 mg $MgSO_4 \cdot 7H_2O$/ml solution was used as described above under reducing conditions. Although only 50% of the Eu carried under these conditions, it was decided to use this step before final separation on the column since the less Y to be contended with the better the column separation should be.

4. *Separation by Ion Exchange.* A separation of Eu and Y was accomplished by combining the preliminary separation using $BaSO_4$, after reduction of Eu, and a subsequent separation of the Eu and Y in the $BaSO_4$ by use of an ion-exchange column.

A solution containing a 1:1 ratio of Eu and Y (5.93×10^6 c/m Eu and 6.05×10^6 c/m Y) was concentrated to two ml. Two ml 400 mg $MgSO_4 \cdot 7H_2O$/ml was added and the solution was made 1 *N* in H_2SO_4. This was heated at 100° C with ~ one gram of amalgamated zinc, adding water to keep the volume constant, and two ml of 1 mg Ba/ml as $BaCl_2$ was added and the mixture heated for five minutes. The $BaSO_4$ was centrifuged and rinsed with five ml H_2O and slurried away from amalgamated zinc with three passes with water. The Eu and Y were leached from the precipitate with three two-ml passes with hot dilute nitric acid. These leachings were concentrated to one ml and the *p*H was adjusted to a value of one. The solutions were then passed through a resin column, consisting of a 126 cm piece of flexible Tygon tubing (I.D. of 0.48 cm) filled with unscreened, air dried Dowex 50 resin which had been equilibrated with *p*H 3.20, 5% citrate. This column had been coiled about a 500 ml mixing cylinder and the resin

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TABLE VII

Coprecipitation of europium and yttrium sulfates with barium sulfate

$EuCl_3$, YCl_3 tracers— 1 ml
$MgSO_4 \cdot 7H_2O$— 1 ml
$BaCl_2$- 1 mg Ba/ml — 1 ml

	10 mg $MgSO_4 \cdot 7H_2O$/ml		200 mg $MgSO_4 \cdot 7H_2O$/ml		400 mg $MgSO_4 \cdot 7H_2O$/ml		Saturated $MgSO_4 \cdot 7H_2O$	
	Eu	Y	Eu	Y	Eu	Y	Eu	Y
c/m in tracer	4920	2398	4920	2398	4920	2398	4920	2398
c/m in $BaSO_4$	4342	603	2300	191	1984	99	1042	71
Percent carried by $BaSO_4$	88.3	25.1	46.7	8	40.3	4.1	21.2	3
Increase in Eu to Y ratio	3.5		5.8		9.8		7.1	

TABLE VIII

Coprecipitation of europous and yttrium sulfates with barium sulfate

$EuCl_3$, YCl_3 tracers—1 *N* H_2SO_4 solution of 1 ml tracer, 1 ml
$MgSO_4 \cdot 7H_2O$, reduced with amalgamated zinc, $BaSO_4$ pptd hot with 1 ml
1 mg Ba/ml as $BaCl_2$

	10 mg $MgSO_4 \cdot 7H_2O$/ml		400 mg $MgSO_4 \cdot 7H_2O$/ml	
	Eu	Y	Eu	Y
c/m in tracer	4737	2268	4737	2268
c/m in $BaSO_4$	3958	419	2540	96
Percent carried by $BaSO_4$	83.4	18.5	53.5	4.2
Increase in Eu to Y ratio	4.5		12.7	

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portion submerged in a constant temperature bath at 50° C. The elutriant was 0.238 *M* citrate at *p*H 3.20, at which *p*H the K_D's for Eu and Y are 14 and 7, respectively. A flow rate of 2.75 ml per hour was used. The column volume was 12.0 ml.

Table IX shows the distribution of activity throughout the experiment and Fig. 39 shows the elution curve with the Y coming off first and the Eu second. No gamma activity was found in the Y fraction. A comparison of the beta to gamma ratio for Eu at the start of the experiment and in Fraction 2 shows Fraction 2 to be of the same composition as the initial Eu. Decay curves are being followed for both fractions.

The percentage of Eu activity carried by the $BaSO_4$ was only 24% instead of the 50% indicated by the batch test. The resultant Eu to Y ratio increased by a factor of only 5.3 instead of the expected 13. A check will be made to see if the increased HCl concentration resulting from concentrating the Eu and Y solutions has caused this.

SEPARATION OF Zr-Cb FROM F. P. MIXTURES

W. H. Baldwin, H. W. Kohn, C. E. Higgins,
J. M. Ruth, A. W. Smith and R. E. Wacker

1. Introduction. In previous reports (ORNL 176, ORNL 229, and ORNL 336) it has been shown that the fission products, Zr and Cb, can be separated from Redox plant waste solutions and should be available in relatively large quantities for certain military applications. No data have been found which show the process to be inoperable, but several problems remain to be solved and data must be obtained with high levels of activity. It is planned to continue investigations on this problem to permit issuance of a feasibility report in September, 1949.

2. Summary. About 30 gallons of the (IAW) raffinate from the first Redox cycle has been obtained from the Redox pilot plant and has been stored for use in the testing of the proposed Zr-Cb separation process at high levels of activity. Facilities in the hot cell are nearing completion and should soon be ready for testing.

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TABLE IX

Distribution of Eu-Y activities for $BaSO_4$ precipitation and ion exchange column run

	ACTIVITY (c/m)*	PERCENT OF TOTAL	PERCENT OF $BaSO_4$ ACTIVITY
Eu	5.934×10^6		
Y	6.054×10^6		
Total activity before $BaSO_4$ precipitation	12×10^6		
Activity left in containers	53,000	0.44	
$BaSO_4$ supernatant	10.16×10^6	84.6	
$BaSO_4$ activity	1.83×10^6	15.2	
Activity in $BaSO_4$ H_2O rinse	114,000	0.95	
Activity left with amalgamated zinc	64,000	0.53	3.5
Activity remaining in $BaSO_4$	21,000	0.18	1.15
Activity in supernatants of $BaSO_4$ after separating from amalgamated zinc	51,100	0.42	2.8
		Percent of component carried by $BaSO_4$	Increase in Eu to Y ratio
Activity in Y fraction (corrected for decay)	276,000	4.6	5.3
Activity in Eu fraction	1.444×10^6	24.4	
Material balance	101%		

* At 10% geometry.

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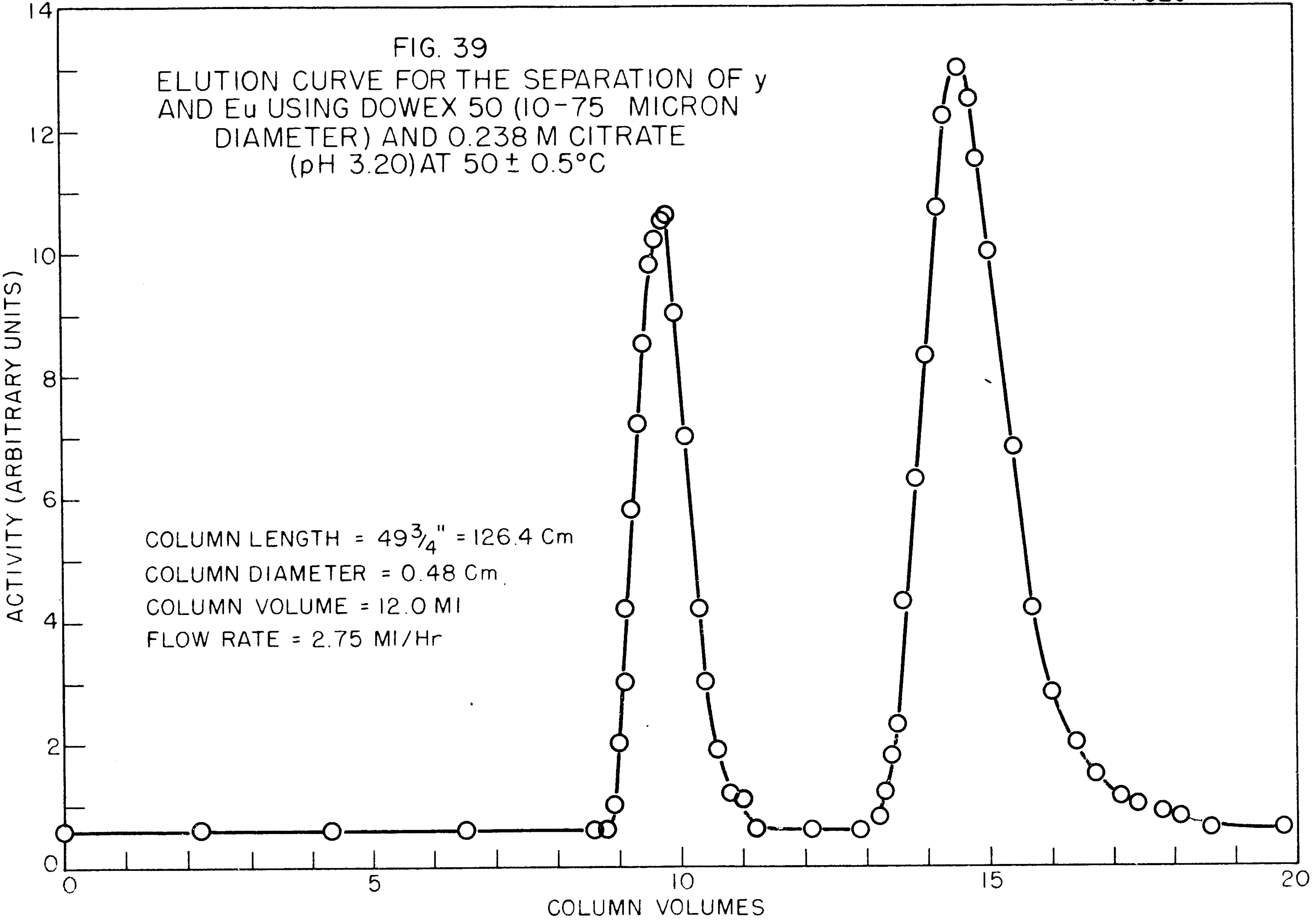

FIG. 39
ELUTION CURVE FOR THE SEPARATION OF Y AND Eu USING DOWEX 50 (10-75 MICRON DIAMETER) AND 0.238 M CITRATE (pH 3.20) AT 50 ± 0.5°C

COLUMN LENGTH = $49\frac{3}{4}$" = 126.4 Cm
COLUMN DIAMETER = 0.48 Cm
COLUMN VOLUME = 12.0 Ml
FLOW RATE = 2.75 Ml/Hr

The acidity and the history of the IAW solutions determine how well the Zr-Cb will be absorbed on silica gel directly. In those solutions of low acidity (near *p*H 2), which are now preferred in the present pilot plant operation, essentially no adsorption on silica gel was observed. However, after HNO_3 had been added to obtain an acidity of 0.3 to 1 *M* HNO_3 adsorption occurred as anticipated.

Zr-Cb were absorbed from dissolver solution, but in those solutions which were not oxidized before treatment, about 12 to 40% of the Pu present accompanied the Zr-Cb.

Data obtained for the absorption of Zr-Cb at various ratios of silica gel to solution fitted a Freundlich isotherm within the limits of experimental error.

Cb was removed somewhat less readily from silica gel than was Zr, heating of the 0.4 *M* oxalic acid being required to elute all of the Cb. Equilibrium distribution data indicate that HF and H_3PO_4 remove Zr more efficiently than Cb.

No method of preventing the absorption of Cr(VI) on the silica gel has yet been found. However, washing of the gel with dilute (0.1 *M* HNO_3) served to remove enough dichromate so that the reduction of the eluting oxalic acid and consequent bubble formation were no longer problems.

The Zr-Cb can be concentrated with respect to the 0.4 *M* oxalic acid eluent by carrying on ferric hydroxide or zirconium hydroxide, formed by the addition of NaOH.

Separation of the Zr-Cb can be made using anion-exchange columns and dilute acid solutions in which the Zr and Cb exist as anions. This is expected to prove useful as an analytical technique in the search for radiochemical impurities in the preparation.

3. *Analysis of IAW Raffinate.* Approximately 30 gallons of IAW waste resulting from the Redox pilot plant treatment of Hanford slugs has been collected from runs 50R and 52R. This solution has been stored underground and will be used for testing with the hot facilities which will soon be available.

The IAW solution has been analyzed and reported to contain about 0.5 curies of Zr and 1 curie of Cb per liter. These radioactivities are somewhat lower than was expected from uranium irradiated at Hanford but can probably be accounted for by the fact that these slugs were irradiated in the areas of lower flux for a period of a year or longer and have cooled the order of 150

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days*.

A request has been made of Hanford chemists to supply us with information on the amounts of Zr and Cb found in Hanford dissolver solutions by analysis.

The recent IAW solutions from the pilot plant differ in composition from those which were originally obtained. The solution which is now obtained by the preferred method of operation of the Redox process is compared below with the original solution.

	ORIGINAL SOLUTION	PREFERRED
HNO_3	0.8 *M*	0.1 *M* HNO_3 to 0.2 *M* acid deficient by NaOH addition
$Al(NO_3)_3$	0.74 *M*	1.15
$Na_2Cr_2O_7$	0.06 *M*	0.06 *M*

4. *Adsorption Studies.* (a) Adsorption from Dissolver Solution (UNH). Dissolver solutions (essentially uranyl nitrate with mixed fission products obtained by dissolving irradiated uranium metal in nitric acid) are considered to be a more generally useful source of the products of fission than are the waste solutions. Early in the plutonium project these solutions were treated with silica gel to obtain plutonium, but it was observed that Zr and Cb were also absorbed by the silica gel (reports CN-601, CN-633, CN-991, CN-1373 and others).

In a crude scouting test (Run 1, Table X) 10 ml of 0.2 *M* UNH solution, containing 1 ml dissolver solution (heels from 706-D special Run 32) and 0.2 *M* in HNO_3, was passed through a column of 200 mesh silica gel (Merck reagent grade) contained in a tube 12 mm i.d. and 70 mm high. The column was washed with 25 ml of 0.1 *M* HNO_3 and then eluted with 25 ml portions of 0.4 *M* oxalic acid at a flow rate of about 10 ml per cm^2 per hour.

It should be pointed out that the original solution was not analyzed and material balances could not be calculated for Test 1.

A second test (Run 2, Table XI) was made using 0.25 ml dissolver solution in 5 ml of 0.2 *M* UNH solution in a manner similar to Run 1 except that washing was more exhaustive with 0.1 *M* HNO_3. Results are shown in Table X, Run 2.

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* Private communication, H. K. Jackson

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TABLE X

Adsorption from UNH solution

Conditions:

Feed = 0.2 *M* HNO_3 containing dissolver solution (see text)
Wash = 0.1 *M* HNO_3
Eluent = 0.4 *M* oxalic acid
Column = 12 mm diameter x 70 mm, 200 mesh silica gel
Flow rate = 10 $ml/cm^2/hr$

	SOLUTION	VOLUME (ml)	GROSS GAMMA (Percent)	Zr GAMMA (Percent)	Cb GAMMA (Percent)	Pu ALPHA (Percent)
RUN 1	Filtrate	11	27	0.8	0.6	5.8
	Wash (0.1 *M* HNO_3)	25	42	1.6	0.4	82.5
	Elution (0.4 *M* oxalic acid)	14	23	74	74	12
	,,	27	7.4	23	23	Not detectable
	,,	19	0.3	0.9	1.5	,,
	,,	22	0.1	0.2	0.6	,,
	,,	25	0.03	0.3	0.1	,,
			Percentages based on the sum of the activities.			
RUN 2	Forerun	5	No detectable activity.			
	Wash (0.1 *M* HNO_3)	15	59	3.1	7.3	41.0
	,,	15	2.1	1.2	0.0	22.4
	,,	20	0.3	0.0	0.0	11.8
	Elution (0.4 *M* oxalic acid)	15	21.7	84.3	56.6	41.3
	,,	18	8.3	19.4	31.3	0.8
	,,	15	1.3	2.5	0.8	0.1
	Material Balance		92.7	110.5	96.0	117.4

[redacted]

[redacted]

TABLE XI

Effect of acidity on adsorption of Zr-Cb

Conditions:

Solution—5 ml IAW (52R), acidity as indicated
Adsorbent—100 mg silica gel (Davison)
Agitation—tumbled end over end at 24 rpm for 24 hours

HNO_3 CONCENTRATION (Molarity)	GROSS GAMMA IN SUPERNATANT (Percent)
None added	100
0.16	93.5
0.31	45
0.47	42.4
0.61	41.0
0.76	49.2
1.46	48.1
2.1	50.2
2.7	51.4

TABLE XII

Adsorption with varied amounts of silica gel

Conditions:

Solution—10 ml of IAW from Redox pilot plant Run 42R made using 30% Hanford irradiated metal and 70% Clinton irradiated metal in the feed. 0.8 *M* HNO_3, 0.8 *M* $Al(NO_3)_3$ and 0.05 *M* $Na_2Cr_2O_7$.
Adsorbent—Silica gel, weight as indicated
Agitation—Tumbled end over end at 20 rpm for 24 hours

SOLUTION	SILICA GEL (gm)	GROSS BETA	GROSS GAMMA	Zr GAMMA	Cb GAMMA
IAW-42R	None	9.9×10^{8} (a)	2.1×10^{8} (a)	4.2×10^{5} (a)	9.3×10^{5} (a)
Supernatant	0.2	97.0%	40.2%	33.8%	19.7%
''	0.4	92.4%	33.7%	24.5%	12.8%
''	0.6	97.0%	31.5%	19.4%	9.5%
''	0.8	95.0%	30.4%	18.2%	8.5%
''	1.0	96.6%	29.0%	16.5%	6.7%

(a) Counts/min/ml at 10% geometry.

[redacted]

[redacted]

With exhaustive washing of the silica gel, plutonium still accompanied the Zr-Cb. It is proposed to test these solutions further using UNH feed solutions which have been oxidized with dichromate before contacting the silica gel and to test the washing of absorbed plutonium from the silica gel with solutions containing dichromate. It is anticipated that Pu(VI) will not be so readily absorbed.

(b) **History of IAW Raffinate.** The solutions, originally used in scouting tests during the search for an absorbent, contained 0.8 M HNO_3 in addition to the other components. It was recognized that it might be desirable to use an IAW solution, which was low in free HNO_3. The original tests made after the neutralization of the free HNO_3 with NaOH revealed little difference in the absorption of Zr-Cb by the silica gel. However, when the IAW from the preferred Redox flow sheet runs was equilibrated in the laboratory, no measureable amount of the gross gamma activity was absorbed from the solution in contrast to the expected amount of about 50%. Tests were made with varied acidity to study the effect of acid concentration on the adsorption by silica gel. An optimum acidity was found near 0.3 M HNO_3 at which 59% of the gross gamma activity was adsorbed in 16 hours (Table XI).

Batchwise equilibrations were made with 5 ml portions of IAW (52R) and 100 mg silica gel (Davison) in an end-over-end tumbler for 16 hours at about 20 rpm. After settling, samples of the supernatant were diluted (25 microliters to 10 ml) and the gross gamma activity was determined on the high pressure argon-filled ionization chamber.

Rate studies were made at 0.31 M HNO_3 from which 8% of the gross gamma activity was adsorbed by silica gel with a half-time of 6 minutes and the remainder with a half-time of 2.3 hours. At an acidity of 0.77 M HNO_3 13.5% of the gross gamma activity was adsorbed with a half-time of 3.8 hours. These results indicate the probability of at least two mechanisms participating in the adsorption of Zr-Cb on silica gel.

(c) **Amount of Silica Gel.** A test was made using different weights of silica gel (0.2 to 1.0 gm Davison 100 silica gel) in 10 ml of Redox pilot plant waste (IAW from 42R) by agitation in an end-over-end tumbler for 24 hours. At the end of this time the silica gel was allowed to settle and 100 microliters aliquots diluted to 10 ml were submitted for analysis.

Analtyical results (Table XII) show that more gross gamma, Zr gamma and Cb gamma were absorbed by more silica gel. No definite trend was detected in

[redacted]

[redacted]

the gross beta activity. A plot (not included here) of log of counts of residual component against the log of counts adsorbed per gram of silica gel show a straight line relationship within limits of experimental error for gross gamma, Zr gamma and Cb gamma. This is interpreted to mean that the adsorption follows the Freundlich relationship.

The silica gel from these tubes was transferred (but not quantitatively) to a small glass column where it was washed first with 0.1 *M* HNO_3 (to remove adhering IAW solution), then with 0.4 *M* oxalic acid at room temperature. Most of the activity was found in the oxalic acid solution and this was found radiochemically to be due to Zr and Cb. A small amount of activity remained on the silica gel and this was put in solution by passing 1 *M* HF down the column thus dissolving most of the silica gel. Radiochemical analysis showed this fraction to be largely Cb, the ratio of Cb gamma to Zr gamma being 26 to 1, showing a considerable concentration over the original ratio of near unity. On the basis of these data it is believed that a separation of Zr from Cb might be effected by choosing the proper composition of oxalic acid solution used for elution.

(d) **Batch Equilibration and Elution.** Some additional information has been obtained on batch tests with tracer activities which were reported in earlier reports (Table XIII). Dilution of the feed with water (1:1) or reduction of the dichromate with H_2O_2 made little difference in the equilibrium absorption. Reagent MnO_2 adsorbed Zr and Cb effectively.

Elution with oxalic acid in batch tests confirmed previous data showing its effectiveness. However, data mentioned elsewhere in this report indicate the difficulty of removing Cb at room temperature and the desirability of eluting at elevated temperatures.

Dilute HF and H_3PO_4 removed Zr more effectively, then they removed Cb. However, HF serves a second purpose, that of dissolving the silica gel and thereby removing the Cb.

(e) **Adsorption of Cr(VI) on Silica Gel.** The adsorption of sodium dichromate and other waste solution components along with the zirconium and columbium on the silica gel was of interest in the study of the silica gel process. Experimental procedures have been worked out, and data on the adsorption of Cr(VI) by silica gel from aqueous solution under varying conditions have been obtained.

(1) **Experimental Methods:** A suitable volume of solution and a weighed sample of silica gel were put into a glass tube of about seven inches overall length, having a usable volume of about 40 ml. For all except three or four

[redacted]

TABLE XIII

Adsorption and elution

Solution— 10 ml of following composition
0.8 *M* HNO3
0.74 *M* Al(NO3)3
0.05 *M* Na2Cr2O7 spiked with IAW from
pilot plant Run 8R
Absorbent— as indicated
Agitation— Equilibrated by tumbling end-over-end for 24 hours
at 26 ± 0.5° C.

ADSORBENT		ADSORPTION (Percent left in solution)			ELUTION	Percent of total eluted		
Substance	G	Gross Gamma	Zr Gamma	Cb Gamma	Eluting Agent	Gross Gamma	Zr Gamma	Cb Gamma
Silica gel	0.561	50	7	8	0.5 *M* HF	31	74	28
Silica gel	0.553	50	7	8	0.5 *M* HF	31	71	28
Silica gel (a)	0.532	50	18	6	0.4 *M* $H_2C_2O_4$	40	89	42
Silica gel (a)	0.572	50	--	6	0.4 *M* $H_2C_2O_4$	40	99	42
Silica gel (b)	0.568	49	11	3	0.4 *M* $H_2C_2O_4$	39	76	68
Silica gel (b)	0.550	49	2	4	0.4 *M* $H_2C_2O_4$	40	67	71
Silica gel (c)	0.532	52	--	--	0.4 *M* $H_2C_2O_4$	21	45	52
Silica gel (c)	0.521	52	--	--	0.4 *M* $H_2C_2O_4$	25	38	52
Silica gel	0.580	50	5	8	0.4 *M* $H_2C_2O_4$	37	69	61
Silica gel	0.536	50	6	8	0.4 *M* $H_2C_2O_4$	37	64	73
MnO_2 (d)	0.869	49	6	3	0.5 *M* HF	16	72	22
MnO_2 (d)	0.887	49	1	2	0.5 *M* HF	16	--	--
MnO_2 (d)	1.120	49	12	2	0.5 *M* H_3PO_4	21	78	45
MnO_2 (d)	1.328	49	11	3	0.5 *M* H_3PO_4	20	--	--
Fe_2O_3 (d)	0.400	71	59	12	--	--	--	--
Fe_2O_3 (d)	0.400	71	--	12	--	--	--	--

(a) Feed diluted with 1 part feed to 1 part H_2O.

(b) H_2O_2 added to feed.

(c) NH_4OH wash used between adsorption and elution in place of H_2O wash.

(d) Reagent grade.

[redacted]

of the points plotted on the following graphs, a volume of 30 ml of solution was measured out to which 10 g of silica gel was added.

The tubes were made with standard ground glass joints in order that the stoppers might be interchangeable with the filter tubes to be described below. Either silicone grease or fluorothene grease was used to prevent leaking. The sample tubes were placed in a tumbling mechanism which was built into a constant-temperature water bath.

Variation of the time allowed in the bath from 4 hours to about 64 hours without any difference in results indicated that equilibrium was established in all cases. It can be noted here that the abrasive action of the gel particles on each other during agitation and the peptization of silica gel at high *p*H both may result in small losses of gel, but these effects were not found to be important in these experiments. (Magnetic stirring was unsatisfactory because of grinding of the gel).

When the tubes were removed from the bath, the stopper was taken out of each, and a tube with a ground glass joint at one end and a coarse glass filter at the other end was inserted in place of the stopper. This filter tube was sufficiently large to hold the contents of the other tube. This appeared to be the easiest way of getting quantitative transfer of the gel to the filter without using any wash other than the solution which is in equilibrium with the gel. In this way, the transfer was accomplished easily and quickly. A solution sample was obtained by filtering or by decanting it from the gel, after which the entire gel sample was centrifuged to remove the adhering solution.

Sodium dichromate and chromic acid were observed to be quickly extracted from the gel by hot water. A continuous drip extractor containing the gel sample was connected by ground glass joints to a flask of boiling water at its bottom end and to a small reflux condenser at its top end. The extraction was usually completed within one to three hours.

The concentration of the solution phase was determined by titration of a measured volume, and the concentration of the absorbed phase by titration of the extract or of an aliquot. The iodine-thiosulfate method with starch indicator was used for all titrations. The *p*H's of the solution phases were measured with a Beckman Model G laboratory *p*H meter.

(2) **Materials Used:** Davison PA 100 Refrigeration Grade Silica Gel was used in all experiments. The moisture content of the material does not appear

[redacted]

to change if the metal can is kept closed. Samples have been kept for moisture determination, but the results are not available yet. There should have been little change. All other materials used were C.P. reagents.

(3) **Effect of pH on Adsorption:** As shown in Fig. 40, changes in acid concentration from $p\text{H} = 2.5$ to an acid content of 0.8 M HCl had little if any effect on the absorption. At a higher pH, corresponding to a change from $Cr_2O_7^=$ to $CrO_4^=$, a new line appeared to be established below the $Cr_2O_7^=$ absorption curve. The transition from one to the other varied with pH and concentration. No particular importance is attached to the two low points, but it should be pointed out that they occurred with solutions which were probably too alkaline for good stability of the gel.

The data can be fitted by the Freundlich equation, giving:

$$\log C_G = 0.82 \log C_S - \log 0.43$$

for the low pH branch of the curve, where C_G = moles of $Cr_2O_7^=$ per 1000 g of gel, and C_S = molarity of $Cr_2O_7^=$ in solution. Here, the original weight of gel directly from the container was used.

(4) **Adsorption by Purified Gel:** Boiling the gel with concentrated nitric acid and washing with hot water had no effect on dichromate adsorption, as indicated in Fig. 41.

(5) Adsorption in the Presence of $AlCl_3$: In order to get a preliminary idea of what effect Al(III) in solution might have on the dichromate adsorption, the extent of adsorption from solutions containing 1 M $AlCl_3$ was determined. Aluminum nitrate will be studied later (because of the necessity for changing the analytical method in the presence of NO_3^-). The curve obtained with $AlCl_3$ is shown in Fig. 42, and can be fitted by the Freunclich equation,

$$\log C_G = 0.63 \log C_S - \log 0.53$$

(6) **Variation of Adsorption with Temperature:** At temperatures of 10°, 25°, and 40° C no difference in the adsorption of dichromate was found. See Fig. 43.

5. *Treatment of 0.4 M Oxalic Acid Solution Containing the Eluted Zr-Cb.* It is unlikely that a solution in 0.4 M oxalic acid would be desirable for final application of the product. Therefore, methods for concentrating the Zr-Cb are being investigated.

NOT CLASSIFIED
DWG. 7314

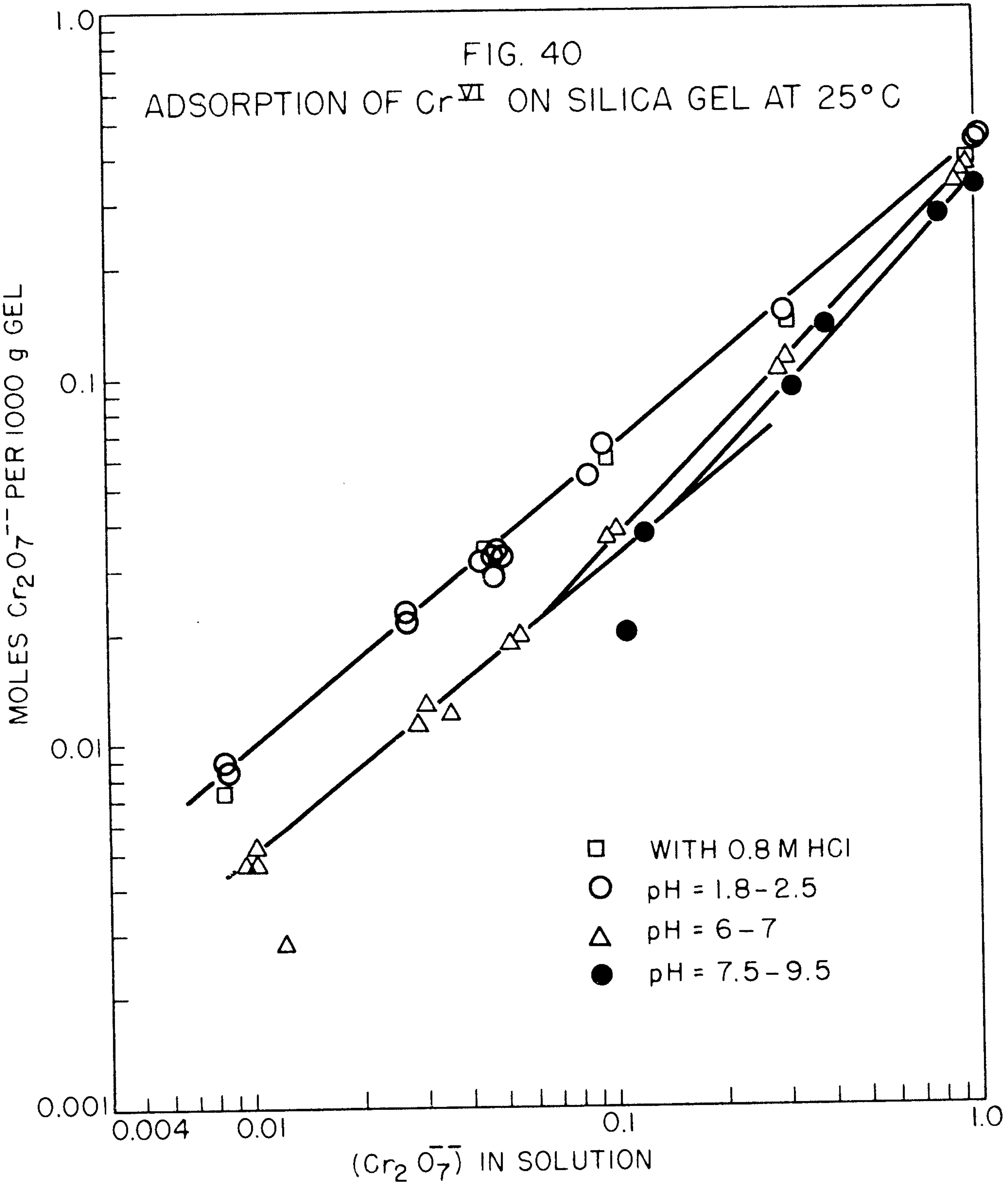

FIG. 40

ADSORPTION OF Cr^{VI} ON SILICA GEL AT 25° C

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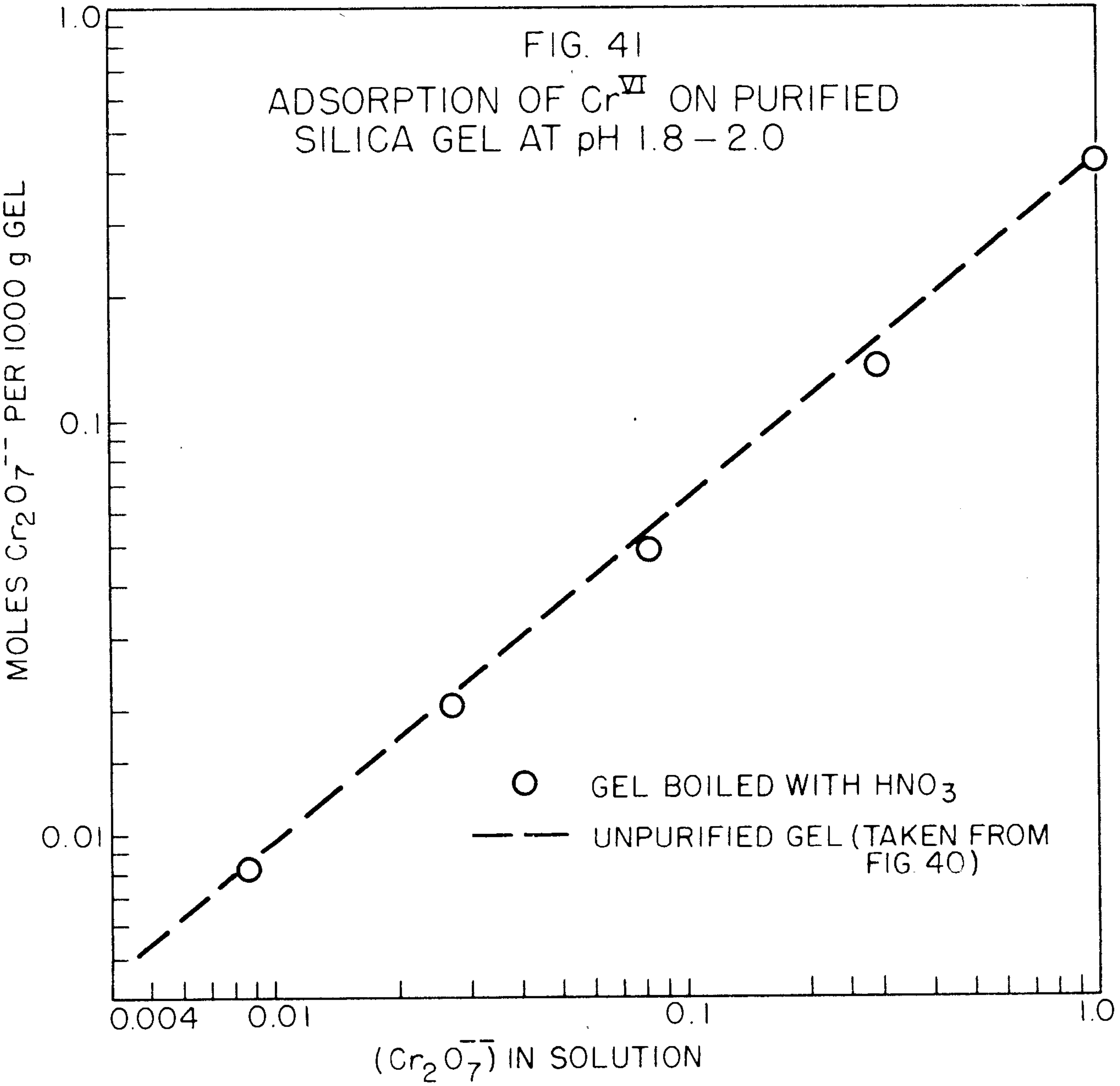

FIG. 41

ADSORPTION OF Cr^{VI} ON PURIFIED SILICA GEL AT pH 1.8 – 2.0

NOT CLASSIFIED
DWG. 7330

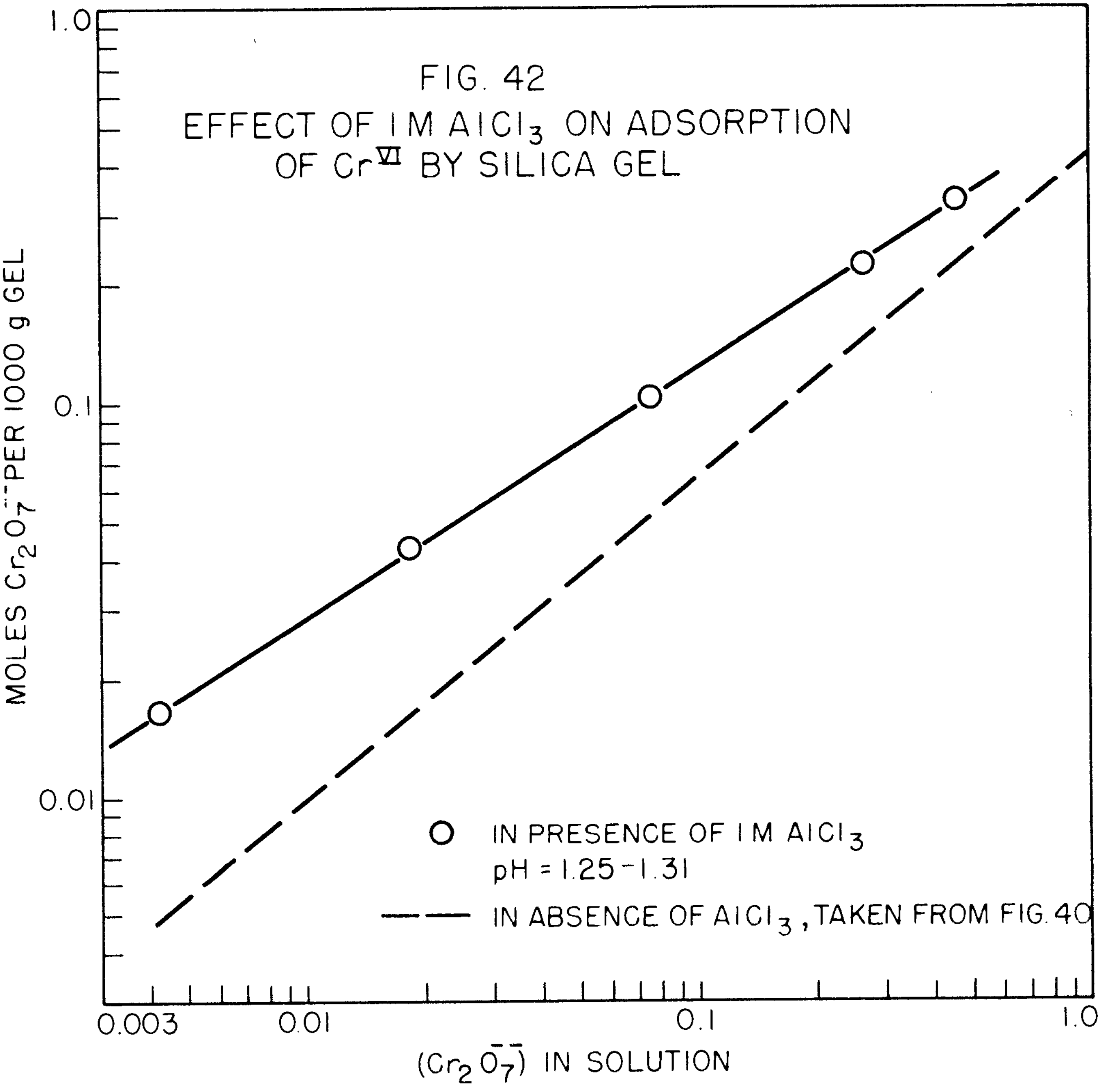

FIG. 42
EFFECT OF 1 M $AlCl_3$ ON ADSORPTION OF Cr^{VI} BY SILICA GEL

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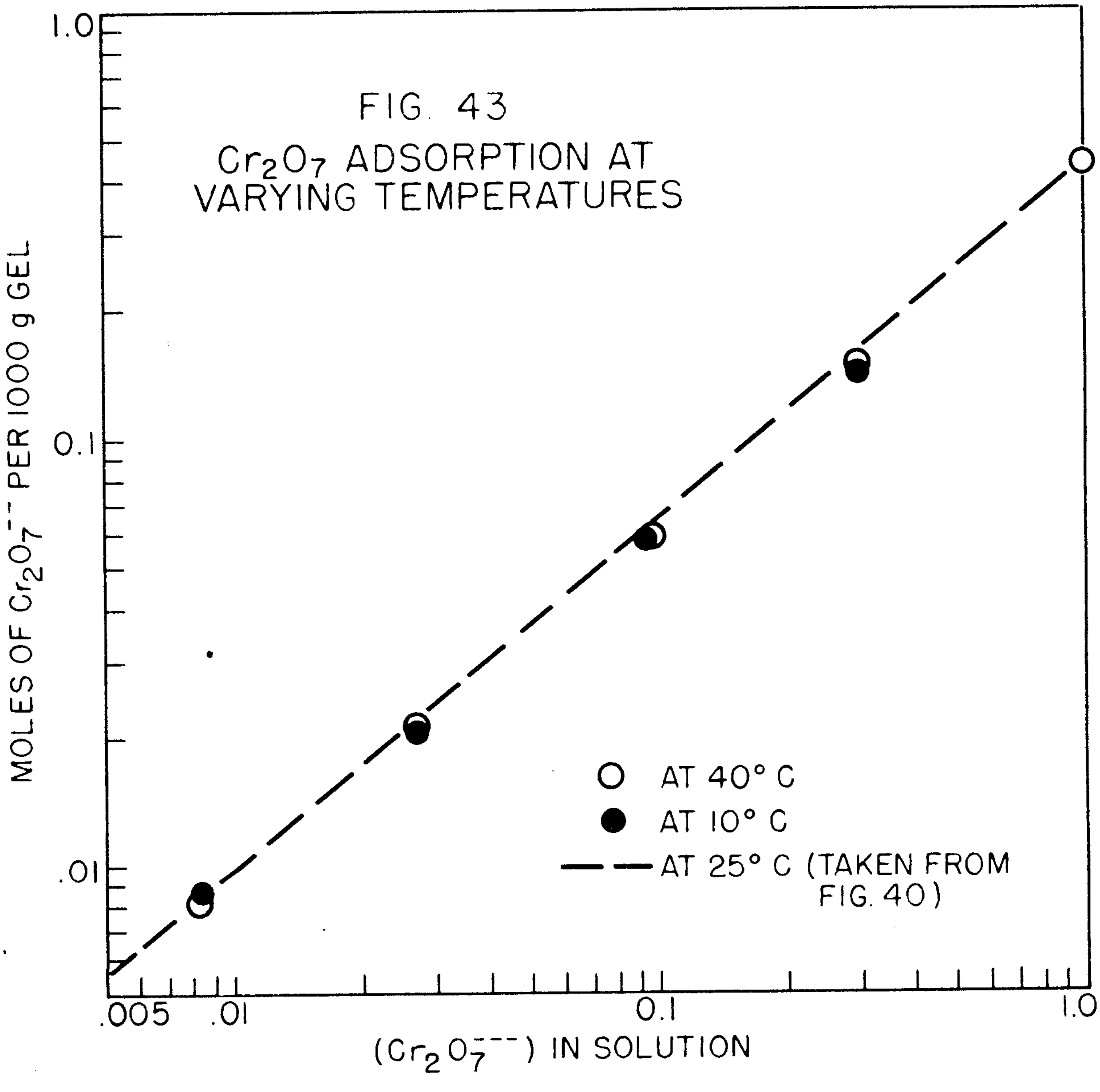

FIG. 43

Cr_2O_7 ADSORPTION AT VARYING TEMPERATURES

It has been found possible to carry the gross gamma emitters from the solution, in a yield greater than 99%, on either ferric or zirconium hydroxide. At present there appears to be no reason to limit the amount of carrier associated with the product to less than 45 mg per curie. Radiochemical purity is a matter for further consideration. Anion exchange resins using oxalic acid systems offer a method for further purification of the Zr and Cb as well as for the analytical estimation of the radiochemical purity.

(a) **Carrying Zr-Cb on Precipitates.** Ferric hydroxide [0.65 g Fe(III)/liter], formed in 0.4 *M* oxalic acid solution by the addition of solid sodium hydroxide until a precipitate appeared, carried 99.6% of the gross gamma activity. The precipitation of zirconium hydroxide by the addition of sodium hydroxide, followed by centrifugation and precipitation of a second portion by the addition of zirconyl chloride carried more than 99.9% of the gross gamma activity (Table XIV).

(b) **Anion Exchange Resin.** K. A. Kraus and coworkers have separated Zr from Cb (and other elements) by elution from an anion exchange resin (Dowex A-1) with solution containing both HCl and Hf at various concentrations. Advantage is, thus, taken of the occurrence of these elements in the anionic form. Zr and Cb were absorbed quantitatively from 0.4 *M* oxalic acid, and batchwise equilibrations (Table XV) indicated the possibility of eluting Zr and Cb from the resin with 1 *M* HCl and 0.001 *M* oxalic acid.

On the basis of this information a separation of Zr from Cb was attempted. A packed column about 6 mm inside diameter was filled to a height of 85 cm with 80-200 mesh Dowex A-1 resin. Ten ml of 0.4 *M* oxalic acid solution containing Zr-Cb tracers passed through the column with subsequent adsorption of the activities at the top of the bed. A solution containing 1 *M* HCl and 0.001 *M* oxalic acid was allowed to flow down through the bed at a rate of 0.45 $ml/cm^2/min$. The results of the elution are shown in Fig. 44 with Zr being present in the first peaks and Cb in the last peak. The first band of activity (Zr rich) appears to consist of four peaks of activity. These have not yet been identified. It does appear that with further development it may be possible to separate Zr and Cb by the use of anion exchangers and perhaps obtain analytical information concerning the radiochemical purity of the product.

6. *Stability of Silica Gel to Radiation.* Samples of silica gel have been irradiated in the ORNL pile for periods up to an including 6 weeks. These

[redacted]

TABLE XIV

Carrying of mixed Zr-Cb from 0.4 M oxalic acid solution

Carrier ($FeCl_3$, or $ZrOCl_2$ solution) was added to 0.4 *M* oxalic acid and the hydroxide precipitated by alkali. In the last test reported Zr carrier was added to the supernatant from the previous precipitation.

PRECIPITATED ION		PRECIPITATING REAGENT		GROSS GAMMA IN SUPERNATANT
	Conc. g/l		Conc.	%
Fe(III)	0.65	NaOH	---	0.4
Zr(IV)	0.074	NH_4OH	1 *M*	2.6, 17.2
Zr(IV)	0.074	NaOH	1 *M*	30.4, 4.04
Zr(IV)	0.37	NaOH	1 *M*	3.2, 1.8
Zr(IV)*	0.37	NaOH	1 *M*	0.06, 0.05

* Supernatant from preceding test was treated with Zr(IV).

TABLE XV

Equilibration of mixed Zr-Cb in oxalic acid with Dowex A-1

Dowex A-1 (anion exchange resin) was equilibrated by tumbling end-over-end in 10 ml solution at 26° C for 24 hours.

DOWEX A-1	SOLUTION		GAMMA ACTIVITY IN SOLUTION		
	HCl *M*	Oxalic Acid *M*	Gross (%)	Zr (%)	Cb (%)
0.54	None added	0.4	0.4		
0.53	None added	0.4	0.1		
0.049	None added	0.4	0.3		
0.047	None added	0.4	2.1		
0.54	1	0.1	20, 17		
0.52	1	0.01	29, 22		
0.127	1	0.001	87, 81	58, 60	42, 50
0.048	1	None added	---	67, 96	100, 100

[redacted]

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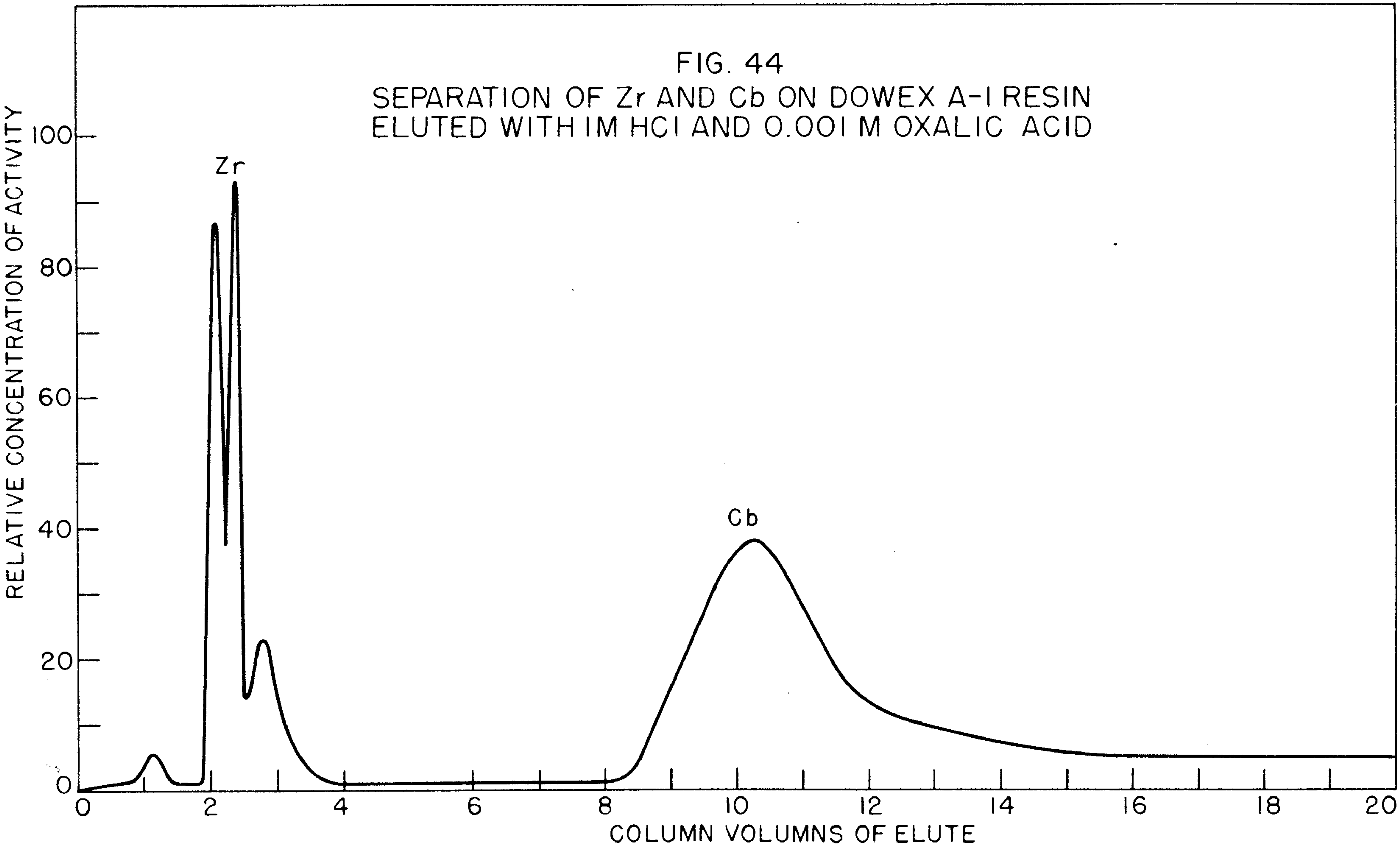
DWG. 7310

FIG. 44

SEPARATION OF Zr AND Cb ON DOWEX A-1 RESIN ELUTED WITH 1M HCl AND 0.001 M OXALIC ACID



samples will be equilibrated with IAW to compare the distribution of gross gamma, Zr and Cb.

A series of batchwise counter current equilibrations has been made using four stages with full Hanford activity level IAW. The silica gel from these tests should prove useful in detecting effects of radiation in solution on the sorption capacities of the silica gel. In one such test a portion of the silica gel had received the equivalent of 10 curie hours of radiation from the absorbed activities without appreciable change in the equilibrium distribution of the gross gamma activities. More analytical data are being obtained from this test.

7. *Program.* It is expected that by September the following additional information will be available:

1. Analyses of Hanford dissolver solutions for Zr and Cb to show the amounts which are available.
2. Adsorption studies on dissolver solutions after an oxidation treatment to minimize the contamination of Zr and Cb with Pu.
3. Capacity tests on silica gel, Vycor and anion exchange resins for Zr and Cb.
4. Data on the stability of silica gel to irradiation.
5. Column studies to investigate the operability and reproducibility of the process which will be proposed.
6. Scouting of methods for the separation of Zr-Cb from wastes existing at Hanford from the present Pu separation process.

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PHYSICAL CHEMISTRY AND CHEMICAL PHYSICS

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SPECTRA OF THE HEAVY ELEMENTS AND RARE EARTHS IN CRYSTALS AND SOLUTIONS

Simon Freed and C. J. Hochanadel

This work was discontinued at ORNL about the middle of May because of the departure of Simon Freed. Communications on some of the work will appear in forthcoming journal articles, while a number of miscellaneous observations are summarized below.

The methods for preparing liquid solutions of salts at the boiling point of nitrogen and for measuring the spectra have been described in previous ORNL quarterly reports (ORNL 176 and ORNL 336). Solutions of the following rare earth salts were successfully prepared and the spectra measured at -196° C and in most cases also at -79° C.

$PrBr_3 \cdot 6H_2O$
$SmBr_3 \cdot 6H_2O$
$GdBr_3 \cdot 6H_2O$
$NdBr_3 \cdot 6H_2O$
$Sm(NO_3)_3 \cdot 6H_2O$
$TmBr_3 \cdot 6H_2O$
$Nd(NO_3)_3 \cdot 6H_2O$
$EuBr_3 \cdot 6H_2O$
$Eu(NO_3)_3 \cdot 6H_2O$
$NdBr_3$

$TbBr_3 \cdot 6H_2O$ was not sufficiently soluble at this temperature to be measurable in a 25 cm optical path. Also, our preparations of anhydrous $EuBr_3$ were very dark in color and not sufficiently soluble to be measured. The solvent employed in all of these solutions consisted of ~10% n-propyl alcohol and ~45% each of propane and propylene. A solution of $UO_2(NO_3)_2 \cdot n\text{-}H_2O$ was made up in a solvent consisting of ~6% di-n-propyl ether in an equal mixture of propane and propylene. The spectrum at -196° C showed somewhat more and narrower bands than at room temperature. However, there were probably a number of different species in solution thereby preventing any pronounced sharpening.

In addition to these salts, several biologically important materials were studied including β-carotene, chlorophyll A and chlorophyll B. These materials were dissolved in equal volumes of propane and propylene. The spectra at -196° C differed from those at room temperature in the number, sharpness and relative intensities of the bands. Also, at low temperatures the bands were displaced toward long wave lengths.

At the start of this work it was necessary to make a rapid study of the behavior of various mixtures of solvents at low temperatures. In Table I are listed the mixtures studied. The relative viscosities were measured by compar-

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TABLE I

Properties of solvent mixtures at low temperatures

PERCENTAGE COMPOSITION																			RELATIVE VISCOSITY AT 77°C	REMARKS
PROPANE	ISOPENTANE	METHYL CYCLOHEXANE	METHANE	PROPYLENE	BUTENE 1	n-PROPYL ALCOHOL	ALLYL ALCOHOL	METHYL ALCOHOL	DIMETHYL ETHER	VINYL CHLORIDE	$CClF_3$	$CClF_2CClF_2$	$CF_3CF = CF_2$	ETHANE	DIETHYL ETHER	Di-n-PROPYL ETHER	n-PROPYL AMINE	ETHYLENE		
30					70														8	
40					60														3.25	
50					50														0.8	
60					40														0.46	
50					50														1.03	
48					48	4													2.25	
45					45	10													6.8	
					95	5													very viscous	mixture turbid
					89	5			6										very viscous	solidified
					53	3			44											solidified
			19		81															solidified sharply
			1		99															solidified slushy
			78		22															solidified sharply
			63		37															solidified sharply
			45		55															solidified slushy
			11		58	31														solidified glassy
60					40														fluid	clear
47					38	5													0.92	mixture turbid
					95		5													phase sep. at fairly high temp.
60					40														fluid	maybe crystal formation
58					38	4													1.05	small crystals present
				50	50														5.67	
	36				64														very viscous	
	50				50														very viscous	
	40			60															4.23	
	38			56		6													11.18	
			50	50																solidified
			7	76		17													1.17	
40			4	45		12													1.0	
				90		10													1.73	
				83		17													~36.	
				81						19										solidified
				40									60							two phases at ~-126° C
				95		5														turbid mixture
60				40															very fluid	
59				39		2														turbid mixture (?)
50				50															0.13	
47				47				6												crystallized
45				45				10												crystallized
45				50			5													two phases separated
48				47			5													high temp. distillation, slow cooling, 2 phases at -144° C
45				50		5													0.22	high temp. distn.—slow cooling
43				47		10													0.42	
46				42		12													0.24	
65				27		8													0.25	
61				26		13													0.5	
													100							froze ~-154° C
	66	22				12														very clear glass
16	55	19				10														glass
91						9													0.25	turbid mixture
94						6													0.17	froze standing overnight
31											69									not miscible at low temp
												100								froze ~-100° C
54												46								froze
73												27								froze
66						8						26								froze ~-180° C
62						13						25								froze
45						10								45						two phases - 180, solid at -196°C
	75														25					solid at 77° K
	50														50					solid at 77° K
82																18			0.5	turbid (?)
88																12			0.25	solid on standing
61	31															8			fluid	turbid
85																15				turbid
74			14													12				solidified
45				45												10			0.3	turbid
88																12			0.25	solidified on standing
44				50												6			0.25	same after 4 hrs.
42				47												11			0.5	maybe crystals present after 12 hrs.
														50				50		solidified
90																	10			crystals at ~-103° C
45				50													5			crystals at ~-103° C
48				43		9													0.4	at 77° K
																			fluid	at 63° K
																			fluid	at 58° K
																			solid	below 58° K

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ing the time to empty a small bulb through a fine capillary under a pressure differential of one atmosphere of helium.

The mixtures which proved to be the most satisfactory at -196° C were:

(a) ~50% propane, ~50% propylene;

(b) ~10% n-propyl alcohol, ~45% propane, ~45% propylene;

(c) ~6% di-n-propyl ether, ~44% propane, ~50% propylene.

In each of these the proportions of propane to propylene can vary over a wide range with little change in viscosity. Solvent (b) was used for preparing most of the solutions. It was found to remain fluid a few degrees below the freezing point of nitrogen (-210° C).

A liquid in glass thermometer was constructed from pyrex glass filled with a mixture of equal volumes of propane and propylene. This thermometer behaves very nicely down to at least -210° C or about 25° beyond the useful range of the commercially available "pentane" thermometers. The 4 mm I.D. pyrex tubing used for the thermometer bulb has satisfactorily withstood the ~10 atmosphere vapor pressure at room temperature.

EXPERIMENTS WITH MOLECULAR BEAMS

E. H. Taylor, P. J. P. Chastagner

The work of the quarter has been in two directions, development of a neutronactivation method for measuring bromine, and simple, orienting experimentation with molecular beams. In addition, the construction in the shop of the apparatus for scattering-reaction experiments has been practically finished.

The neutron-activation method for measuring bromine deposited from beam experiments was previously reported to require a chemical separation of the bromine, because of the high counting rate after irradiation of even the supposedly best material for a collector foil, polystyrene. It has been decided to use a separation by volatilization in vacuo, since this appears likely to be the most nearly quantitative type of separation. Preliminary experiments

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have shown the essentials of a satisfactory procedure, and it remains only to confirm the accuracy of the separation on known amounts of radio-bromine.

A typical experiment was as follows: A minute amount (probably less than a microgram) of KBr was evaporated onto a short fibre of fused silica which was then irradiated overnight in the pneumatic tube of the pile. After a few hours cooling, the fibre was transferred to a silica tube connected to a glass system which was then evacuated. Gaseous Br_2 (roughly 10^{-8} mole) was admitted from an ampoule through a break-seal and allowed to exchange with the activated sample. The exchange was carried out for 8 minutes at a temperature (obtained by flaming) of roughly 600° C, as judged by the color of the silica tube. The gaseous Br_2 was then allowed to react with a film of K deposited previously in vacuo on a glass disc. This was then removed and counted with a standard end window G-M tube.

The first conclusion from this experiment is that Br_2 gas does exchange with KBr at a measurable (although yet unknown) rate at about 600° C, as shown by the counting rate observed, 2600 c/m (fourth shelf, 2.4% geometry) 14 hours after removal from the pile. Second, the separation appears quite clean, for only three half-lives were observed in the decay of the sample, two corresponding to the bromine activities of 4.4 and 34 hours, and one, showing no decay apparently being the long-lived chlorine of half-life about 10^6 years. Since no pains were taken to clean the fibre before irradiation, it appears that extraneous activities (except halogens) are sharply eliminated by this method. The exchange proceeds also at much lower temperatures, being appreciable in an hour at about 300° C.

Potassium was not entirely satisfactory as a mount because the hydroxide formed in air from the excess metal is hygroscopic. Calcium appears to be better and has the further advantage of a much lower vapor pressure. Sliver was tried but proved slow in reacting with the Br_2.

Molecular beams have been produced in a glass-metal apparatus to learn something of techniques and to test ovens and collectors. Zinc, K and KBr have been used, and such details as oven temperatures and collector temperatures studied in a preliminary way, using the visible spots produced after fairly long collection to characterize the sharpness of the beam.

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Details of possible interest include the facts that Zn and K are not condensed at every collision with glass at room temperature, and that Zn at least is rather mobile on glass at temperatures not far above room temperature.

CALORIMETRY OF RADIOACTIVITY

G. H. Jenks, F. H. Sweeton

As stated in the previous quarterly report, this group has undertaken to design and construct an extremely sensitive calorimeter to be used in the study of easily absorbed nuclear radiations and also to be used to test the feasibility of a calorimeter of similar design and sensitivity but containing enough mass to absorb hard gamma radiations. The high sensitivity is to be achieved through the use of liquid helium.

Design and construction of this calorimeter have now been completed. The assembly of the necessary auxillary equipment such as Dewar flasks and liquid helium transfer tubes has also been completed. No tests of the calorimeter with liquid helium have as yet been made. However, to the extent possible using liquid nitrogen, the various parts of the calorimeter have been tested and found to be satisfactory.

In principle and, in many respects, in design, the present calorimeter is similar to the β-calorimeter developed by Cannon and Jenks(1). The β-calorimeter operated at the temperature of liquid nitrogen and used the rate of vaporization of nitrogen, under constant pressure, as a measure of the heat input. The calorimeter just completed, which will be called the He calorimeter, is planned to operate in the same manner but with the liquid nitrogen replaced with liquid helium.

Several factors tend to make a calorimeter of this type more sensitive when liquid helium is used than when liquid nitrogen is used. The product of the heat capacity of the calorimeter and its temperature fluctuation determines the quantity of heat which can be stored in the calorimeter and not appear as

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(1) C. V. Cannon and G. H. Jenks MonC-410, October 16, 1947.

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a change in the volume of vapor. This factor in turn determines the length of time required to carry out a rate observation and limits the sensitivity of the calorimeter. Temperature fluctuation in the liquid in every case is determined by the degree of control of vapor pressure over the liquid, but dT/dP for liquid helium is smaller than that for liquid nitrogen by a factor of about ten. In addition and more important, the heat capacity of most substances at 4° K is 10^2 to 10^3 times less than at 77° K. An increased sensitivity of 10^3 to 10^4 is then indicated for a calorimeter operating at the lower temperature.

In order to achieve this increased sensitivity, variations in background gas evolution from the calorimeter must be held to an amount which is negligibly small compared to that caused by the heat input of the source. Also, it must be possible to measure the rate of gas evolution from the calorimeter with sufficient accuracy at the low heat inputs. Considerations of these two factors have, to a large extent, determined the design of the calorimeter. An outline of the design of the He calorimeter follows. No drawings of the calorimeter are included, but the report on the β-calorimeter by Cannon and Jenks contains a drawing of a calorimeter of the same general nature. The container in which the heat source (resistance heater or radioactive sample) and a few ml of liquid helium are to be placed in a closed copper cylinder having an I.D. of 11.4 mm and an internal depth of 30.8 mm. The walls are about 1 mm thick. This container is suspended by means of a stainless steel tube (.025 in. O.D., .019 in. I.D.) within a larger copper cylinder. The small tube also serves as a connection between the space in the inner cylinder and the pressure control and gas measuring device which is outside the calorimeter and at room temperature. Connections are provided so that the space between the two cylinders can be highly evacuated or filled with helium gas for temperature equilibration purposes. For heater connections, two manganin wires, .003 in. in diameter, pass from the outer cylinder into the inner one through platinum-soft glass seals. The combination of the two copper cylinders will be called the calorimeter flask.

The calorimeter flask is surrounded by a closed stainless steel Dewar type flask which is to be filled with liquid helium. Provisions are made for controlling the pressure of vapor over the liquid in this flask. Surrounding the

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stainless steel container is a glass Dewar flask which is to be filled with liquid helium and which is open to the atmosphere. This flask in turn is placed in another glass Dewar which is to contain liquid nitrogen.

Computations indicate that with above design the background heat input to the calorimeter can be held to 10^{-9} cal/sec or less if the temperature of the liquid in the bath surrounding the calorimeter is within 5×10^{-4} deg of the calorimeter temperature. To maintain the bath and calorimeter temperatures equal within the 5×10^{-4} deg, it is only necessary that the difference in vapor pressures over the two liquids be less than 0.5 mm. This degree of control of relative pressures is quite feasible with the pressure control apparatus which has been developed for use with the calorimeter.

The question of measuring the rate of gas evolution ($\sim$0.4 cc/hr for a heat input of 10^{-7} cal/sec) from the calorimeter remains to be discussed. The problem in this case is that of leading the gas from liquid helium temperature through the liquid-vapor interface and out to room temperature in such a manner that changes in temperature distribution along the tube conducting the gas remain negligibly small. The device shown in Fig. 45 was constructed for that purpose. It consists of two different lengths of heavy copper rod sealed within a silvered glass sleeve. The two rods and the glass sleeve are identified in the drawing as A, B and D, respectively. A 25 mil stainless steel tube, through which the gas from the calorimeter passes, is soldered along the length of the two rods and projects beyond the copper at each end. The copper rod at B' is soldered to the cap of the stainless steel Dewar, and the small tube at this end connects with the calorimeter. The copper at A' is in contact with air at room temperature, and the steel tube at A' joins the pressure control apparatus.

In operation, liquid helium will cover the glass vacuum jacket to a point near the break in the copper rod. The rod B will then be at liquid helium temperature and the rod A at room temperature. All of the temperature gradient in the small tube should then occur along the 3 cm section at C and differences in liquid level around the jacket should not effect the temperature gradient appreciably.

In addition to the above apparatus, two new pressure control systems for use with the He calorimeter have been assembled. However, the design of each is similar to that of the pressure control apparatus used with the β-calorimeter and will not be described here.

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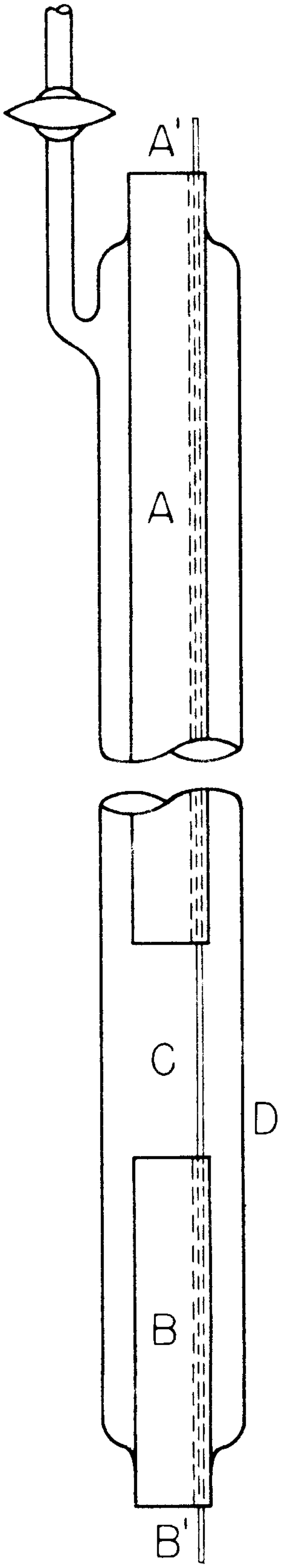

FIG. 45

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MICROWAVE SPECTROSCOPY

Ralph Livingston

A cooperative program in microwave spectroscopy has been initiated between the Laboratory and the Duke University Physics Department where Dr. Walter Gordy has had an extensive microwave program under way for some time. He and his co-workers are handling the microwave aspects of this new program with the Laboratory. The ORNL Chemistry Division is handling the synthesis of needed radioactive compounds and assists in carrying out actual measurements at ORNL. Microwave spectrometer development work is done at Duke.

This report will deal primarily with the chemistry aspects of the work and to some extent with the actual setting up of equipment and the making of measurements at ORNL. The purpose of the first studies undertaken is the measurement of the nuclear spin, quadrupole moment and magnetic moment of several iodine isotopes. The iodine measurements are made by observing the spectra of a rotational energy transition of methyl iodide.

Chemistry. The initial specifications set on the methyl iodide synthesis could only be formulated approximately since spectrometer development for the study was at an early stage. The purity requirements likewise could not be established definitely. However, taking into account the general availability of radioactive iodine isotopes, and the degree to which spectrometer development could reasonably be pushed in a short time, it appeared that the first work on I^{129} should be done on a level in the vicinity of 10 micrograms of total iodine isotopes per experiment with this quantity reduced, if possible, for later experiments on shorter lived iodines. The methyl iodide should be quite free of foreign gases to minimize pressure broadening effects on the spectral lines. The desired isotope should be present in at least 10% relative abundance, and if possible much higher. The chemistry should also be easily resolvable to remote control techniques.

The general chemical method considered was to react the iodine, as an alkali iodide, with dimethyl sulfate or methyl p-toluenesulfonate (methyl tosylate) so as to obtain methyl iodide requiring little or no subsequent purification. Methyl tosylate was preferred to dimethyl sulfate because of its reported lower vapor pressure and lesser toxicity. Work centered about

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the organic part of the synthesis. It was believed that the inorganic part of the synthesis could be developed after a suitable organic method was found.

Initial work was patterned after standard methods in the literature(2,3). Two macro-scale experiments were carried out by dissolving 20 g potassium iodide in 90 ml water, adding 22.4 g methyl tosylate and distilling off the product methyl iodide. Considerable water also distilled over, and it was immediately apparent that a non-volatile solvent was needed if the methyl iodide was to be used without further purification.

All subsequent work was with butyl phthalate as the solvent. Methyl tosylate was found miscible with butyl phthalate, but sodium iodide is insoluble in butyl phthalate.

Three experiments were carried out on a one gram sodium iodide scale. The apparatus consisted of a 200 ml round bottom flask sealed directly to the bottom of a four bulb reflux condenser. A 19/38 standard taper joint at the top of the reflux condenser was connected to a U-tube trap which could be cooled in liquid nitrogen. The exhaust side of the trap was connected to a mechanical vacuum pump and to a closed tube manometer.

In the first experiment one g sodium iodide was placed in the flask and 90 ml butyl phthalate poured over it. Two grams of methyl tosylate was added and the system was evacuated to about one mm. The trap was cooled in liquid nitrogen. The reaction mixture bubbled vigorously. After the initial bubbling stopped, the reaction mixture was warmed, and the mixture allowed to bubble for about one hour more. About 0.1 cc of product weighing 0.26 g was poured from the trap. Its refractive index was 1.505 compared with the accepted value of 1.529 for methyl iodide. It appeared that methyl iodide was synthesized, but considerable impurity was present, either from the reagents or from complicating reactions. The residue in the reaction flask contained considerable white flocculent material, presumably sodium p-toluenesulfonate.

In the second experiment the butyl phthalate was first freed of volatile matter by refluxing under vacuum for one hour. The experiment was carried out with 1.0 g sodium iodide to which was added 50 g of butyl phthalate containing 2 g methyl tosylate. About 0.13 cc product weighing 0.35 g was collected. Its refractive index was 1.524 and the odor was like that of methyl iodide. The

(2) Peacock and Memon, Quart. J. Indian Chem. Soc. 2, 240 (1925).

(3) Tipson, J. Org. Chem. 12, 133 (1947).

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yield of product collected was 37%. In a third experiment lasting three hours, instead of one hour as previously a 58% yield of methyl iodide was collected from the trap.

The procedure was next tried on a smaller scale. A new series of experiments was started using a microwave spectrometer, supplied by Dr. Gordy, as an analytical tool. It operated in the 4 mm (75,000 Mc) region, and the $J = 4 \rightarrow 5$ transition of methyl iodide was observed. The energy was obtained by tripling from a K band klystron (2K33). The absorption cell was one meter of J band guide (0.276 × 0.124 I.D.) having a volume of 22 cc. The optimum pressure of methyl iodide was about 10^{-2} mm. The wave guide cell was cooled in dry ice to give greater sensitivity.

Four experiments were conducted. The general method was to prepare reagents and set up all glassware needed for a single methyl iodide experiment. The microwave spectrometer was next put into operation and "peaked up" using commercial methyl iodide. As soon as all equipment was operating correctly, the methyl iodide was pumped from the wave guide cell. The progress of the pumping could be followed by observing the spectral lines on the spectrometer oscilloscope. The experiment was then carried out and the synthesized methyl iodide immediately transferred to the wave guide cell. The intent was to use successively smaller quantities of sodium iodide in each experiment and still try to get good methyl iodide lines on the oscilloscope.

The glassware used was similar to that developed for radioactive experiments as shown in Fig. 46. The experiments were carried out on a high vacuum system. The reactor was the same 200 ml round bottom flask sealed to a four bulb reflux condenser which was used in the previous macro-scale runs. A side tube was sealed to the flask and to this was connected the ampoule of reagents needed for an experiment. The connection was first made with a standard taper joint, but later the ampoule was sealed directly to the side tube. Reagent ampoules, to be described more fully later, were made by attaching a break off seal to a 20 ml flask. The ampoule was loaded through a small side tube with the solution of methyl p-toluensesulfonate in butyl phthalate, evacuated and then sealed off. The ampoule was next provided with a magnetic break off plunger (iron nail sealed in glass tube) and connected to the reactor. The desired amount of sodium iodide, usually as an aqueous solution, was placed in the bottom of the reactor vessel, and the unit was connected to the vacuum system and pumped on until all water was removed. A small deposit of dry

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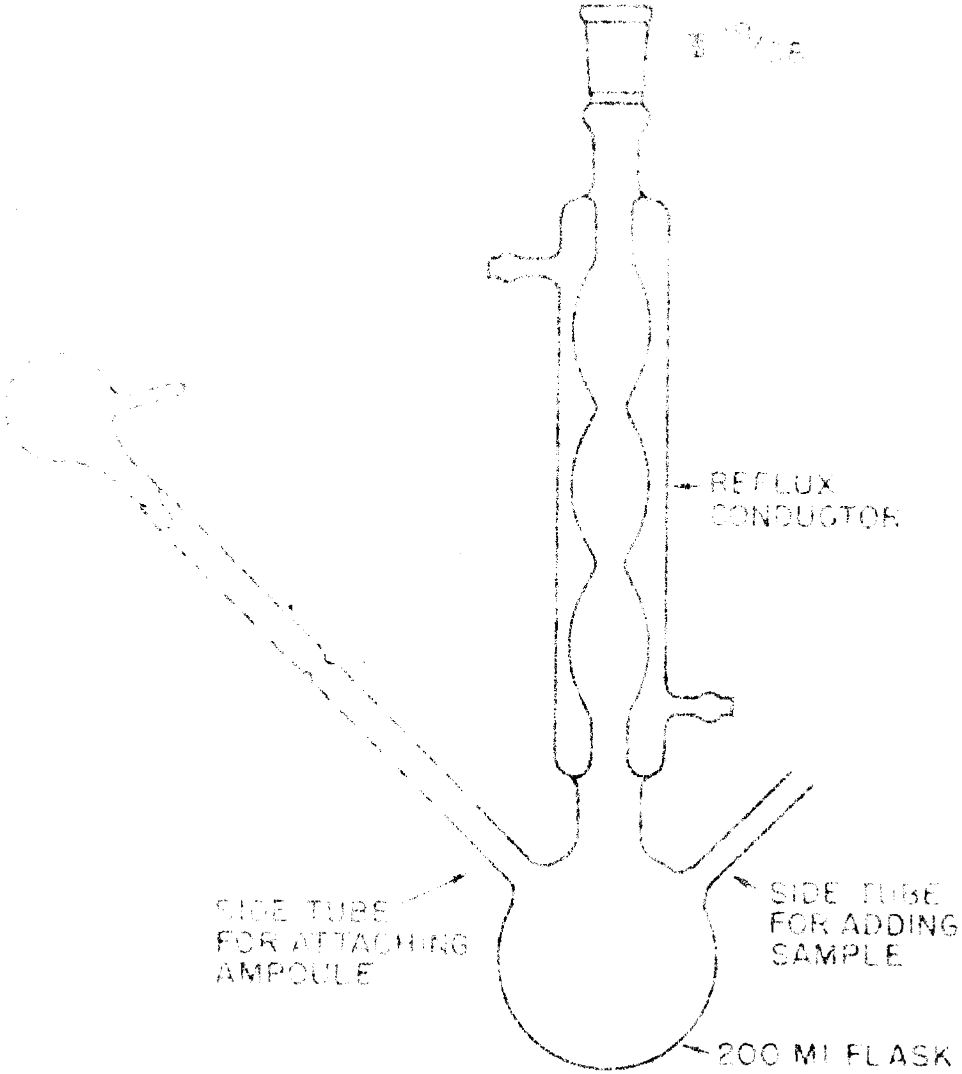
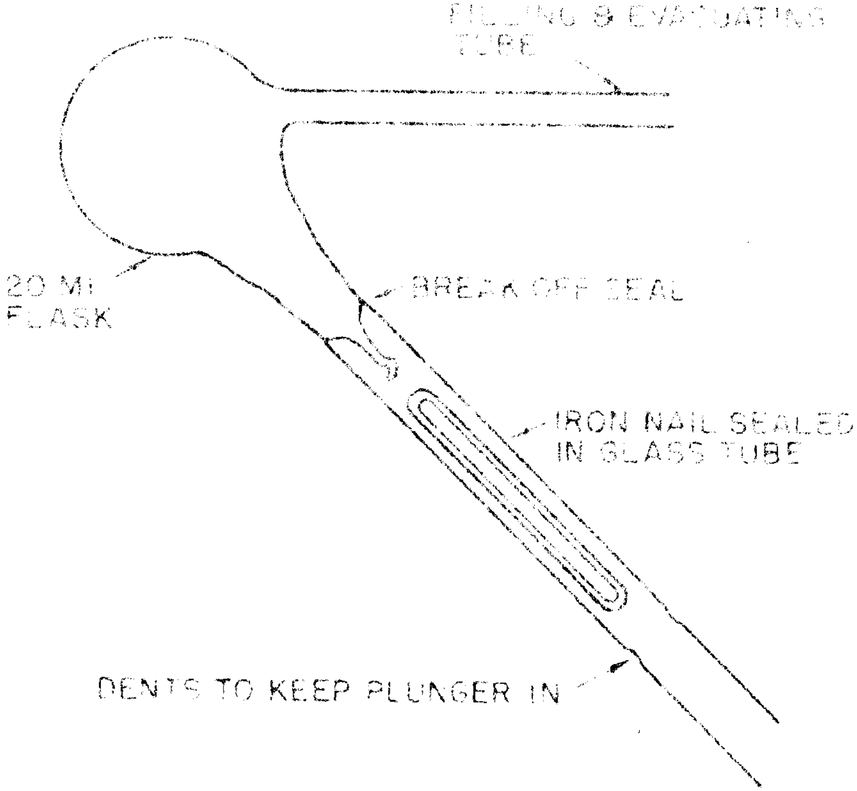


REACTOR



AMPOULE

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sodium iodide was left on the bottom of the reactor flask. The synthesis was carried out by breaking the seal on the ampoule and allowing the reagents to flow over the sodium iodide deposits. The solution was flash boiled for several minutes and the product transferred to the wave guide cell. To facilitate measuring small quantities of sodium iodide a standard solution of sodium iodide in water was made up to contain just 100 μg iodine per ml.

In the first run 200 μg iodine as sodium iodide was used. The ampoule, in this case, was made from a 50 ml flask and contained 1.65 g methyl tosylate in 27.5 ml butyl phthalate. The product formed was led directly to the wave guide cell. A few very broad lines were seen with difficulty. The lines sharpened and then disappeared when the cell was pumped on. The very bad broadening effect observed indicated the presence of considerable foreign gas. The butyl phthalate was freed of volatile impurity by refluxing under high vacuum for six hours, and a second experiment was carried out. In this second run 50 μg iodine was used with an ampoule of reagents containing 1.3 g methyl tosylate in 25 cc of the purified butyl phthalate. The vacuum line was also modified. Instead of taking the methyl iodide directly from the reactor and introducing it to the wave guide cell, a small trap of about 25 ml volume was included. The synthesized methyl iodide was first condensed in the trap, cooled in liquid nitrogen, the trap isolated from the reactor by a stopcock, and then the trap warmed to dry ice or room temperature and opened to the wave guide cell. This procedure greatly improved the volume efficiency of the methyl iodide transfer and was used in all subsequent work. Methyl iodide has an appreciable vapor pressure at dry ice temperature. At first it was felt that warming the trap to dry ice instead of room temperature would hold back traces of less volatile materials. This was later found to be unnecessary. In this second run, methyl iodide lines were seen, but they were still badly "pressure broadened".

Both organic chemicals were vacuum distilled in all glass equipment. The pressure during the vacuum distillation was maintained well under 10^{-3} mm. Both materials distilled very smoothly. A solution of 3.20 g methyl tosylate in 100 ml butyl phthalate was made up and 15 ml of the solution used per ampoule in subsequent runs. Prior to sealing the ampoules off on the high vacuum line, they are heated and the solution allowed to boil in order to

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effect further degassing. In Run 3, 50 μg iodine was used. The methyl iodide synthesized gave good lines in the spectrometer. The quantity of methyl iodide appeared slightly high for optimum line sharpness. In Run 4, 15 μg of iodine was used. The reaction mixture was flash boiled intermittently over a four minute period in this run. It was found that in this period of time, most of the methyl iodide comes off. The lines obtained were at optimum sharpness and were fully as good as lines from commercial methyl iodide. It was estimated that two-thirds of the volume of the trap-wave guide cell system was outside of the wave guide cell proper. Hence, if the trap and connecting tubing volumes could be made small compared to the wave guide cell, an experiment on a 5 μg scale might give equally good results on this analytical spectrometer. Rather than go below a 15 μg level at this time, it was decided to set up for running I^{129}.

The final reactor developed for radioactive iodine experiments is shown in Fig. 46a. The reactor is a 200 ml round bottom flask sealed to a three bulb reflux condenser. There are two side tubes from the flask. To one of these is sealed the ampoule of reagents. The other is used for introducing the solution of sodium iodide from a pipette. Once the iodide is added, this side tube is sealed off. The ampoule design is shown in Fig. 46b. The ampoule is made from a 20 ml flask. To this flask is sealed the break off and a side tube for filling and evacuating. The side tube is located so that when it seals to a vacuum system, prior to sealing off, the solution in the ampoule can be boiled by heating with a burner. The iron plunger is shown in place in Fig. 46. It is actually put in place after the ampoule has been filled and sealed off. It is prevented from falling out by three small dents formed in the glass tube.

The Spin of I^{129}. All equipment was rebuilt and the new spectrometer brought from Duke University by Dr. Gordy. The equipment was set up in a large hood as shown in Plate I. Lead bricks were piled around the spectrometer and glassware, not for the I^{129}, but for use in later runs with shorter lived activities. The new spectrometer operated in the 6.75 mm region (45,000 Mc) and the J = 2→ 3 transition was worked with rather than the J = 4→ 5 in order to give a simpler spectrum to analyze. This was expected to prove especially

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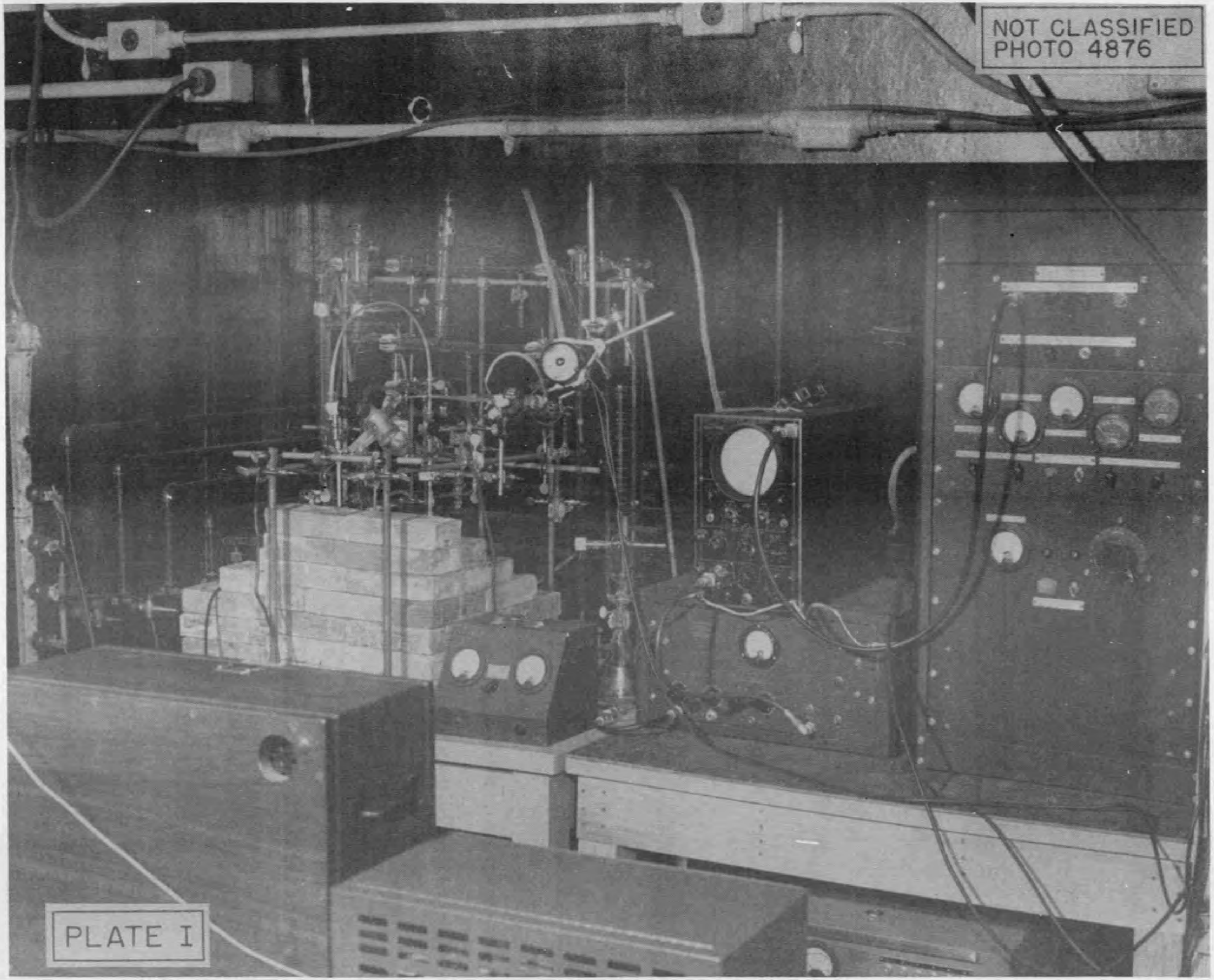

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PLATE I

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helpful if the iodine spins involved proved to be high. The equipment shown in Plate I includes the klystron power supply and saw tooth modulator in the relay rack at the right, the detector high gain amplifier and oscilloscope, and further to the left, the Pirani gauge and lead bricks which surround the spectrometer proper. The vacuum system is at the rear of the hood to the left. The wave guide cell was a coil of I band guide (0.180 in. × 0.086 in. I.D.) about two meters long and immersed in dry ice. Its volume was about 20 cc.

Five runs were carried out. The fission produced I^{129} was isolated by G. W. Parker and G. Hebert. The first sample used was an iodide solution containing a considerable excess sodium sulfite and some excess sodium hydroxide. Only two lines were seen on the oscilloscope with difficulty, and it was apparent that considerable foreign gas was present. The chemical yield was also low. This was checked roughly by following with a G-M probe the trace of I^{131} which was present in the original iodine sample. In the later work samples of iodine in carbon tetrachloride were obtained. This was extracted with very dilute sodium sulfite solution. After extraction the excess acid was neutralized with sodium hydroxide. This source of sodium iodide contained far less excess salt than the first sample used, and, as was hoped, the chemical yield in later runs became high. The presence of foreign gases still gave difficulty, but the situation was gradually improved by more thoroughly pumping the dry salt residue in the reactor, preparatory to carrying out the run, and by more thoroughly outgassing the ampoules of reagents used. Sufficient information was obtained from the first four runs to establish reasonably well the spin and quadrapole moment. The chemistry worked perfectly in the fifth run and gave complete confirmation of the moments.

The observed spin of I^{129} was found to be 7/2. The quadrupole coupling, $eQ(\partial^2 V/\partial r^2)$, was -1422 mc which gives a ratio of quadrupole moments of I^{129} to I^{127} of 0.7353. The actual value would be -0.43×10^{-24} cm^2 using the microwave value for I^{127} or -0.34×10^{-24} cm^2 if the atomic spectra value for I^{124} is used. More complete details are to appear in a letter to the Physical Review.

Magnetic Moment of I^{129}. The magnetic moment was determined by observing the Zeeman splitting of the hyperfine structure of methyl iodide. The spectrometer was rebuilt using a coiled wave guide cell between the pole pieces of a magnet. Details are shown in Plate II. The cell was coiled so that the magnetic field was perpendicular to the wide side of the guide or parallel to the E

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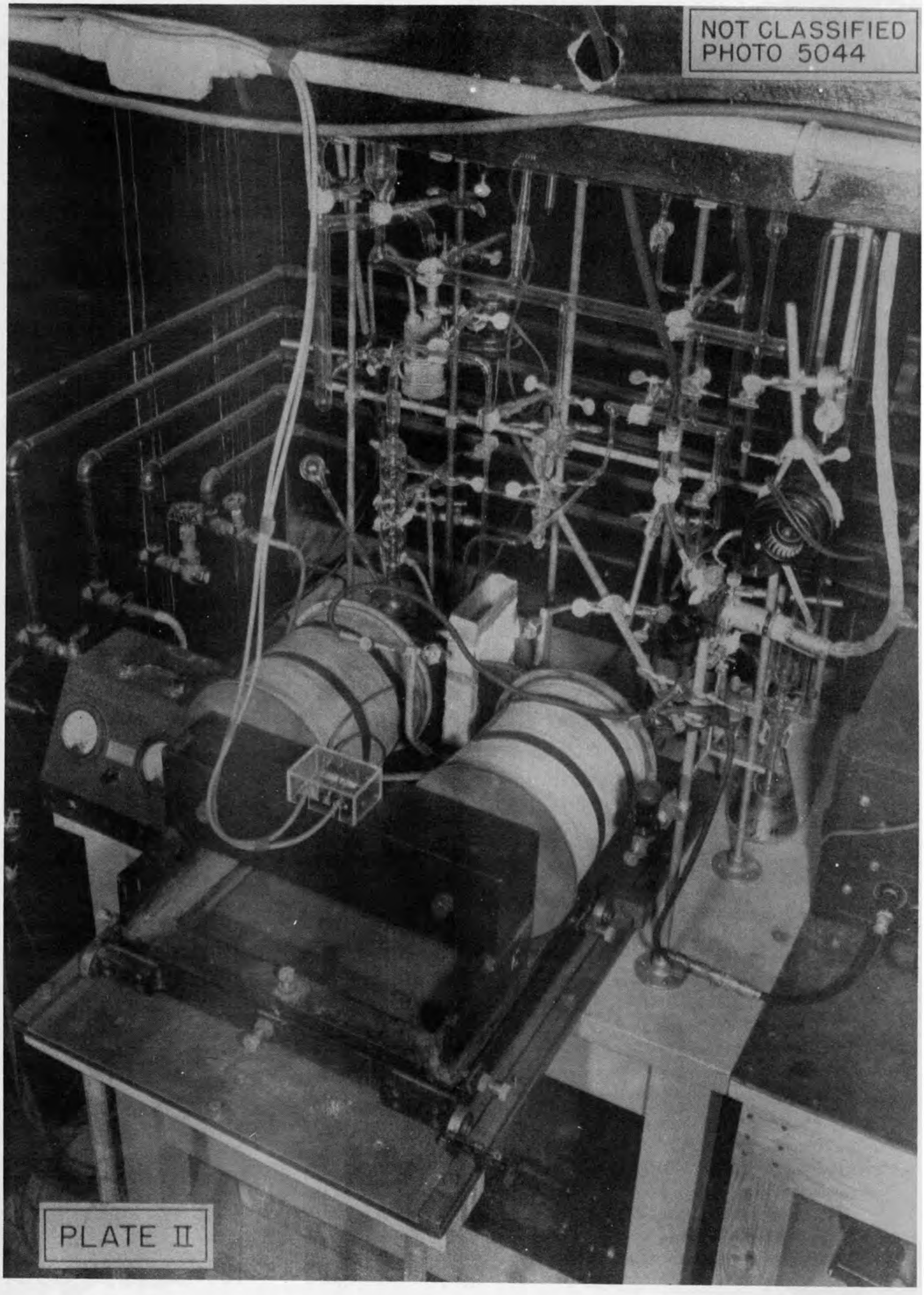

PLATE II

vector of the radiation. This gave transitions with the $\Delta M_F = 0$ selection rule and eliminated $\Delta M_F = \pm 1$ transitions. The cell was placed in a can that could be filled with dry ice. It can be seen in Plate II. The reaction vessel with ampoule can also be seen at the left side of the vacuum system. Two runs were carried out with I^{129}. The chemistry worked ideally. About 10 μg I_2 was used in the first run and 6.5 μg in the second. I^{127} was also run to give a check on the method. A value of 2.74 nuclear magnetons was found for the I^{129} moment and is estimated to be within 5%. The sign of the moment cannot be determined by the microwave method, but it most likely should be positive. More complete details will appear in a letter in the *Physical Review*.

Present plans include a redetermination of the magnetic moment to an accuracy, we hope, of 1%. Work is also underway on studies of the spectra of I^{131} as methyl iodide.

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RADIATION CHEMISTRY

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DECOMPOSITION OF AQUEOUS SOLUTIONS OF FISSIONABLE MATERIAL

J. W. Boyle, E. H. Taylor

Apparatus has been completed and is being tested for the continuous measurement of pressures up to 5000 lb/in.^{2} over solutions in the pile. It consists of a stainless steel bomb with removable liner (at present of Pt) connected to a Statham Transducer which measures the pressure by the deformation of a wire attached to a diaphragm, the deformation of the wire being followed by measuring its electrical resistance.

This apparatus will be used to extend to higher pressures and temperatures the work of E. Shapiro(1) on the decomposition of uranyl sulfate solutions in the pile.

GENERAL

C. J. Hochanadel, D. M. Richardson, E. H. Taylor

The 2 Mev Van de Graaff generator has been assembled and is expected to be in operation as soon as the system has dried out enough to sustain the voltage. The work of assembly has been done jointly by members of the Physics Division, the Instrument Department and the Chemistry Division.

Consideration has been given to the design and construction of a calorimeter for the measurement of energy absorbed from the electron beam, and measurements with this will probably precede the use of the beam in chemical studies. Irradiation of solids for studies of stored energy (J. A. Ghormley and H. A. Levy) and experiments with aqueous solutions (C. J. Hochanadel) are planned as the first chemical uses of the Van de Graaff machine.

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(1) Monthly Progress Reports of the Chemistry Division, Clinton Laboratories, 1945-1946.

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PHYSICAL MEASUREMENTS AND INSTRUMENTATION

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I. ELECTRON AND OPTICAL MICROSCOPY, ELECTRON DIFFRACTION

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

1. *Metallography.* (a) **Beryllium.** Metallographic examination of a machined beryllium rod which corroded in air at room temperature was finished and a report submitted (C.F. No. 49-3-207). The corrosion product was white in color and amorphous by X-ray diffraction. This material, although it could not be definitely identified, is probably an amorphous hydroxide formed by hydrolysis of beryllium carbide present in the sample. Beryllium carbide is hydrolyzed by steam in approximately 24 hours to give a similar substance.

Another result of the examination of this specimen was the demonstration of beryllium oxide in the beryllium grains and at the interfaces. The oxide, identified by X-ray examination by M. Bredig, occurred in the form of small inclusions $\frac{1}{2}$ to 3 microns in diameter and 3 to 7 microns in length. The hexagonal nature of these inclusions could be seen distinctly with the use of polarized light at high magnification.

Other beryllium samples, recently submitted by the Technical Division, are being examined. One, used as a control in a series of corrosion tests where extensive corrosion took place, appeared to contain an excessive amount of beryllium carbide. Another, similar to the material reported on in report No. 49-3-207, showed a high percentage of the oxide by X-ray and microscopic examination. Some beryllium grains seemed to contain an abundance of oxide.

Both samples examined exhibited thermal checking, which appeared in some instances to have taken place apparently at the cleavage planes of the beryllium grains rather than at grain boundaries. It is probable that this checking took place when sections were prepared on the cutoff wheel or during the grinding operation.

(b) **Corrosion of Beryllium.** A large number of macrographs of beryllium, before and after corrosion, have been done for the Corrosion Section of the Technical Division.

(c) Assistance has been given the Solid State Section of the Physics Division in the mounting, polishing and etching of single crystals of copper and copper-gold alloy.

(d) Additional samples of zirconium have been examined metallographically in continuation of our study of metallographic polishing and etching techniques for this material.

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2. *Chemical Microscopy.* (a) A number of samples of uranyl ammonium phosphate submitted by W. K. Eister of the Technical Division have been examined microscopically to determine crystallite size, size range, and structure in connection with filtration problems.

(b) At the request of the New York office of the AEC a series of samples of precalcined beryllium oxalate prepared by the Clifton Products Co. have been examined microscopically to determine particle size and shape.

(c) Electron micrographs of pure chromic oxide, pure red iron oxide, hydrated yellow iron oxide, powdered quartz, hydrated chromic oxide, and mapico red were made at the request of K-25 to determine particle size, size distribution, shape, and degree of aggregation.

(d) Slurry from the filter house has been examined for A. C. Jealous of Technical Division to determine ultimate particle size.

(e) Electron micrographs of carbonyl iron (spherical) have been taken to determine particle size and size range.

(f) Determination of particle size and shape of a silicon-aluminum alloy was made for J. B. Ruch of the Technical Division.

3. *Resinography.* In cooperation with Dr. G. E. Boyd, work is being continued on a study of the physical characteristics of various exchange resins. This included several samples of resins (Dowex 50) which have been irradiated in the pile.

4. *Photography.* A number of slides were made for members of the Chemistry Division in connection with meetings and seminars which took place during this period. Copies of graphs, and pictures previously taken were made on requests from various members of the Laboratory and K-25. Color photographs of the nitride of element 61 were taken at low power. A number of enlargements of line spectra were done. A series of photographs was taken for the Medical Division. In addition, approximately 1000 prints were processed.

5. *Particle Problem.* Electron micrographs of fly ash spill and particles on CWS filter removed from the pile filter house have been taken for J. Gost of the Technical Division.

6. *K-25.* (a) During this period a large number of samples have been submitted by K-25 in connection with their barrier program. This work consisted of both optical and electron microscopy. Because of the secret classification of the material and work involved a report of this activity cannot be given here. Reference is made to completed reports, C. F. Nos. 49-3-261, 49-

[redacted]

[redacted]

4-34, 49-4-83, and 49-4-230.

7. Evaporation of Metallic Films. A considerable amount of time was spent in connection with the research work of other laboratory personnel where the evaporation of metallic films on various surfaces was required. These included the coating of mica sheets with gold, the coating of formvar films with gold and silver, coating small bulbs with aluminum, coating plastic cones with silica, coating Geiger counter part with zirconium, shadow casting polished metal specimen of beryllium, and making first surface mirrors with an aluminum reflecting surface.

8. Research and Development. (a) Some time has been spent in studying the evaporation of various metals on formvar films with our equipment to determine optimum conditions as to film thickness, age, distance, evaporation time, and current intensity.

(b) A technique of shadow casting directly on metallographically polished samples is being tried.

(c) Equipment for more efficient photographic reproduction of electron diffraction patterns, a fixed focus negative reducer for lantern slide production, and a tilting stage for stereo micrographs have been designed and built during this period.

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II. INSTRUMENT RESEARCH AND DEVELOPMENT

BETA PROPORTIONAL COUNTERS

C. J. Borkowski, E. Fairstein

The rate of increase of gas amplification as the center wire voltage is increased in a proportional counter is strongly dependent on the amount of polyatomic gas present in admixture with argon as shown in Fig. 47. The data were taken with a 7 cm cathode diameter counter and one mil center wire. With pure argon it is seen that gas amplifications over 1000 cannot be used. Admixture of 10% methane with the argon gives stable gas amplification up to 10^6 for beta counting. The usual gas amplification for beta counting is between 10^4 and 10^5. 50% argon and 50% methane will give voltage plateaus somewhat longer than 10% methane and 90% argon but at an operating voltage which is about 500 volts higher.

Pure methane gives the longest plateaus but at operating voltages which are 900 volts higher than the 10% mixture. The higher operating voltages introduce high voltage leakage problems so that it is advisable to operate at voltages below 2000 volts when using an amplifier with a 1 millivolt input sensitivity.

In Table I are given the voltage plateaus using various percentages of argon and methane in a permanently filled counter having a 7 cm cathode diameter and 1 mil center wire. The gas pressure was 1 atmosphere.

Figure 48 shows the effect of wire size and gas pressure on the threshold voltage and plateau of Eck-Krebs type counters. 40 cm pressure of CH_4 and a ½ mil wire give an operating voltage of about 1600 volts, a comfortably low operating voltage.

The design of a continuous flow type beta proportional chamber which will accommodate two inch sample plates is shown in Fig. 49. An O-ring gasket insures a gas tight seal between the slide and chamber.

This chamber is also being used as an alpha proportional counter with excellent results. Two inch sample plates can be used. A point alpha source moved across any diameter on the sample holder shows less than 1% change counting rate from center to edge.

A method suggested by W. C. Bradley to reduce the distribution of pulse heights out of a beta proportional counter was investigated and found to work

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DWG. 7523

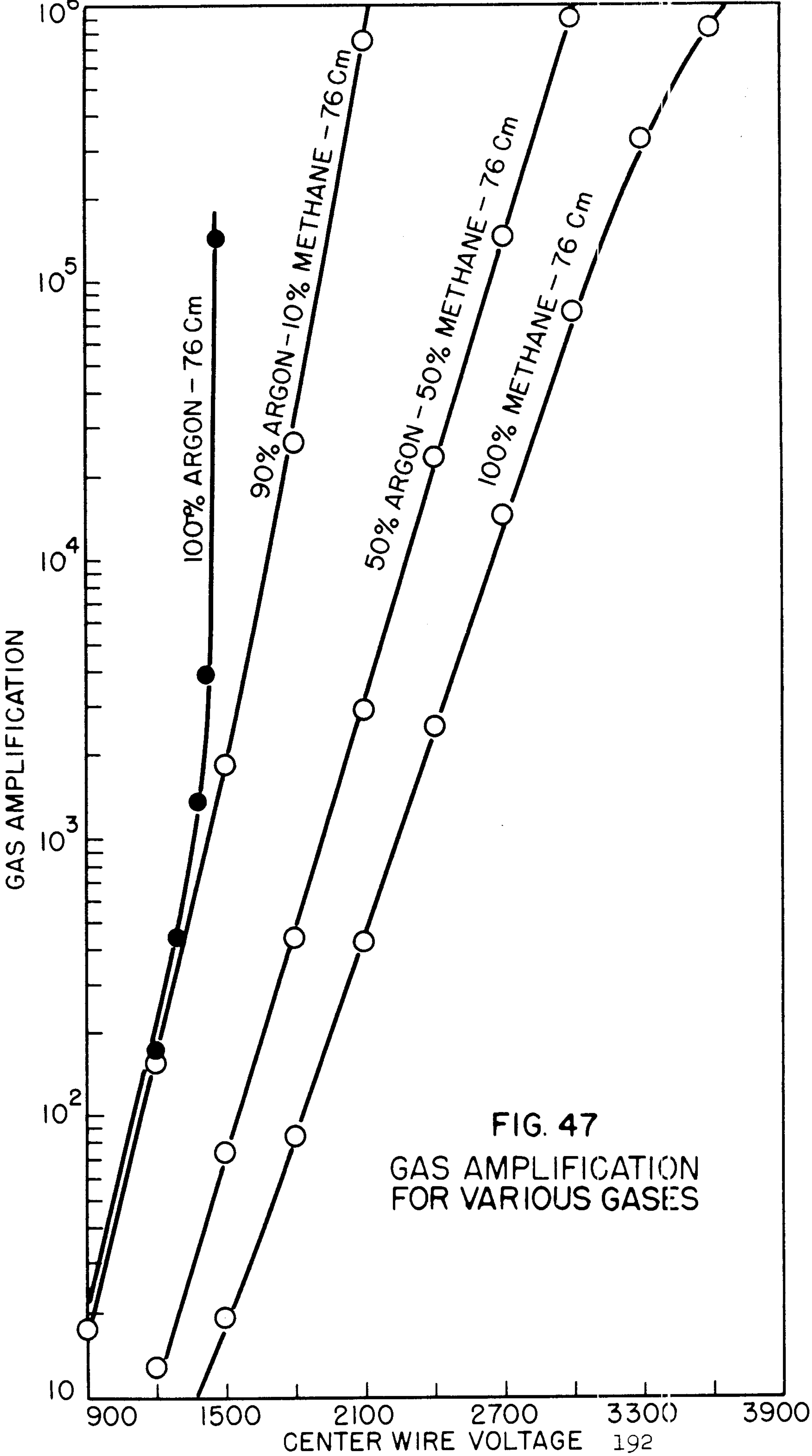

FIG. 47
GAS AMPLIFICATION
FOR VARIOUS GASES

[redacted]

TABLE I

Voltage plateaus using various percentages of argon and methane in permanently filled counter

Counter has 7 cm cathode diameter and 1 mil center wire
Gas pressure—One atmosphere

VOLTAGE	100% ARGON	90% ARGON 10% METHANE	50% ARGON 50% METHANE	100% METHANE
1425	6500			
1470	122700			
1500		10800		
1590		24900		
1680		37900		
1725		38400		
1800		38900		
1845		38800		
1890		39500		
2100			29200	
2190			37500	
2280			38300	
2370			38300	
2490			38600	
2580			38600	35800
2670			38600	38100
2790			39200	38200
2880			39800	38300
2970			41900	38300
3090				38500
3180				38600
3270				39100

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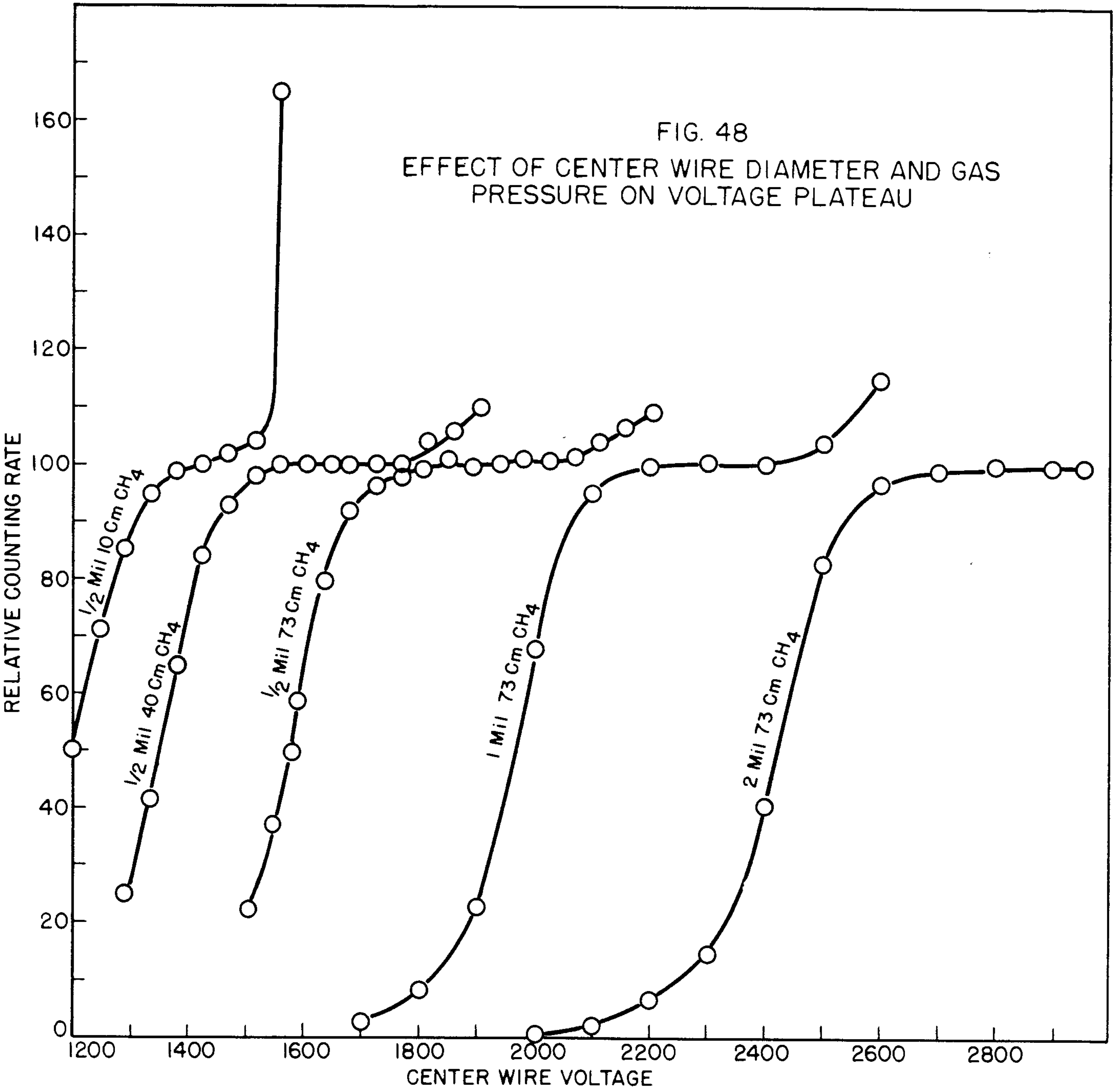

FIG. 48

EFFECT OF CENTER WIRE DIAMETER AND GAS PRESSURE ON VOLTAGE PLATEAU

[redacted]

KEY TO FIGURE 49

ITEM NO.	QTY.	NAME	SIZE	MATERIAL
1	1	Slide	3.250 W x 6-15/16 Lg.	304 SST
2	1	Rod	1/4 Dia x 1 Lg.	24 S Al
3	1	Stop	1/16 x 3/8 x 1-3/16	Brass
7	4	Screws, Flat Head Mach.	2-56 NC-2 x 3/16	Brass
8	1	Jaw, LH	3/8 x 11/16 x 3-15/16	24 ST Al
9	4	Screws, Flat Head Mach	10-24 NC-2 x 3/4	304 SST
11	3	Screw, Pressure	1/4-28 NF-3 x 5/8	304 SST
12	1	Knob	1 Dia	Lucite
13	1	Body (Chamber)	1-1/2 x 3-15/16 x 4-1/4	17ST or 24ST Al
14	1	P-Ring	No. S - 8 - 10	Syn Rubber
15	1	Jaw, RH	3/8 x 13/16 x 3-15/16	17 ST or 24 ST Al
16	1	Insulator	From Amphenol Fitting	No. 82-805
17	3-7/8	Wire	.0005 Dia	SST
18	1	Connector	From Amphenol Fitting	No. 82-805
19	1	O-Ring	S - 7 - 12	Syn Rubber
20	1	Amphenol Fitting	No. 82 - 805	--------
21	2	Tube Fitting	1/8 Tube	Brass
22	4	Screws, RH Mach	4-40 NC - 2 x 1/4	Brass
23	1	Stop	1/16 x 3/8 x 13/16	Brass
24	1	Gib	1/16 x 9/16 x 3-15/16	Brass

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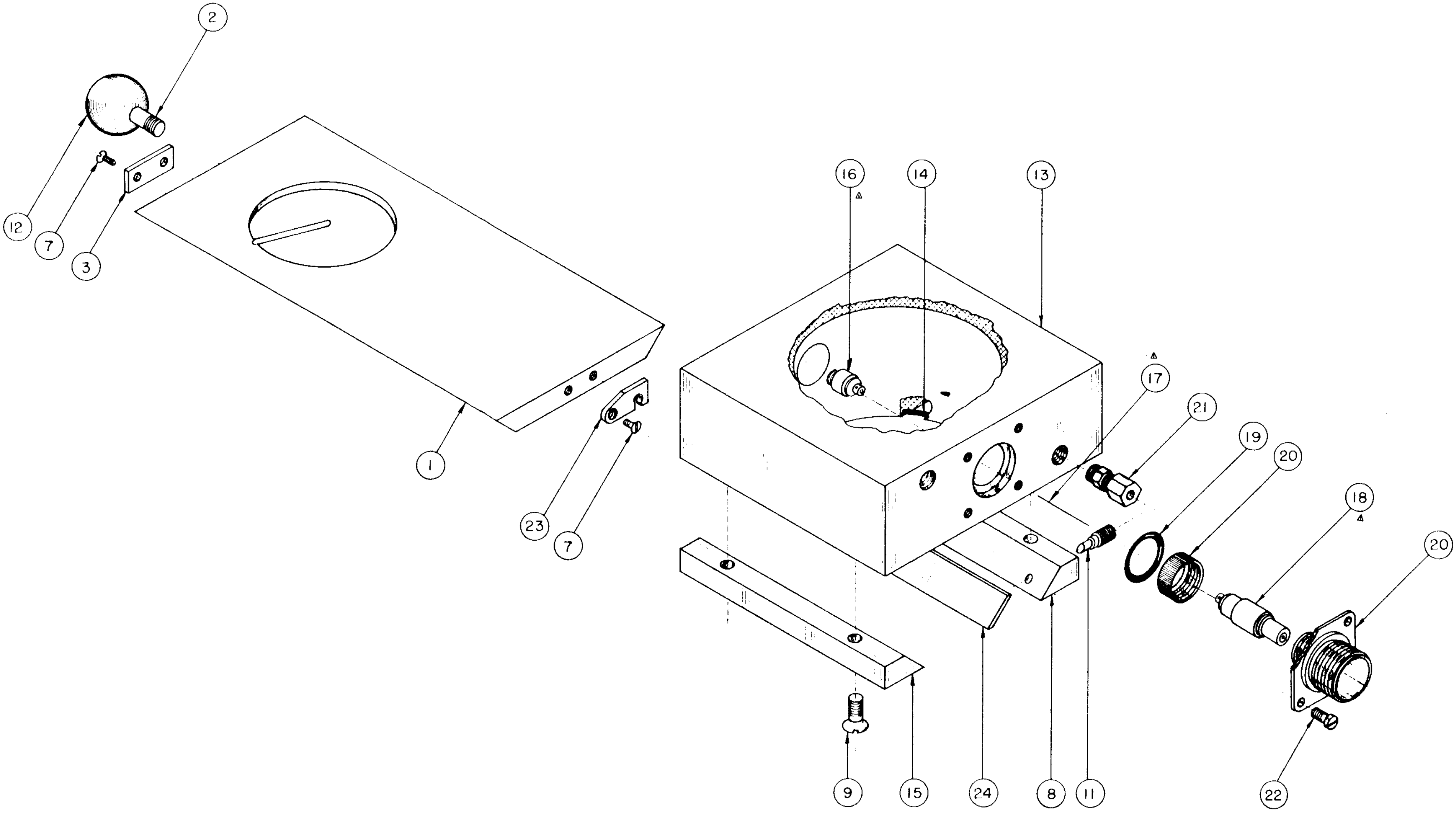

FIG 49
ALPHA AND BETA PROPORTIONAL FLOW TYPE CHAMBER

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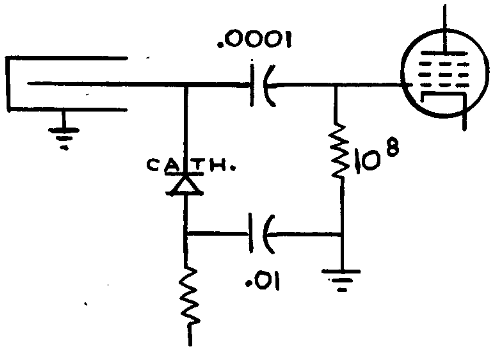
very satisfactorily. A 1N34 germanium diode with a high back resistance is used as the load on the chamber in place of the conventional 100 K resistor. The following input circuit is used:



The 1N34 diode can be used with equal effectiveness in place of the 10^8 ohm grid resistor, thus,

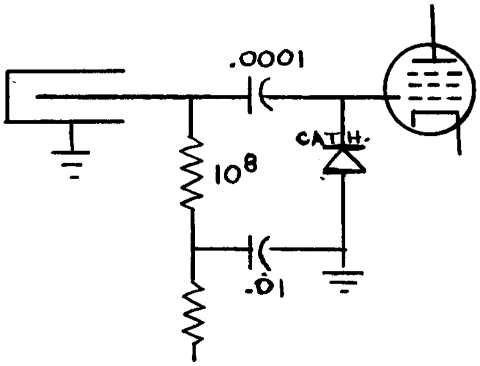


Figure 50 shows how the use of the 1N34 diode limits the maximum pulse voltage from the chamber from a maximum of 1 volt down to 100 millivolts in the operating region of the beta proportional counter. Thus the amplifier is required to handle a distribution of pulse heights of only 100 to 1.

1. The Amplifier, Input Circuit. The input circuit requires special consideration and for this reason it will be discussed in some detail.

To prevent extraneous noise pick-up and interaction with the output stages, the input circuit is enclosed in a shield of its own. Within this shield are placed the chamber decoupling network (consisting of a resistor and capacitor), the chamber load resistor, the coupling capacitor, and the grid resistor of

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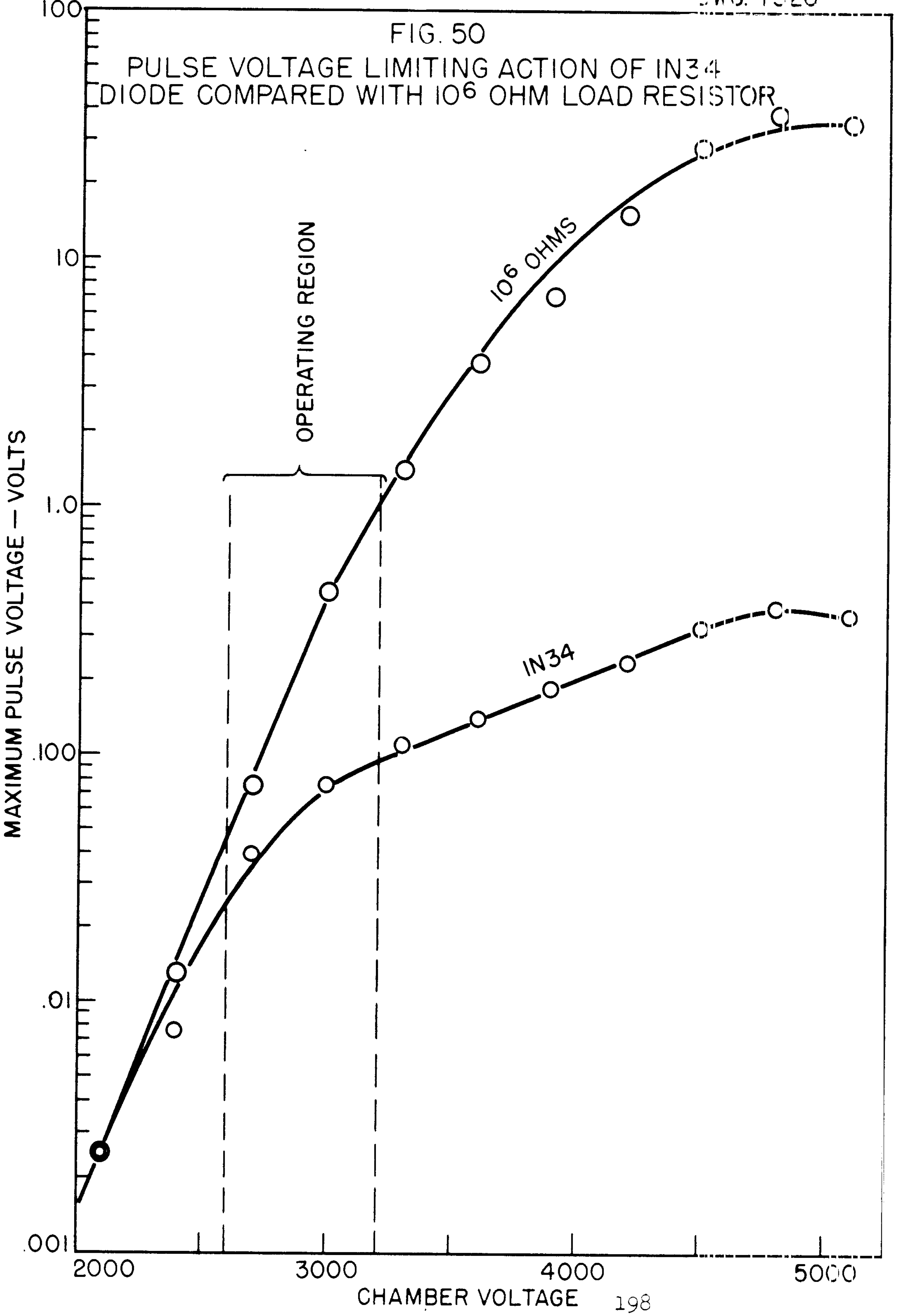

FIG. 50

PULSE VOLTAGE LIMITING ACTION OF IN34 DIODE COMPARED WITH 10^6 OHM LOAD RESISTOR

[redacted]

the first amplifier stage. For trouble-free operation, it is also desirable to shield the decoupling network from the amplifier input. The various coupling resistors are mounted in a manner which results in one end being shielded from the other. Grommets are provided for openings through which high voltage leads pass. This is to reduce the possibility of corona.

The choice of coupling and decoupling capacitors is very important, since surface leakage and corona losses in these two components will produce spurious counts in the system. The most satisfactory units found to date are the Centralab type 850 (ceramic) for use as the coupling capacitor, and the Plasticon Glassmike type ASG-30 for use as the decoupling capacitor.

In humid climates, it is necessary to treat the surfaces of these units to further reduce their electrical leakage.(1)

The high-voltage and input connectors are also very important. Connectors with teflon inserts specially designed for low electrical leakage (such as the Amphenol 82-804 and 82-805) are by far the most satisfactory.

The surfaces of all the components just described should never be touched with the bare fingers. Gloves should be worn during installation.

2. *Amplifier Requirements.* The desirability of a long counting rate plateau coupled with the continuous pulse height distribution of a beta, gamma, or X-ray emitter makes it necessary for the amplifier to accept a wide range of input signals without introducing spurious responses and without blocking. A linear amplifier is unnecessary. The basic requirement is that the trigger circuit be tripped once for every pulse which arises in the chamber.

The maximum sensitivity of the amplifier should be such that input circuit noise is just below the counting threshold. For a good amplifier, this is about 100 microvolts. In actual practice, threshold sensitivities up to 1.5 millivolts are acceptable.

The range of input signal acceptance should be at least 300 to one before spurious responses or blocking effects occur. A good amplifier will have an acceptance range of 1000 to one. An amplifier with this range will have a plateau length of at least fifteen percent of its threshold voltage. A range of greater than 1000 to one will afford no improvement, because the chamber

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(1) The usual treatment is described in 'Methods for Reducing Insulator Noise and Leakage' by Floyd M. Glass, ORNL 191.

[redacted]

[redacted]

itself produces multiple pulses.

The rise time of the amplifier should be one microsecond or less. The fall time should be approximately five to ten times the rise time. This figure represents a reasonable compromise between gain, noise transmission, and dead time.

The gain of the amplifier will normally be determined by the sensitivity of the trigger circuit which follows it, since the input sensitivity is more or less fixed. With a trigger circuit sensitivity of 250 millivolts, an amplifier gain of 250 to 1000 is desirable.

3. *Spurious Responses and Blocking.* The output voltage of a chamber produced by an ionizing event approximates a step function. When this signal passes through an interstage coupling network, it is converted to a pulse of the form $V_0 e\,(-t/RC)$, where V_0 is the height of the step appearing at the input terminals of the coupling network, and RC is the time constant formed by the coupling capacitor and plate load and grid-leak resistors.

When the signal passes through two such networks, the alternate charging and discharging of the second capacitor causes the output voltage to cross the baseline. This effect produces a pulse of opposite polarity to the initiating pulse, and is known as an overshoot.(2) The magnitude of the overshoot is a function of the ratio of time constants. For an overshoot of one percent, the two time constants should differ by 100 to one.

Each additional network produces one more overshoot. Since even numbered overshoots are of the same polarity as the original signal, they cannot be discriminated against, except on an amplitude basis. If they are large enough to trip the trigger pair, they result in spurious responses.

For a signal acceptance range of 1000 to one, it is necessary that the second overshoot be no greater than 0.1 percent.

In an ordinary resistance coupled amplifier, a large voltage pulse at the input will cause a tube near the output end of the amplifier to be driven into the positive grid region, causing it to draw grid current; when this occurs, the interstage coupling capacitor becomes charged quite rapidly. When the signal disappears, the discharge of the coupling capacitor through the grid-leak causes the stage to be cut off, usually for a period considerably longer

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(2) For complete discussion of overshoots and blocking, see Vacuum Tube Amplifiers, Section 3-2 by Valley and Wallman.

[redacted]

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than the duration of the initiating pulse. This effect is known as blocking, and results in the loss of small signals which immediately follow a large one. The effect is to cause a drop in the plateau at the higher chamber voltages.

Blocking effects can be reduced by causing the output stage to be driven negatively, rather than positively.

The amplifier should consist of two or three stages. (A feedback pair is considered as one stage). The signal is differentiated at the chamber with a time constant of approximately one microsecond, and again at the coupling network between the amplifier output and trigger circuit input with a similar time constant. All intermediate coupling networks have time constants at least 300 times greater. (Differentiation at the chamber is accomplished by using a low valued chamber load resistor. The time constant is the product of this resistor and the input capacitance of the amplifier with the chamber connected). Differentiation at the input prevents blocking effects due to pulse pile-up at high counting rates, and differentiation at the output attenuates noise components arising from hum and microphones.

4. *Trigger Circuits.* The trigger circuit used with the counter should be stable, have a sensitivity of about 0.25 volts, respond to one polarity signal only, be capable of handling large signals without drawing grid current or producing other undesired responses and should produce a pulse no wider than the signal causing it. A Schmidt circuit is one type which has these characteristics and has been used successfully.

5. *High Voltage Power Supply.* The high voltage supply must be regulated, but not to any great degree. A shunt type regulator using one type 6BG6 tube (with the first and second grids tied together and used as the control grid) provides ample regulation.

6. *Low Voltage Supply.* The low voltage supply must be well filtered, but need not be regulated.

Using a chassis ground return in the heater circuit does not introduce undesirable hum. Generally, it is desirable to shield the heater lead going to the first amplifier stage.

In most units, it will be found necessary to provide the amplifier with r.f. noise filters in both filament and plate leads to eliminate power line interference. A well built unit will have a zero background count due to line noise and high voltage leakage over a twenty-four hour period.

7. *Scalars and Ratemeters.* Scalars and ratemeters will not be discussed,

[redacted]

[redacted]

since any standard circuit can be made to operate with the system.

8. *Construction of Beta Counters.* The development of routine counting equipment has been divided into two broad classifications, (1) conversion of existing equipment, and (2) development of new circuits.

The first experiments on beta proportional counters were performed using the Simpson alpha proportional counter. It was found necessary to add a pre-amplifier (consisting of two 6AK5's connected as a feedback pair) and a germanium diode across the output to eliminate some of the overshoot. It was also necessary to improve the filtering in the low voltage power supply.

The unit has given excellent results and is still in use after two years of continuous operation. The plateau length is about 300 volts. The dead time is about 1.5 microseconds, corresponding to a loss correction of about one percent per 400,000 counts per minute. This figure is as good as that of the original alpha counter.

Since then, numerous other types of alpha and Geiger-Mueller counters have been converted, all giving good results.

The simplest unit to convert is the Nuclear Instrument and Chemical Corporation Model 162. This model does not require the addition of a pre-amplifier. The circuit and necessary changes are indicated in Fig. 51. Its operating characteristics are similar to those of the converted Simpson unit.

An alternate method for conversion is to replace the chamber load resistance with a type 1N34 diode, as previously described.

Attempts were made to develop new units which would yield longer plateaus and be simpler to build. However, after quite some time was spent on this project it was found that in most cases the plateau length was limited by multiple pulsing arising in the chamber itself, rather than in the circuitry.

One circuit developed which does contain fewer components than the usual counter is the three stage amplifier shown in Fig. 52. The resolving time is about two microseconds and the plateau length about the same as the converted commercial units.

With counting rates greater than 25,000 per minute, a drop in the counting rate occurs at the upper end of the plateau. The effect becomes increasingly pronounced with higher counting rates. It is due to blocking in the second stage. The effect can be eliminated by replacing the chamber load resistance with a type 1N34 diode.

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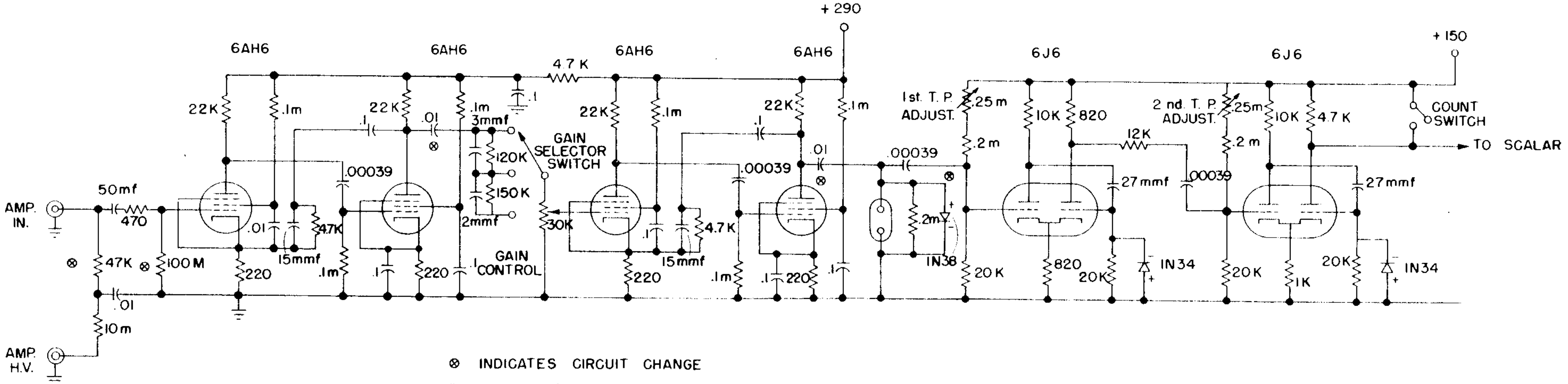

⊗ INDICATES CIRCUIT CHANGE

R IN OHMS, (IN mf. UNLESS OTHERWISE NOTED.)

FIG. 51

I. D. L. MODEL 162 ALPHA PROPORTIONAL AMPLIFIER CONVERTED TO BETA PROPORTIONAL COUNTING

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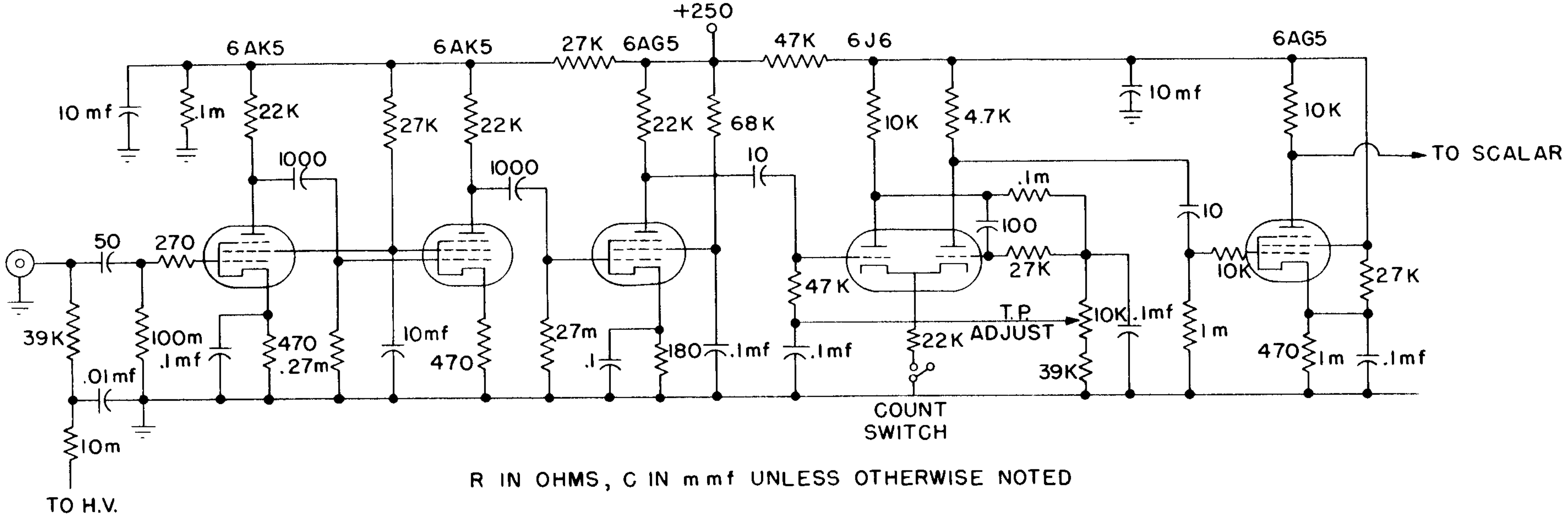

R IN OHMS, C IN mmf UNLESS OTHERWISE NOTED

FIG. 52
THREE STAGE BETA PROPORTIONAL AMPLIFIER

[redacted]

It should be pointed out that a combination of blocking and multiple pulsing can occur in such a way that exact cancellation of the two effects takes place. The result is a false plateau which may be twice as long as a normal plateau. This effect exists for a small range of counting rates only, and care must be taken to ascertain that the sample used for standardizing the system does not lie in this range.

All the counters placed in operation exhibit plateau lengths of fifteen percent of the plateau threshold. While this is adequate for all normal applications, a longer plateau would be desirable for use by untrained personnel.

One method for doing this is to use an automatic gain control, which causes a decrease in amplifier gain with an increase in chamber voltage. The control voltage for the AGC system can be derived from the high voltage supply and used for decreasing the screen voltage or increasing the grid bias on one or more of the amplifier tubes. A complete system using this method has not been built, but a few experiments have indicated its feasibility.

A FOUR-CYCLE LOGARITHMIC VOLTMETER

C. J. Borkowski, E. Fairstein, B. Zemel

A four-cycle logarithmic voltmeter circuit has just entered the development stage. Preliminary tests have given encouraging results.

The intended use for the voltmeter is as an indicator for a ratemeter circuit, although it will probably have other applications as well.

When used with a ratemeter, it will be possible to obtain decay curves through a counting rate variation of four decades without switching ranges. It will also provide a means of monitoring in situations where the counting rate varies between wide limits.

The advantage of this system over existing systems is that it is expected to have the low zero drift and permanence of calibration normally associated with a linear count-rate meter circuit. Its primary disadvantage is its relatively high cost.

A description of the apparatus is as follows: A one-cycle logarithmic potentiometer capable of continuous rotation is mechanically linked to a switching mechanism which trips a micro-switch after each complete revolution. The

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potentiometer can be turned through four revolutions. Three switches are required. The switches change fixed shunt resistances across the potentiometer. The potentiometer has a voltage applied to it from a 300 volt power supply. The switching mechanism makes it possible to derive a voltage from the potentiometer which can vary continuously in a logarithmic manner between the limits of .01 and 100 volts, except for the discontinuities in the immediate neighborhood of the switching points.

This combination is part of a feedback system. The signal voltage (which is any voltage we are interested in measuring) and the voltage derived from the potentiometer are both applied to a sensing element in such a way that the sensing element sees no signal when the two voltages are equal. In this case, the sensing element is a Brown Recorder amplifier whose output drives a servomotor mechanically linked to the potentiometer. The system automatically hunts the balance point, the angular position of which is a measure of the signal voltage.

The potentiometer actually used in the test was a linear unit with nine equally spaced taps. Fixed shunting resistances of the proper values were connected between the taps to give an approximately logarithmic voltage distribution. The maximum deviation from a true logarithmic distribution was approximately one-half of one percent.

COINCIDENCE CIRCUIT FOR USE WITH BETA PROPORTIONAL COUNTERS

R. A. Dandl

There has been a need for a coincidence circuit to be used with beta proportional counters. The design considerations stressed in the circuits now being made were stability and flexibility. Since the rise time of the conventional beta amplifiers is in the 0.25 to 0.5 μ-sec region, speed in the coincidence circuit was no problem. Stability was insured by taking two precautions other than the orthodox precautions usually taken. Since the pulses from the beta counter trigger circuit are non-uniform in amplitude, to assure proper operation of the resolution time controlling triggers in the coincidence circuit, the pulses from the counter were used to cut off an amplifier

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with a diode damped inductance in the plate. Secondly, the coincidence circuit trigger pairs were made as fast as possible, consistent with obtaining flat topped variable width pulses. The flat topped pulses are important in defining a resolution time and making the coincidence circuit proper non-critical. The coincidence circuit proper which consists of cathode follower driven diode clamps is very satisfactory. Two gear coupled pots in R.C. circuits in the triggers allow panel adjustment of the resolution time from 0.15 to 4.0 μ-sec. The usual resolving time is of the order of 0.5 μ-sec in order to avoid missing true coincidences resulting from delays due to small pulses triggering at time "t" (amplifier rise time) after a large coincident pulse. Several of these circuits are in operation and have proven satisfactory for their application. Figure 53 shows a schematic of the circuit.

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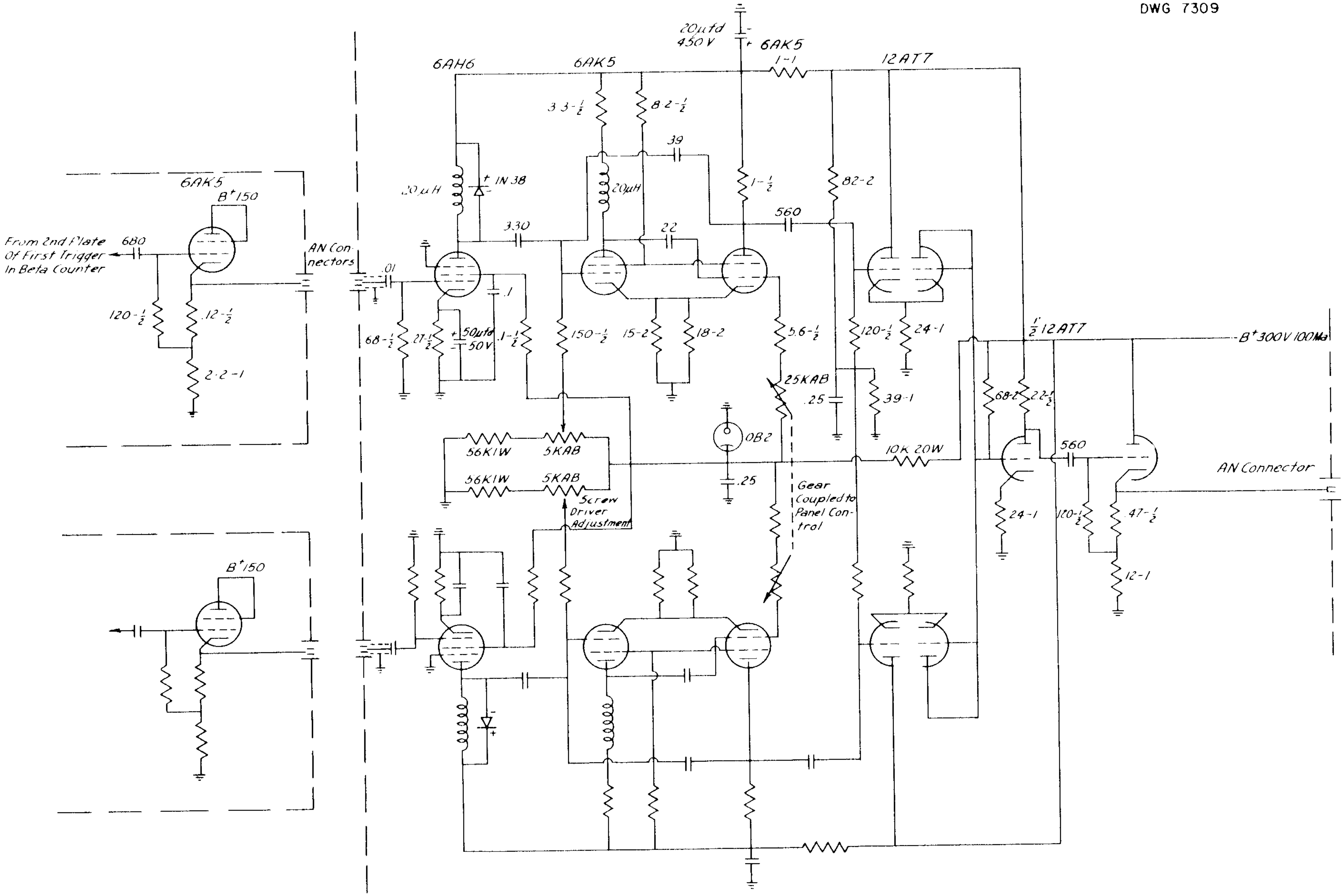

All 6AH6's on filament supply with one side grounded.
Remaining tubes on supply with center top connected to OB2

FIG. 53
COINCIDENCE CIRCUIT FOR BETA PROPORTIONAL COUNTER

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ANALYTICAL CHEMISTRY

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IONIC ANALYSES—RESEARCH AND DEVELOPMENT

Summary. The major portion of the work has been directed toward the development of analytical methods for the various control groups. A new polarograph has been installed in 205 Building for the Pilot Plant Control Group. It will be used primarily for the determination of uranium in the 25 recovery process streams.

The Precision Dow Recordomatic titrator is being adapted to a micro volumetric uranium determination. The volumetric procedure will be used as a referee method for the 25 process streams.

A polarographic method has been used for the determination of micro amounts of iodine in radioactive solutions.

Service analyses included UAP samples from K-25 and non-routine samples from the radioisotope production group and the technical chemical development group.

***Automatic Titration of Microgram Quantities of Uranium* (*F. J. Miller, P. F. Thomason*).** The Precision Dow Recordomatic titrator(1) has been adapted to drive a Kirk micro burette by a simple gear arrangement. This enables one to automatically titrate with volumes as small as 10 λ. It will be a decided advantage for the analyses of the highly radioactive 25 process solutions.

Preliminary titrations by the ferric sulfate procedure(2) of uranyl sulfate solutions, made from Bureau of Standards MS-ST U_3O_8 dissolved in sulfuric acid, have shown well defined breaks. However, the titration curve is somewhat erratic, resulting in rather poor precision. This is thought to be due to mechanical trouble in titrating such a small volume. The coupling of the micro burette to the titrator is positive. However it was found that the air space in the burette between the titrant and mercury caused a lag in the titration. This was overcome by removing the mercury from the burette and filling the entire burette with the titrant. As the chart travel of the recorder is a measure of the volume of titrant added, it is not necessary to read a meniscus on the centimeter scale of the burette. The burette plunger was gold plated to prevent corrosion by the titrant.

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(1) ORNL 336, pp. 110-112.

(2) Nessle, G. J., et al, Potentiometric Titration of Uranium with Ferric Sulfate MDDC-1123.

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The titration cell assembly consists of an aluminum heating block with a small hole for a one ml beaker. The temperature of the block is automatically maintained at 90° C by a Wheelco thermostat. The assembly is placed on a magnetic stirrer and stirring is accomplished by a short piece of No. 22 iron wire sealed in a small glass tube which will fit in the 1 ml beaker. A piece of No. 18 platinum wire is used as the indicator electrode with a small salt bridge connecting the No. 270 Beckman calomel electrode. The electrodes are mounted in an inverted glass crystallizing dish which will fit over the cell assembly. Carbon dioxide atmosphere is maintained in the cell during the titration.

Twenty lambda of a 10 mg U/ml standard uranyl sulfate was pipetted into the one ml beaker with a micro pipette, adding the rinsings to the beaker. Ten lambda of concentrated H_2SO_4 was added and the beaker placed into the assembly. Chromous sulfate was added until the recorder registered +400 mv on the $+\frac{1}{2}$ to $-\frac{1}{2}$ scale; usually 250 λ of 0.1 *N* chromous sulfate was sufficient to show an excess. The tip of the burette and the electrodes were inserted into the solution and the titrator started. The titration curve was completed in approximately five minutes.

The first jump in potential was in the order of 150 millivolts and indicated the oxidation of the excess chromous ion. The second break, which was less pronounced (approximately 50 millivolts) indicated the completion of the U^{+4} oxidation to U^{+6} by the $\sim$0.1 *N* ferric sulfate. The chart travel between the two breaks is a measure of the uranium present and can be calibrated in terms of micrograms of uranium per inch of chart travel.

Theoretically 200 λ of uranium in the 20 λ of solution will require 16.3 λ of 0.1029 *N* $Fe_2(SO_4)_3$. As the average chart travel was 5.6 inches for this titration, 2.92 λ of solution should be delivered per inch of chart travel by this particular burette. Typical results of this titration are shown in Table I and a titration curve is shown in Fig. 54. While these results are encouraging, the titrations of 250 γ of uranium show comparatively less chart travel than with the 200 γ titrations. This could be due to non-uniformity of the burette plunger. Work is continuing on the calibration of the device and the problem of eliminating nitrates in the process samples. Very small amounts of nitrate may be tolerated provided an excess of chromous sulfate can be obtained. However, due to the small volumes involved, the volume of chromous sulfate is limited to approximately 500 λ.

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TABLE I

Micro uranium titration with the recordomatic titrator

SAMPLE NUMBER	URANIUM PRESENT	CHART TRAVEL BETWEEN BREAKS	MICROGRAMS OF U PER INCH OF CHART
1	200 γ	5.6 inches	35.7
2	200 γ	5.6 inches	35.7
3	200 γ	5.6 inches	35.7
4	250 γ	6.8 inches	36.5
5	250 γ	6.6 inches	37.8
6	250 γ	6.7 inches	37.4

TABLE II

Diffusion current versus uranium concentration

MICROGRAMS OF U PER MILLILITER	DIFFUSION CURRENT MICROAMP x 100	MICROAMPS PER MICROGRAM OF U x 100
0.53	0.24	0.45
1.59	1.50	0.94
2.12	2.19	1.03
5.3	6.42	1.21
7.42	9.0	1.21
9.01	11.1	1.23
10.07	13.1	1.30

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DWG. 7556

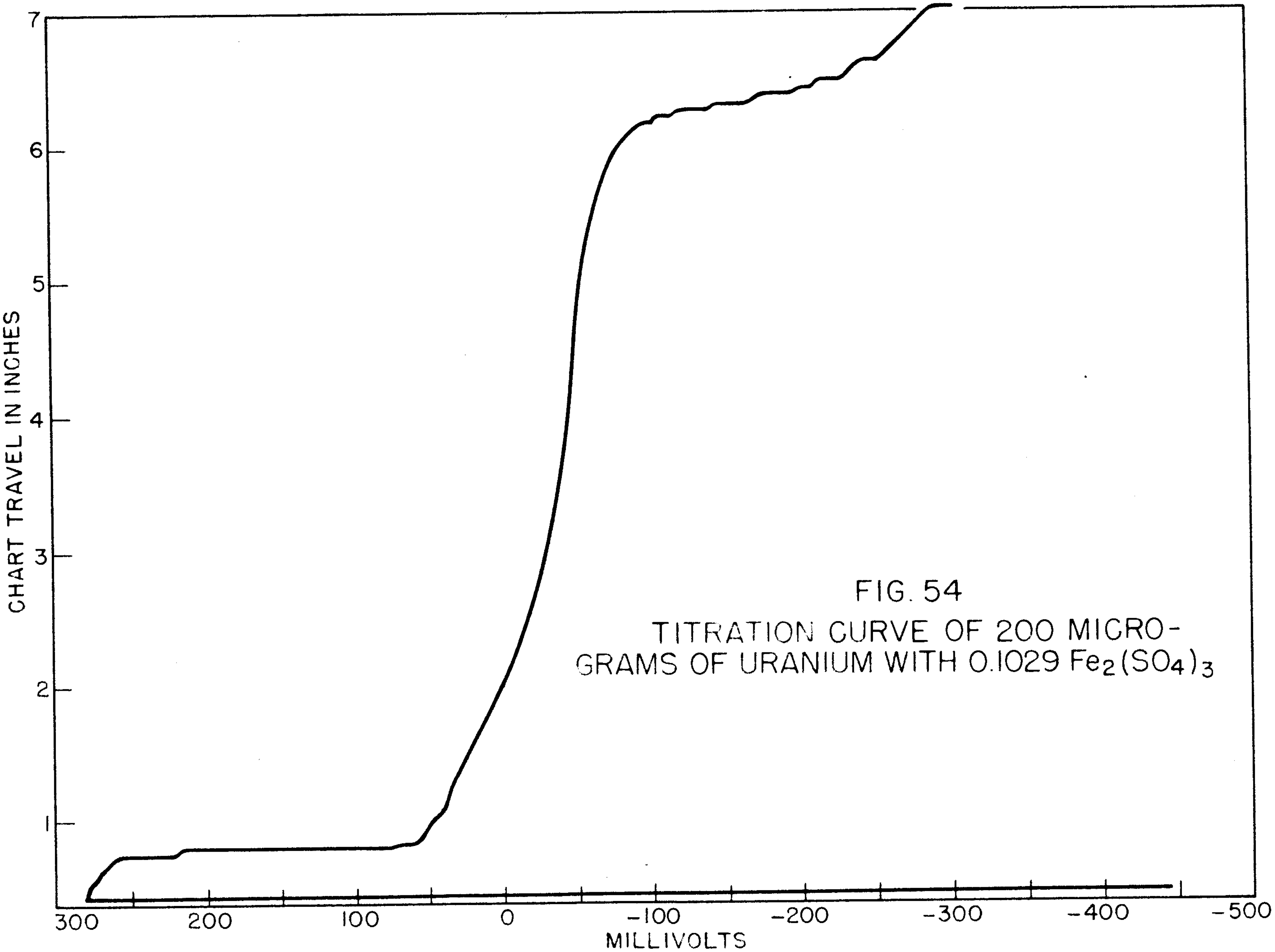

FIG. 54

TITRATION CURVE OF 200 MICROGRAMS OF URANIUM WITH 0.1029 $Fe_2(SO_4)_3$

[redacted]

Determination of Ferric and Ferrous Iron in a Mixture (F. J. Miller, P. F. Thomason). Mr. A. S. Kitzes of the Technical Division is making a study of the effect of high beta and gamma radiation on a ferrous iron solution. He requested a method for the determination of both ferric and ferrous iron, preferably some continuous type of measurement. As the Kolthoff and Lingane (3) polarographic determination met this requirement, a simple manual polarograph utilizing a Brown Electronik Recorder was installed and calibrated.

A stationary platinum microelectrode, 4 mm long and 0.5 mm in diameter, was sealed into the polarographic cell which consisted of a 2½ in. diameter plastic beaker with a sodium sulfate salt bridge connecting a saturated calomel electrode. Ten milliliters of solution was necessary to adequately cover the bottom of the beaker. It was unnecessary to remove the dissolved oxygen from the solution as the entire current-voltage curve occurred at a potential so positive that the reduction of oxygen did not interfere.

It was possible to determine simultaneously the ferrous and ferric iron in a mixture of 0.001 *M* ferrous sulfate and 0.001 *M* ferric sulfate in a 0.5 *M* sulfuric acid solution by recording the cathodic-anodic wave from +1.0 volt to 0.0 volts with the half-wave of the ferric-ferrous system at approximately +0.53 volts. The Brown recorder was adjusted so that the current measured was 0.5 μa per centimeter of chart. This allowed the complete cathodic-anodic wave of approximately 14 μa to be recorded. The instrument was placed at the disposal of Mr. Kitzes.

Polarography (W. H. Davenport, Jr.). (1) **Aluminum.** An investigation was made of two methods of determining aluminum polarographically. One method is based on the reduction of the aluminum ion in a $BaCl_2$ or $Th(ClO_4)_4$ supporting electrolyte. The other is based on the reduction of one tautomer of the dye Pontachrome Blue-Black. The amount of dye which is present in solution in this form is directly proportional to the concentration of aluminum present. Neither of these methods seems to be very applicable to analytical purposes. They are subject to many interferences and a critical control of *p*H must be maintained in both cases. Some use may be found for either or both procedures in special solutions containing aluminum relatively free from interfering ions.

(2) **Iodide.** Neutral or slightly acid iodide solutions may be oxidized to the iodate using Br_2 water. After removal of excess bromine by boiling, the iodate concentration may be determined polarographically using a buffered 0.1 *M* KCl + 0.1 *M* acetate supporting electrolyte suggested by Kolthoff and

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(3) Kolthoff, I. M., and Lingane, J. J., Polarography, New York 1941 (pp. 169 and 276).

[redacted]

[redacted]

Orlemann.(4) The half-wave potential is -0.5 V. *versus* the saturated calomel electrode. Reduction waves were obtained for solutions containing as little as 0.127 γ I/ml. These waves are not reliable. A more desirable concentration range 1 γ I/ml—5 γ I/ml, was used to prepare a satisfactory calibration curve. A solution of 5 γ I/ml gave a diffusion current of approximately one microampere.

Polarograph for Routine Uranium Control Analyses (M. T. Kelley, G. R. Wilson, H. H. Miller). In the previous quarterly report (ORNL 336) a brief description of a recording polarograph for uranium determination was given. This instrument has been further modified by incorporating a high impedance preamplifier into the Brown recorder similar to that described by Rosenbaum and Stanton.(5) The use of this preamplifier in place of the usual transformer input to the Brown eliminated the effects of stray magnetic fields which sometimes caused random shifts of the recorder pen. A second instrument of the same design has been constructed and is now in use in the Pilot Plant Control Laboratory.

The tests of the performance of this instrument have been even more promising in the low concentration range than had been hoped. The diffusion currents found for several concentrations in the range from 0.5 to 10 micrograms of uranium per milliliter are as shown in Table II.

The surprising factor in these measurements is the apparent decrease in diffusion current per microgram of uranium below concentrations of 5 micrograms per milliliter although the diffusion current curve is almost perfectly linear from this point to 300 micrograms per milliliter. It has been concluded that although the use of the polarograph for determination of uranium in the concentration range of 1 microgram per milliliter (4×10^{-6} *M*) is feasible a better understanding of the decrease of diffusion current would be highly desirable. To this end the present polarograph is being further modified so that its most sensitive range will be of the order of 0.05 microampere for full scale deflection with the result that sensitivity of the instrument will not be a limiting factor in the measurements. Studies will also be made of other ions in this concentration range to see if they show similar behavior.

Special Analytical Apparatus (H. L. Hemphill). The hydraulic pipettor has been revised by replacing the rubber diaphragm with a teflon sealed piston control. This control features a combination coarse and fine adjustment that

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(4) Kolthoff, I. M., and Lingane, J. J., Polarography, New York 1941 (pp. 319-320).

(5) Rosenbaum and Stanton, Anal. Chem. 19, 794 (1947).

[redacted]

will accurately pipette either milliliter or lambda volumes of solution.

A small portable electric stirrer has been devised using a micro electric motor which is driven by two No. 935 flashlight cells that are contained in the handle of the device. This compact stirrer will efficiently mix a small volume of liquid in a test tube or centrifuge cone and is particularly convenient when it is necessary to stir radioactive solutions.

RADIOCHEMICAL ANALYSES—RESEARCH AND DEVELOPMENT

1. *Summary*. Investigation of the decay scheme of Ba^{140} has disclosed evidence for two previously unreported gamma rays. The half-life and mode of decay of Cl^{36} have been established. Significant work on beta and gamma counting efficiencies of standard counters has been finished. Radiochemical methods for Pu, Am, (+Cm), and Zr are being devised. Activation-analysis methods are under investigation, and certain activation cross sections have been determined.

2. *Decay Scheme of Ba^{140} (W. S. Lyon)*. The method of purification of Ba^{140} was given in the previous report.(6) The continuous beta spectrum is given in Fig. 55 and the Kurie Plot in Fig. 56. With a large source of Ba^{140} the spectrum of unconverted gamma rays was determined, using uranium, gold, and columbium radiators. This information confirms the conversion-electron peaks observed in the Kurie plot. That all observed radiations are due to Ba^{140} has been shown by use of sources of different bombardment and cooling times, and by following decay of various portions of the spectrum on the spectrometer. Coincidence counting, employing a coincidence circuit with conventional G-M tubes, gave useless results because of too rapid growth of La^{140} gamma radiation. Use of proportional counters with a coincidence circuit will make possible a reliable study of beta-gamma coincidences.

Ba^{139} has been reported to have a 0.163 Mev gamma ray.(7) The close approximation in energy to the Ba^{140} gamma given above made an investigation seem desirable. A source of Ba^{139} was prepared by irradiation of ~1.5 g of $Ba(NO_3)_2$ in the ORNL reactor for two hours. This material was then mounted as a gamma source in the spectrometer. A columbium radiator was used, and photoelectrons of energy about 0.16 Mev were sought. A K photoelectron peak corresponding to a gamma energy of 0.165 Mev was found. Repeated measurements indicated a half-life for this gamma of ~70 minutes, essentially confirming the assignment to Ba^{139}.

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(6) Chemistry Division Quarterly Report, ORNL 336 (1949).

(7) L. R. Shepherd and J. M. Hill, Nature 162, 566 (1948).

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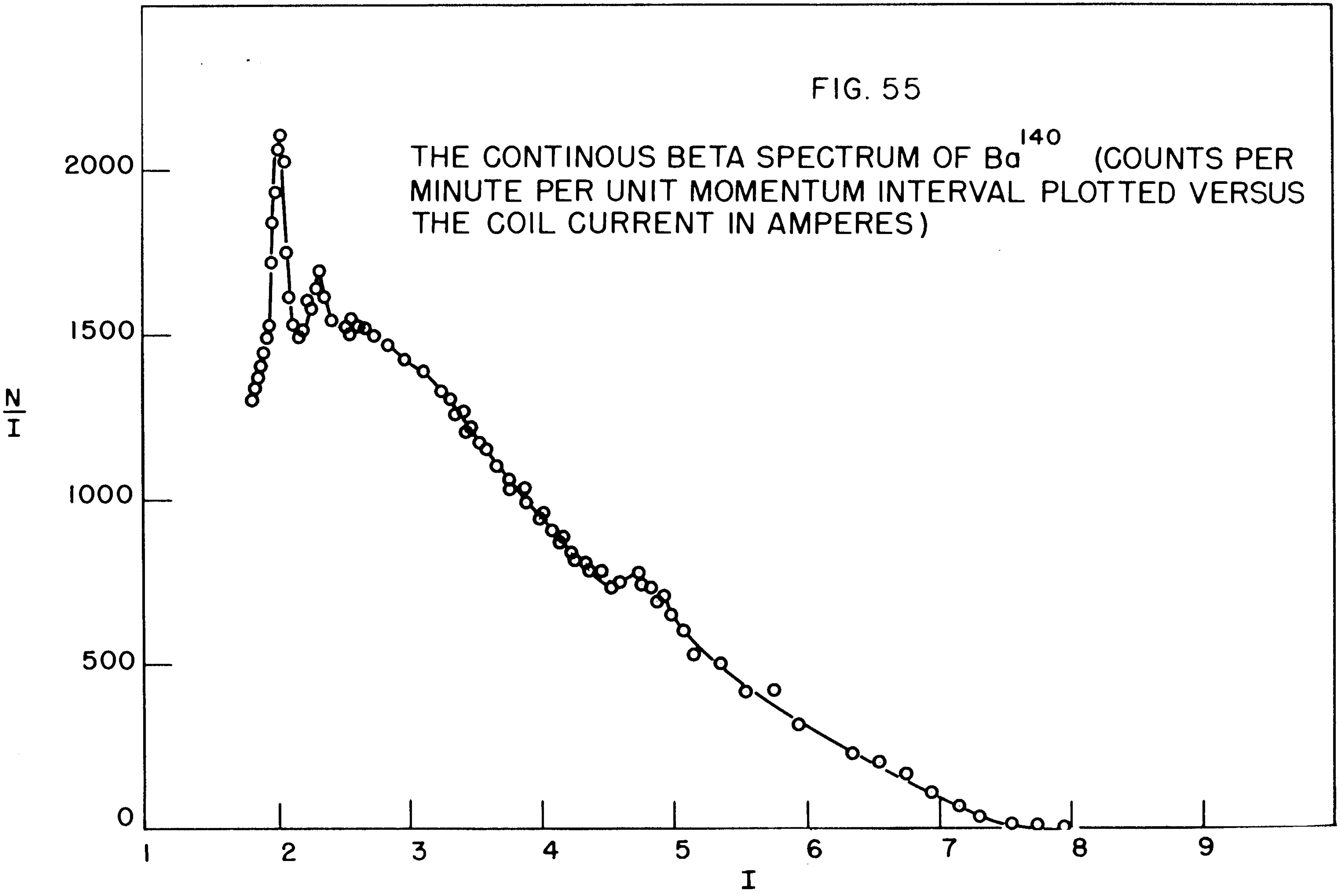

FIG. 55

THE CONTINOUS BETA SPECTRUM OF Ba^{140} (COUNTS PER MINUTE PER UNIT MOMENTUM INTERVAL PLOTTED VERSUS THE COIL CURRENT IN AMPERES)

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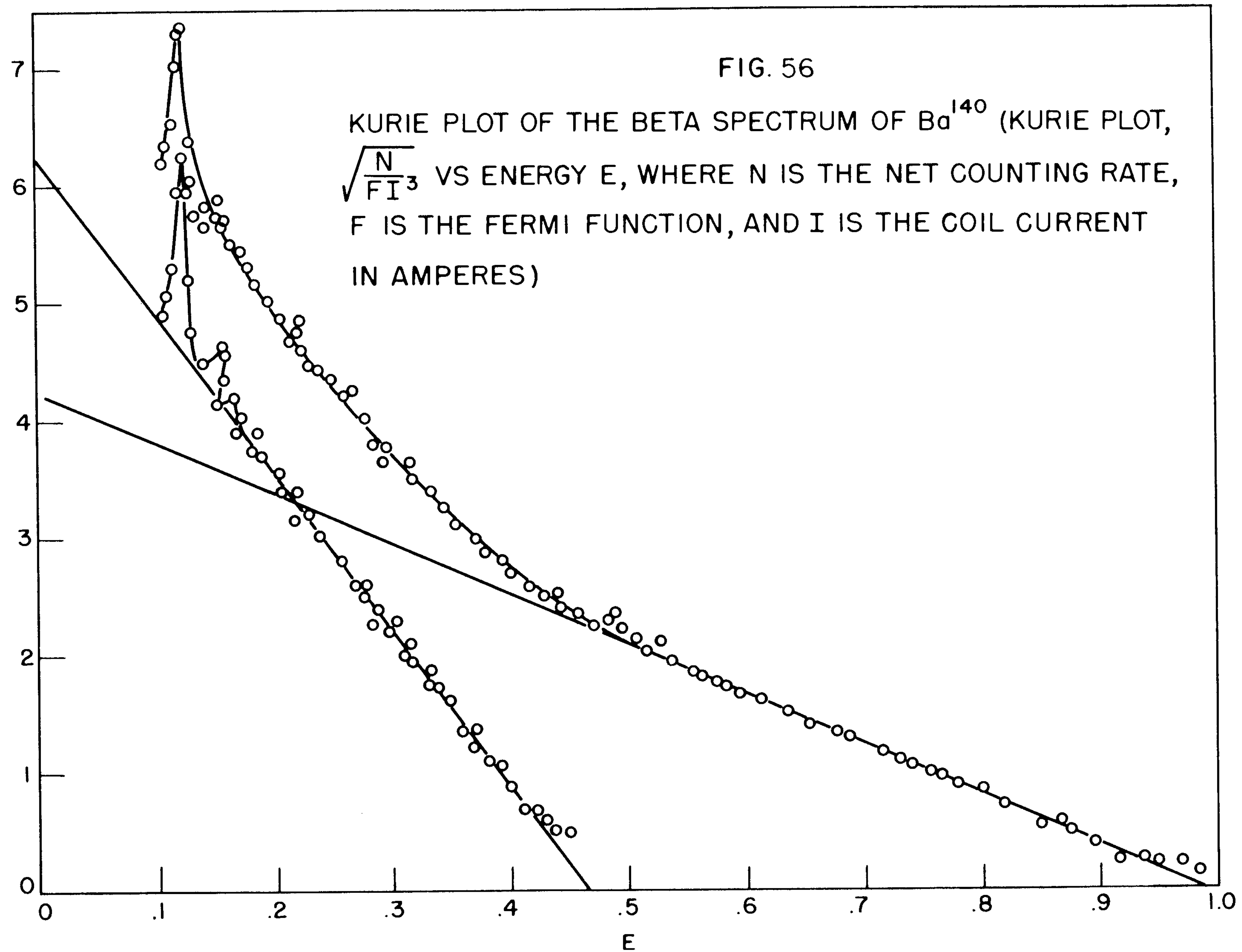

FIG. 56

KURIE PLOT OF THE BETA SPECTRUM OF Ba^{140} (KURIE PLOT, $\sqrt{\frac{N}{FI^3}}$ VS ENERGY E, WHERE N IS THE NET COUNTING RATE, F IS THE FERMI FUNCTION, AND I IS THE COIL CURRENT IN AMPERES)

[redacted]

3. *Radioactivity of Cl^{36} (S. A. Reynolds).* Three samples of Cl^{36} have been studied. Two were prepared by bombardment at Hanford and were purified by Mr. E. Beauchamp of the Operations Division. The third was purified from KCl bombarded almost two years in the ORNL reactor. The purification consisted of AgCl precipitation, solution in ammonia, $Fe(OH)_3$ "scavenging," reprecipitation of AgCl by addition of HNO_3, fusion with Na_2CO_3, leaching the resulting NaCl with water, and distillation of HCl from sulfuric acid. Aluminum absorption curves on the conventional end window G-M counter show a maximum beta energy of 0.73 Mev (by Feather analysis) (Fig. 57). This agrees roughly with the results obtained by Overman, 0.66 Mev (8), and by Graham and Walke, 0.64 Mev. (9) By use of the proportional beta counter and gamma chamber, K-capture and B^+ emissions were shown to be absent. The half-life was calculated by two methods: (1) employment of the equation

$$T_{½} = 0.693\ N_T\ \sigma\ ft/A,$$

where N_T is the number of target atoms (Cl^{35}), σ is the capture cross section per atom, f is neutron flux, t is time in seconds, and A is activity in disintegrations per second; and (2) from the equation

$$T_{½} = 0.693\ N/A,$$

where N is the number of Cl^{36} atoms. In case (1), the cross section was taken to be 32.3 b, after Overman (8); f was furnished by J. A. Cox (Operations) for two samples (10) and was determined by means of a Co monitor for the third; and A was determined by absolute beta counting. In the second case, the number of Cl^{36} atoms was calculated from data furnished by Dr. C. H. Townes (Columbia Radiation Laboratory) on the abundance of this isotope in one sample prepared by Mr. Beauchamp. (11) Dr. Townes determined the abundance by a microwave spectrometric technique. In both cases, the probable errors are unknown, but the approximate agreement between the two methods is encouraging.

4. *Beta Geometries (W. A. Brooksbank, T. H. Handley).* In a preliminary report (12) L. R. Zumwalt published the *observed* percentage back-scattering of RaE betas from silver as 52-53%. It was indicated by Zumwalt and by J. W. Jones (13) that the true figure should be 67-70%, corrected for absorption and

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(8) R. T. Overman, Radioactivities Produced in Neutron Irradiation of Chlorine, MDDC-857 (1947).

(9) Graham and Walke, Phys. Rev. 59, 109 (1941).

(10) J. A. Cox, bombardment data furnished by Hanford Operations.

(11) C. H. Townes, personal communication, March, 1949.

(12) L. R. Zumwalt, Absolute Beta Counting Using End-Window Geiger-Mueller Counter Tubes, MDDC-1346 (1947).

(13) J. W. Jones and L. R. Zumwalt, personal communications, March, May, 1949.

[redacted]

[redacted]

TABLE III

Energy values for Ba^{140}

β Max.	0.990 ± 0.01 Mev
	0.465 ± 0.02
γ	0.160 ± 0.01
	0.310 ± 0.01
	0.535 ± 0.01

TABLE IV

Half-life of Cl^{36}

From abundance	3.6×10^5 yr
From bombardment data	2.0×10^5 yr (average of three)

TABLE V

Comparison of counter geometries

COUNTER	ZUMWALT GEOMETRIES			NBS	
	Std. B (Percent)	G (Percent)	F (Percent)	3098	2093
1	7.8	8.2	8.0	8.2	8.2
5	7.3, 7.4	7.6, 7.5	7.5	7.5	7.4
6	8.1, 8.2	8.3	---	---	8.3
10	7.2	7.4	---	7.2	7.2

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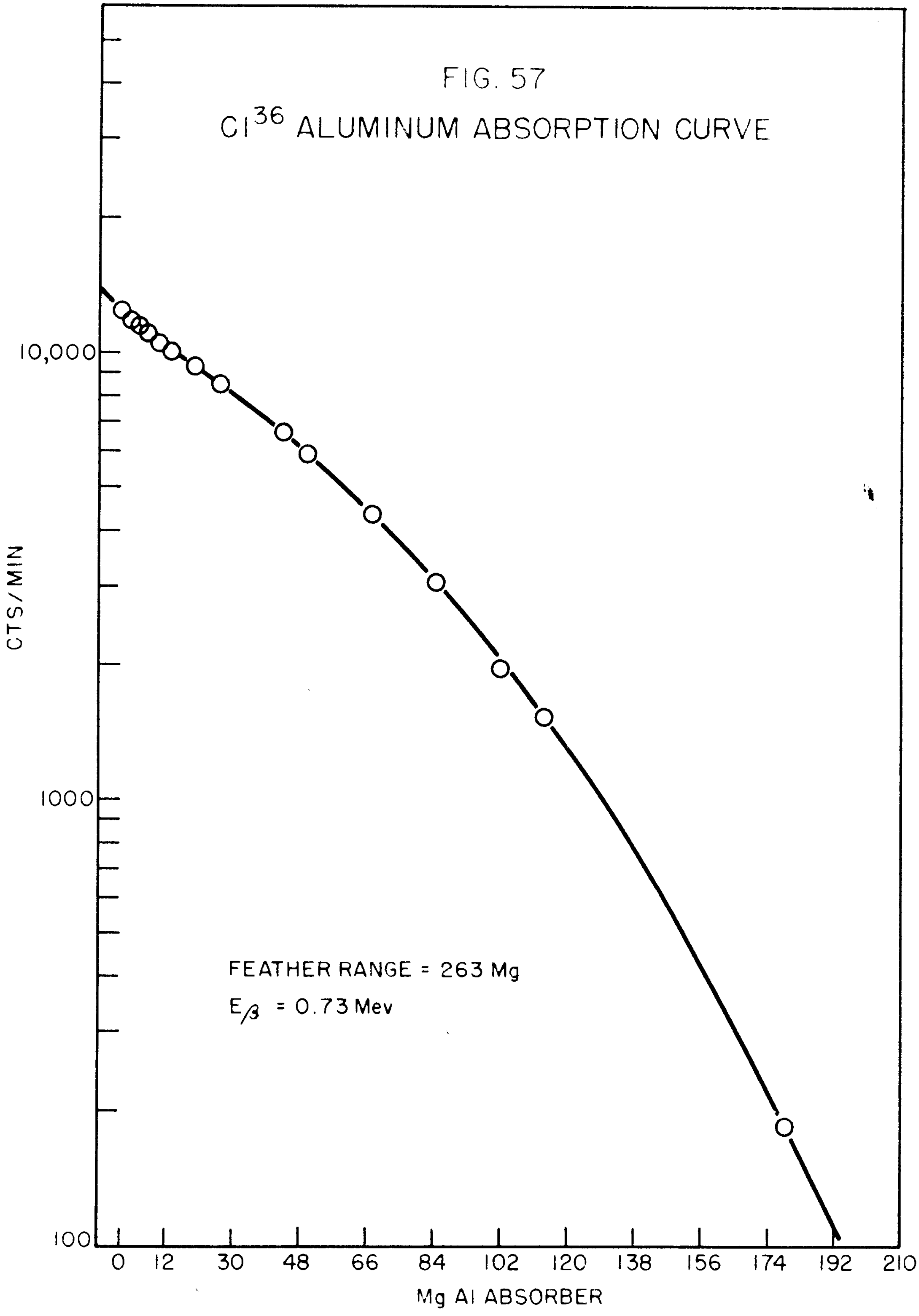
FIG. 57

Cl^{36} ALUMINUM ABSORPTION CURVE



[redacted]

scattering by air and the mica window. Applying the latter figure to data obtained using two National Bureau of Standards RaDEF standards, the geometries of four counters were determined. The geometries of these counters were also determined by use of secondary RaDEF standards prepared by Zumwalt. The results are tabulated in Table V. It will be noted that the results agree within experimental error.

In an experiment to check the back-scattering percentage given above, a RaE preparation was made, and equal aliquots were mounted on 1 mil polystyrene, 6 mil rhodium, and 4 mil platinum. Counts were made on a standard G-M counter, keeping the surfaces of all mounts in the same plane. A short absorption curve was taken on each sample, and extrapolation was made to zero absorber as usual. Comparison of the extrapolated rates shows that the percentage back-scattering from Rh is 67%, and that from Pt is 82%, in good agreement with Zumwalt's observations. Rh was chosen for the experiment because of its proximity in atomic number to Pd, which is used to coat the silver discs on which the RaDEF is mounted in the NBS standards. The following procedure was used in preparing the RaD and RaE used in the experiment:(14) Ten micrograms each of Pb and Bi were added to a $RaCl_2$ solution, which was made about 40% in ammonium citrate. The solution was made alkaline to phenol red by addition of NH_4OH, 0.3 g of KCN was added, and the RaD (Pb) and RaE (Bi) were extracted together by shaking with a 0.003% diphenylthiocarbazone ("dithizone") solution in chloroform. After washing, the Pb and Bi were stripped from the chloroform with 1:100 HNO_3. The *p*H of the aqueous solution was adjusted to about 3 (first Meta-Cresol Purple end-point), and the Bi was extracted with dithizone. After washing, the Bi was stripped with HNO_3, and, after allowing short-lived activities to decay, the RaE was used in the back-scattering experiment. Decay and absorption studies were made on the product, identifying it as pure RaE. To the aqueous phase from the Bi extraction were added NH_4OH and KCN, and Pb was extracted with dithizone. The growth of RaE and RaF activities is being followed.

5. *Gamma Counting Efficiency (W. S. Lyon).* The gamma counting efficiency of end-window counters (such as used in routine analytical work) defined as

$$\frac{\text{counting rate}}{\text{disintegration rate}} = E$$

[redacted]

(14) Snell, Colorimetric Methods of Analysis, Sandell, Colorimetric Determination of Traces of Metals, Reynolds, Routine Methods for Radioisotope Analysis (1948).

[redacted]

has been determined for Au^{198}, Cb^{95}, Zr^{95}, Co^{60}, Sc^{46}, and Na^{24}. Disintegration rates have been obtained by measurement on the 100% geometry ion chamber(15), by absolute beta counting, and, in the case of Co^{60} and Na^{24}, by coincidence counting. To obtain the gamma counting rates, the samples were mounted in the standard manner for gross gamma measurement, i.e., on one-inch watch glasses supported on scotch tape stretched across the bottom of 1-1/16 inch hole in the center of an aluminum card which was placed in the second shelf of the standard tube support. Betas were absorbed by the standard "sandwich." The observed counting rates were normalized to a radium gamma standard of the type now in use in all analytical groups. A plot of the efficiency against gamma ray energy is given in Fig. 58.

6. *Counting Standards (W. A. Brooksbank, S. A. Reynolds).* Alpha standards containing Pu^{239} are being prepared for use by analytical groups requiring use of alpha counters. These will be "Krylon" coated stainless steel discs. Standardization will be done by counting on all available proportional alpha counters in analytical groups. High-level (~1 mc) beta sources will be provided for checking beta sensitivity of alpha counters. These will contain Sr^{90} with its Y^{90} daughter. The sources will be used in daily checks of alpha counters to indicate beginning of beta-sensitivity, with resultant inaccurate counting of certain alpha samples.

At the suggestion of P. R. Bell (Physics), R. Luman (Instruments), and others, additional uranium (metal) normalizing standards (for beta counting) are being prepared. Standards of Co^{60} are also in preparation. Some of the standards will be calibrated as secondary geometry standards by counting on counters whose geometries have been determined by RaD and by coincidence counting. The standards will be made available to any project group desiring them. Requests have already been received from the ORNL Health Physics Division, and NEPA.

7. *Activation Cross Sections (G. W. Leddicotte, S. A. Reynolds).* To monitor neutron exposures, the Co-Mn-Al alloy prepared for R. T. Overman is used. The alloy contains 0.53% Co and 0.21% Mn.(16) The cross sections are taken to be 33 b and 13.5 b, respectively.(17)

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

(16) R. T. Overman et al., Descriptive Manual of Radioisotopes Produced by Neutron Bombardment in the Clinton Pile, ORNL 4 (1948).

(17) J. W. Jones, et al., Activation Measurement of the C-Neutron Flux in the Clinton Reactor, MonC 398 (1948).

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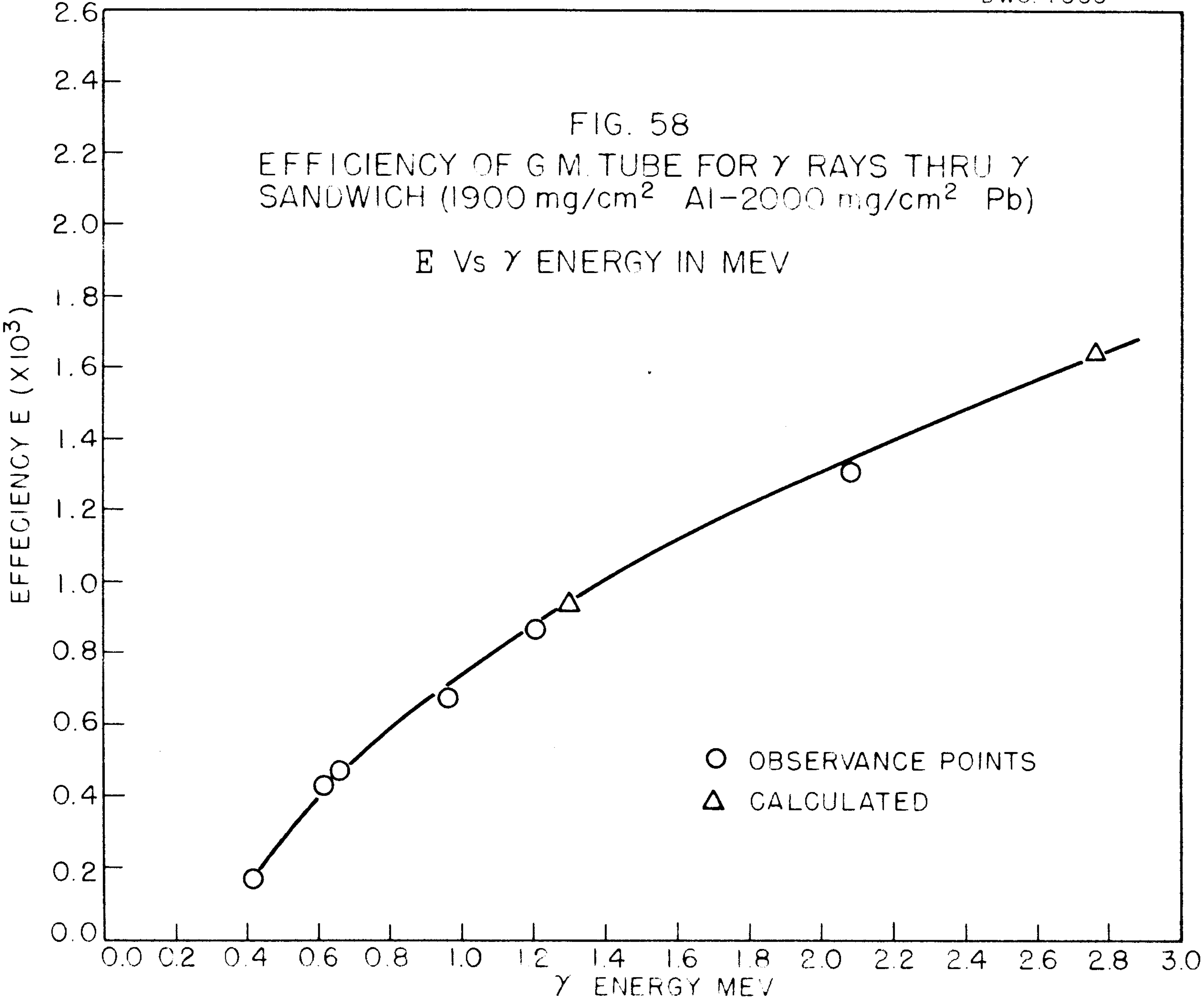

FIG. 58

EFFICIENCY OF G.M. TUBE FOR γ RAYS THRU γ SANDWICH (1900 mg/cm^2 Al–2000 mg/cm^2 Pb)

E Vs γ ENERGY IN MEV

[redacted]

By bombarding enriched Ge^{70}, the 11 d Ge^{71} K-capture activity was produced, as well as the 40 hr positron-emitting isomer. A conventional beta counter was calibrated for counting X rays in the Ga region by means of a Zn^{65} sample, whose disintegration rate was determined by measuring its gamma activity on the ion chamber. The decay scheme assumed was that of Good and Peacock (18), showing 98.7% K-capture, with 1.14 Mev gamma accompanying 46% of the K-capture processes. The overall efficiency for second-shelf counting (about 8% geometry) was found to be 0.14%. The "observed" counting rate on the Zn standard as well as the Ge was obtained by extrapolation of a Be absorption curve (after subtracting the gamma in the case of Zn). The cross section of Ge^{70} for production of 11 d Ge^{71}, was found to be ~2.3 barns. It is believed that this result is accurate within 40%. H. S. Pomerance has reported a value of 3.3 b, using the pile oscillator. (19) The Ge X-ray activity was found to decay with a half-life of 11.6 d, in good agreement with earlier results. (20) Decay of the induced gamma activity of the Ge^{70} sample was followed on the gamma ion chamber. No 40 hr period was noted. If the total gamma activity, most of which decayed with a 14 hr period, was assumed to be Ge^{71}, the cross section for production of this isomer would be ~0.02 b. If the half-life of the Ge^{70} isomer is 40 hr, the cross section for its production is surely less than 2 mb.

The cross section of Zr^{94} for production of the familiar 65 d Zr^{95} activity was determined by bombarding samples of enriched $Zr^{94}O_2$ in "rabbits" in the pneumatic tube. Cobalt monitors were used. Activities were determined by means of the ion chamber, and corrections for Cb growth were made. Cadmium ratios were taken on the monitors as well as the samples so that thermal-neutron cross sections could be calculated. The thermal-neutron activation in each case was taken to be the difference between the activity observed in the sample bombarded without shielding and the activity found when the sample was inclosed in a cadmium cup during bombardment. The cross section for pile neutrons was found to be 0.074 ± 0.01 b, and the thermal cross section was found to be 0.060 ± 0.01 b.

The cross section of Zr^{96} for production of 17 hr Zr^{97} is being investigated. Apparently resonance capture is important in this case, for very low

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(18) [illegible]. M. Good and W. C. Peacock, Phys. Rev. 69, 680 (1946).

(19) H. S. Pomerance, personal communication, May 16, 1949.

(20) G. T. Seaborg and I. Perlman, Table of Isotopes, Rev. Mod. Phys. 20, 598 (1948).

[redacted]

[redacted]

cadmium ratios have been obtained in pneumatic tube bombardments.

8. *Radioisotope Target Materials (G. W. Leddicotte, S. A. Reynolds).* Determination of product yields for various radioisotope target materials and identification and quantitative analysis for impurities have continued. The materials were especially prepared by Mallinckrodt Chemical Co., and were submitted for study by J. A. Cox of the Operations Department. Complete details will be given in a report to be published in the next quarter. The activities found in the various materials after bombardment are given in Table VI.

9. *Radiozirconium Procedures.*

a. TTA Separation with Colorimetric Determination of Carrier Yield (R. H. Powell). (1) Colorimetric Method. To a 125 ml separatory funnel add 1 mg Zr carrier and an appropriate aliquot from the radiozirconium solution. Add 1 mg conc. HCl and shake to mix. (If original sample contains oxalic acid, it may be destroyed by treatment at this point with 1 ml of 5% $KMnO_4$, followed by destruction of the excess $KMnO_4$ by hydroxylamine hydrochloride.) Add 5 ml of 0.5 *M* TTA in xylene. Shake for ten minutes. Add 45 ml of xylene and mix by shaking. Withdraw and discard aqueous phase. Wash organic phase twice with 10-15 ml 6 *M* HCl. Draw organic phase into a fresh separatory funnel containing 1 ml of 0.221% NaF and 10 ml of 9 *M* HCl. Shake ten minutes. Withdraw the aqueous strip. Evaporate suitable aliquots for counting, and determine the yield of carrier by the following colorimetric method.

Ten ml volumetric flasks are used to contain colorimetric samples and blank. Into each flask, pipette solution containing 20 micrograms of Zr as "spike." To blank add 0.05 ml of 0.221% NaF. To flasks for samples add 0.5 ml of aqueous strip (above). To blank add 0.5 ml 8.2 *M* HCl. To blank and samples add 0.5 ml 0.75 *M* NaOH. Fill each flask to mark with color-forming reagent (see notes). Mix contents of flasks and let stand for $1\frac{1}{4}$ hours. Read transmittance of samples against blank on a spectrophotometer at 5300 Å. Determine amount of Zr in unknowns by comparison with a standard curve.

Notes Color-forming reagent: (a) sodium alizarin sulfonate, 1.25 mg/ml in 95% ethanol, (b) 8.75 g H_3BO_3 in 300 ml of isopropyl alcohol containing 0.5 ml conc. HCl. For working reagent mix one part of (a) and nine parts of (b). This reagent has been found to be stable for at least 24 days. The separatory funnels are kept closed during shaking, rather than using air bubbling for mixing, because it has been found that HF is lost during air agitation. The

[redacted]

[redacted]

TABLE VI

Activities induced in target materials

MATERIAL	INDUCED ACTIVITIES
$CaCO_3$	Ca^{45}, 180 d β; P^{32}, 14 d β; Sr^{89}, 55 d β
$AgNO_3$	Ag^{110}, 225 d β, γ (K ?)
Fe_2O_3	Fe^{59}, 47 d β, γ; Fe^{55}, ~4 yr K; P^{32}; S^{35}, 87 d β
As_2O_3	As^{76}, 26.8 hr β, Sb^{124}, ~60 d β, γ
$Cd(NO_3)_2$	Cs^{115}, 2.3 d β, ; Cd^{115m}, 43 d β, γ; Cd^{117}, ~3 hr β; In*
TiO_2	Ti^{51}, 72 d β, γ; P^{32}, Fe*, S^{35}
Na_2CO_3	Na^{24}, 14.8 hr β, γ; S^{35}; Ca^{45}; Sr^{89}; Cs^{134}, ~2 yr β, γ

TABLE VII

Yields of Zr carrier and tracer

RUN	PERCENT CARRIER RECOVERED	PERCENT TRACER RECOVERED
1	88.9	91.2
2	56.1	60.7
3	27.9	26.5

TABLE VIII

Comparison of fluozirconate and colorimetric methods

RUN	FLUOZIRCONATE	COLORIMETRIC
1	4.71×10^{-2} mc/ml	4.76×10^{-2} mc/ml
2	4.90×10^{-2}	5.17×10^{-2}

[redacted]

[redacted]

fluoride concentration is critical in stripping and in the colorimetric analysis. The percentage stripped has been found to be a function of the HCl concentration, the best strip occurring with highest acidity. Use of high acidity necessitates partial neutralization with NaOH, because of the *p*H-dependence of the color-formation step. The original aliquot taken for analysis must have at least ten times the activity that is desirable for counting, because of the dilution involved. A Coleman spectrophotometer, Model 14, has been used for transmittance determinations. A Burrell Wrist Action Shaker has been used for mixing.

(2) **Evidence for Interchange.** Occurrence of interchange between tracer and carrier has been shown where oxalic acid was present (the case in many radioisotope preparations), but uncomplexed solutions have not been tested. The data are given in Table VII.

(3) **Comparison with Fluozirconate Method.** Two comparisons have been made between the colorimetric method and the "standard" fluozirconate method.(21) Absolute beta counting was done on aliquot from the aqueous strip in the colorimetric run. In the fluozirconate analysis gamma counts were made, and these were corrected to beta disintegrations by a suitable "factor" for gamma efficiency. The results are summarized in Table VIII. The samples were "Zr-Cb mix" materials. The colorimetric method has not yet been tested on general fission-product mixtures. The time required for four analyses, exclusive of time for color-development, is slightly over one hour. Thus in actual working time the colorimetric method is somewhat shorter than the fluozirconate method.

b. Simple TTA Separation without Carrier (F. L. Moore). Little development of this procedure has been done during the past quarter. The General Radiochemical Analysis Group made a number of runs using the method as given in the previous quarterly report.(6) Results are good in phosphate-free solutions. On a typical sample 14 TTA analyses were performed averaging 2.54 × 10^8 cts/min/ml with an average deviation of 0.06 × 10^8 (2.4%); and 6 fluozirconate analyses, averaging 2.00 × 10^8, with an average deviation of 0.08 × 10^8 (4%). The latter is a typical deviation. The TTA analysis is higher than the fluozirconate because of self-absorption of the beta particles in the latter. Thus it is evident that in certain types of materials the TTA analysis

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(21) D. N. Hume et al., A Manual of the Radiochemical Determination of Fission Product Activities, CN-2815 (1945).

[redacted]

[redacted]

for radiozirconium is at least as reproducible as the "standard" method, and gives more nearly absolute results.

10. Plutonium Analysis (F. L. Moore). The TTA analysis for total Pu[22], involving depolymerization with nitric acid, has given reasonably satisfactory results on Redox, 23, and 25 process solutions. The 1AW samples in Redox have been troublesome because of low Pu activity, presence of Am and Cm, high beta-gamma activity, and considerable amounts of aluminum and chromium. A suggestion of K. A. Kraus that fluoride should be used to destroy the Pu(IV) polymer was investigated and found to be satisfactory. Two methods were used: (1) usual precipitation of LaF_3 carrying Pu, followed by dissolving the precipitate in H_3BO_3-HNO_3 mixture and extracting with TTA-xylene, and (2) treatment with HF, followed by complexing of the fluoride with boric acid, and TTA extraction. The first method was used only briefly because of the obvious advantages of the second. The first method gave 95-100% Pu yields on synthetic polymer solutions containing 15% and 46% polymeric Pu(IV). The second method gave 90-100% extraction with two half-volume TTA-xylene passes after ten-minute treatment with HF in concentrations from 0.33 M to 2 M with solutions initially containing 46-65% polymer. Most extractions were over 95% effective. Members of C. L. Burros' group ran a number of 1AW samples (Redox process) by the usual HNO_3-depolymerization method and by method (2) above. Typical results are given in Table IX. It is evident that good agreement was secured in most analyses.

11. Americium and Curium Analyses.

a. TTA Extraction (F. L. Moore). On all analyses of 1AW samples from the Redox process results for total "Pu" by LaF_3 precipitation were observed to be higher than by TTA extraction, even though repeated depolymerization treatments were made. It was believed that appreciable quantities of Am^{241} were present. This would carry on LaF_3 but would not extract with TTA from 1 M HNO_3 solution, as will Pu(IV). It is known that Am and Cm will extract with TTA at a *p*H of about 4. A determination of percent extraction of Am as a function of *p*H was made (Table X), using equal volumes of aqueous and 0.5 M TTA-xylene. A ten-minute mixing period was used. In the determination of Am by TTA extraction on 1AW solution a complexing agent should be used to prevent precipitation of $Al(OH)_3$ at the *p*H used. Tartaric acid (2.6%) was tried, but at *p*H 4.48 only 14-15% of the Am was extracted. A *p*H 5 buffer containing ammonium acetate and nitric acid was next used. In the absence of Al

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[22] F. L. Moore and J. E. Hudgens, ORNL 153 (1948).

[redacted]

[redacted]

TABLE IX

Comparison of Pu methods (TTA)

SAMPLE	USUAL TTA	METHOD (2)
I-AW-A	2.97×10^4 c/m/ml 3.09×10^4	2.67×10^4 c/m/ml 2.72×10^4
I-AW-B	8.6×10^3 7.8×10^3	9.1×10^3 7.0×10^3
III-AW-A	2.9×10^4	2.3×10^4
III-AW-B	6.2×10^3 5.5×10^3	9.5×10^3 8.4×10^3
52R-1AW	5.8×10^3 6.2×10^3 6.7×10^3	6.1×10^3 6.0×10^3 5.7×10^3
54R-1AW-200-2	3.00×10^4	3.01×10^4
54R-1AW-400-1	2.92×10^4	2.87×10^4
54R-1AW-500-2	3.44×10^4	3.33×10^4

TABLE X

Extraction of Am as a function of pH

pH	PERCENT EXTRACTION	pH	PERCENT EXTRACTION
0.23	0.0	3.90	92.3
1.03	0.0	4.33	95.3
1.22	0.0	4.60	98.5
2.02	0.3	5.32	98.0
3.10	43.1	5.88	98.2
3.62	85.0		

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over 90% of Am tracer was extracted, but when Al was present precipitation took place immediately after extraction was begun.

The alpha pulse analyzer is a valuable tool for determination of alpha energy, which serves for characterization. The beta tolerance is so low, however, that such determination cannot be made on alpha from 1AW solutions directly. Therefore, the alpha emitters must be decontaminated from beta activity in a preliminary step. After exhaustive extraction of Pu from a 1AW sample at low *p*H, the *p*H was adjusted to 3.45 and the material was extracted with a half-volume of TTA. The organic phase was diluted with an equal volume of xylene and stripped with 1/7 volume of 8 *M* HNO_3. The above procedure serves to decontaminate from most fission products, but of course does not give quantitative yield of Am or Cm. The extracted material was identified as 60-65% Cm^{242} and ~35% Am^{241} by pulse analysis by E. Fairstein. This is in agreement with a prediction made by K. A. Kraus. Thus it has been demonstrated that considerable Am and Cm activity is present in 1AW samples, and the Pu(IV) polymer is not the source of difficulties in analysis. This was also shown by comparison of two depolymerization procedures (see above).

b. Precipitation (S. A. Reynolds). The method given below has been found useful in analysis for Am or Cm in the presence of Pu when little or no materials are present which interfere in the usual LaF_3 analysis for Pu (e.g. Al).

Procedure Pipette a suitable sample into a 3 ml cone. Add 0.25 mg La carrier and three drops of conc. HNO_3. Add 0.4 ml of 1 *M* $Na_2Cr_2O_7$, dilute to 2 ml, and mix well by stirring with a platinum wire (usual Pu technique throughout). Heat to 90-95° C, and maintain at that temperature for fifteen minutes. Cool to room temperature, and add three drops of conc. HF which has been treated with $Na_2Cr_2O_7$ until an orange color persists. Digest five minutes. Centrifuge five minutes. Remove supernatant, and wash twice with 0.5 *M* HF-0.5 *M* HNO_3, as in Pu analysis. Slurry and transfer as usual to a stainless steel or platinum disc. Evaporate to dryness, flame gently, and count alphas in a proportional alpha counter.

Notes A single oxidation step as above gives a decontamination factor from normal Pu of about 300. If Pu(IV) polymer is present, HNO_3 treatment may be necessary to destroy the polymeric material. Yields of Am in the absence of interferences are 97-100%.

12. Analysis for Rare Gas Activities (W. A. Brooksbank). A literature search for methods of analyzing rare gases has been completed. It has been

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decided that adequate separation of Kr and Xe activities can be obtained by adsorption on an desorption from charcoal under controlled conditions.

SPECTROCHEMICAL ANALYSES - RESEARCH AND DEVELOPMENT

Analytical Development

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

1. *Aqueous Solutions.* Procedures were worked out for spectrochemical analysis of the following samples by the porous cup method with the accuracy and precision estimated as ± 2-3%.

   (a) 5-100 ppm Al in a 25% Th solution. (0.005-0.100% Al referred to Th.)

   (b) 0.5-15 ppm B in plant tissue (referred to wet weight).

   (c) 0.1-20 ppm Ca in distilled water.

   (d) 0.01-0.1% Pb, 0.05-0.4% Sn, 0.005-0.100% Cu, and 0.002-0.030% Mn in Bi metal (run as 10% solution in HNO_3).

   (e) 1-20 ppm Al in 1.8% Th solution.

2. *Non-aqueous Solutions.* (a) Al/Th ratios: A technique was developed for analyzing 2% solutions of Th in diglycol dichloride and tributyl phosphate by the porous cup technique without any chemical treatment. Hexane-tributyl phosphate mixtures could be safely run by the porous cup method only after elimination of the hexane, or addition of tributyl phosphate to the mixture. By using aqueous standard solutions, a curve was constructed for an Al/Th range of 6×10^{-5} to 9×10^{-4} by weight in the organic substance.

3. *Analysis of Uranium Compounds for Impurities.* (a) An attempt was made to regulate distillation of the AgCl in the carrier distillation method for the spectrochemical analysis of U_3O_8 by surrounding the electrode containing the sample with a heated jacket. The carrier was volatilized, but the necessary sensitivity for detection of traces was not achieved.

   (b) Preliminary work was performed on the application of 1:4 tributyl phosphate-hexane mixtures to the trace analysis of uranium. Extraction of the uranium from the impurities leaves an aqueous solution which may be analyzed in any conventional way. Since this reagent also extracts thorium,

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the technique presumably can also be applied to analysis of thorium compounds. With regard to the application of spectrographic techniques, this extraction method, combined with the porous cup technique, offers the following advantages over the carrier distillation method currently used for the spectrographic analysis of U_3O_8.

(1) It permits an accuracy and precision of 2-3% in values obtained for trace concentrations, compared to the ± 30-50% usually obtained by the carrier distillation technique.

(2) All trace elements soluble in 5 *N* HNO_3 and not extracted by the reagent (see below) can be analyzed for; this introduces the possibility of analyzing for Al, rare earths, and other elements which are difficult or impossible to volatilize by the carrier distillation technique.

(3) Any uranium or thorium compound soluble in 5 *N* HNO_3 can be handled by this technique. This for instance, includes $UO_2(NH_4)PO_4$, UF_6 and UF_4, which cannot be handled by the carrier distillation method without chemical treatment. Such treatment introduces the danger of loss of the impurities being determined.

(4) If the aqueous layer is concentrated by evaporation after extraction of the U or Th, there is no theoretical limit to the sensitivity relative to U (or Th) which can be achieved. In the carrier distillation method, on the other hand, relative sensitivity is limited by sample size.

(5) No uranium is consumed by the analysis; uranium can be returned to the laboratory submitting it, in a highly purified condition.

(6) In the case of U^{235} and U^{233} preparations, the separation removes the uranium from the vicinity, thus eliminating the danger of contaminating the operator during the spectrographic exposure. The exposure is made using the impurities only.

A study was made to determine the extent to which common metals in the quantities likely to be present in U or Th samples were extracted into the organic layer. A solution was prepared containing the indicated quantities of metals in 5 ml of 5 *N* HNO_3. Two ml of this solution was shaken for one minute with 10 ml of a 1:4 tributyl phosphate-hexane mixture. The aqueous layer was drawn off and discarded, and the organic layer heated until the hexane was eliminated. Its volume was made up to 2 ml with pure tributyl phosphate, and this was analyzed directly by the porous cup method. Results are given in Table XI.

None of these elements was detected in the organic layer. The only exception to this was the appearance of vary faint lines of Ca. Since very

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TABLE XI

Extent of extraction of impurities into tributyl phosphate-hexane

TRACE ELEMENT	CONCN. OF TRACE EL. IN AQ. LAYER (ppm)	μg OF TRACE EL. IN AQ. LAYER	APPROX. DETECTION LIMIT BY PCE (ppm)	UPPER LIMIT FOR DISTR. COEFF. (org. mixt./aq.)
Al	20	100	1	2×10^{-3}
B	20	100	0.5	1×10^{-3}
Ca*	10	50	0.1	0.4×10^{-3}
Cd	200	1000	100	2×10^{-2}
Co	20	100	2	4×10^{-3}
Cr (as $CrO_4^{=}$)	50	250	2	1.6×10^{-3}
Fe	20	100	2.5	5×10^{-3}
Mn (as Mn^{++})	50	250	2	1.6×10^{-3}
Mo	100	500	3	1.2×10^{-3}
Ni	200	1000	10	2×10^{-3}
Pb	200	1000	10	2×10^{-3}
Y	20	100	0.2	0.4×10^{-3}
Zn	500	2500	25	2×10^{-3}

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faint Mg lines also appear and no Mg was added to the aqueous solution, it appears that the presence of Ca lines was due to contamination of the electrodes, rather than extraction of Ca by the tributyl phosphate.

Maximum values were calculated for distribution coefficients of the impurity metals between the tributyl phosphate-hexane mixture and the aqueous phase. The upper limits of metallic trace concentrations in the evaporated mixture were taken to be those characterizing the porous cup electrode technique in general (AECD-2392).

In addition to these elements, Zr, Cb, and Ru have been shown by the Technical Division to have extraction coefficients of less than 1×10^{-3}.

4. *Qualitative Analysis of Inhomogeneous Metallic Surfaces with a Micro Spark.* Work is $\sim$75% complete on an arrangement which will permit the qualitative spectrographic analysis of metallic inclusions, 0.2 mm in diameter. A tiny high-voltage D.C. spark between an Al wire and the specimen is photographed with a medium quartz spectrograph. Correlated motion of specimen and photographic plate, combined with photographing of the specimen before and after exposure, permits identification of individual grains.

This arrangement is modeled after a similar arrangement in use at the Ford Company laboratories in Detroit.

ANALYTICAL SERVICE

In general, the demands for analytical service made by the Laboratory during the past four months have not changed radically. There has been a decrease in the requirements of the Pilot Plant resulting from completion of the work of Redox by the Technical Division. However, because of the higher levels of radioactivity now being handled, the analytical personnel requirements have not changed. During the next period the Pilot Plant will be occupied with the 25 recovery process. The analytical requirements for this process are very similar to those of the Redox process and little change is necessary except for the greater care necessary in handling the enriched 25 samples.

A greater number of samples was submitted by the Laboratory and Semiworks Sections of the Technical Division and also by the Radioisotope Development Section of the Operations Division. In addition, a trend toward more stringent requirements on the part of radioisotope customers has placed an added load on the Radioisotope Production Control Group.

A summary of service analytical work is given in Table XII.

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TABLE XII

Summary of service analytical work for period

March 1—June 30, 1949, Number of Analyses Reported

	RADIOCHEM. DEV.	IONIC DEV.	SPECTRO-CHEM. GROUP	GENERAL RADIOCHEM. GROUP	GENERAL IONIC GROUP	WATER ANALYSES	LAB. AND SEMI-WORKS CONTROL	PILOT PLANT	PRODUCTION CONTROL	TOTALS
PERSONNEL										
Tech.	8	4	4	4	4	1	2	5	8	40
Non-Tech.	4	2	-	6	1	4	10	21	18	66
Biology	Less than 1% of time devoted to analyses									
Physics			46		3*	11				60
Chemistry		23	137	4	40	24			785	1013
Technical		226	88	4920	25	1408	10,698	11,295	2757	31417
Metallurgy			66		32		119			217
Operating Div.			73	65		84			10840	11062
Health-Phys.			1	164			24			189
K-25		48	7	470						525
Misc.			42							42
		297	460	5623	100	1527	10,841	11,295	14382	44525

*Time of 1-1/3 people devoted to preparation of compounds for Physics Division.