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CHEMISTRY DIVISION

QUARTERLY REPORT

FOR THE MONTHS DECEMBER, 1948, JANUARY AND FEBRUARY, 1949

J.A. SWARTOUT, Acting Director

[redacted]

OAK RIDGE NATIONAL LAB

OPERATED BY
CARBIDE AND CARBON CHEMICALS CORPO
FOR THE
ATOMIC ENERGY COMMISSION
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CHEMISTRY DIVISION

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Date Issued:

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Carbide and Carbon Chemicals Corporation
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ABSTRACT OF QUARTERLY REPORT
CHEMISTRY DIVISION

During the past Quarter steps were initiated to strengthen certain phases of the research program of the Division. Likewise, research groups which were weakened by personnel losses during the past year are being, or will be, bolstered by a number of additions to the staff. Research in the field of radiation chemistry was resumed by a group reconstituted under Dr. E. H. Taylor. Plans for strengthening fundamental and applied research in separations processes were formulated and adopted.

The results of principal interest during the period, December, 1948 through February, 1949, are summarized below.

Nuclear and Chemical Properties of the Heavy Elements - The measurement of equilibrium constants for the formation of thorium complexes in aqueous solutions was continued with studies of iodate and fluoride complexes in nitrate media. Evidence was found against the existence of complexes containing both iodate and nitrate, but for complexes containing fluoride and nitrate.

Additional data have been obtained on the solution chemistry of U(V). The second order rate constant for the disproportionation of UO_2^+ was found to be strongly dependent on acidity and on ionic strength of the solution. The disproportionation is catalytically accelerated, and the mechanism for the reaction is altered, by the presence of polymeric particles of U(IV). Oxidation-reduction potentials of the U(V) - U(VI) couple in chloride solutions have been measured and found to be practically invariant with chloride concentration. In connection with this research, a precision method for measuring pH with glass electrodes utilizing a vibrating reed electrometer was developed.

An anion exchange procedure for separating protactinium from other metal ions in chloride systems appears very promising. Separations from thorium, zirconium and columbium have been thus achieved.

Phase studies of the system, uranyl sulfate-water, have been completed from the trihydrate-ice entectic to 374° C with the exception of the essential determinations of vapor compositions and vapor pressures.

Nuclear and Chemical Properties of Elements in the Fission Product Region - The preparation of Xe^{135} on a "large" scale for neutron transmission measurements was continued throughout this quarter. With the possible exception of a few more preparations to improve the accuracy of measurements which may appear in question as the result of current computations, the chemical phase of the work has been essentially completed.

In the course of developing an assay method for Xe^{135}, evidence has been found for an 11 d isomer of Xe^{131} formed in about 0.8% of the decay of 8 d I^{131}.

A long-lived palladium activity has been isolated from fission. The maximum half-life of this activity, which is believed to be Pd^{107}, is estimated to be about 7×10^6 yr.

The results of research using calutron enriched isotopes of zirconium, molybdenum and tin for clarification of the radiation characteristics and identities of the radio nuclides of these elements and of technetium are included but are too extensive to summarize effectively.

Studies to identify the γ -activities of uranium fission of sufficient energy to eject photo-neutrons from deuterium have continued with examination of the iodine fraction from pile-bombarded uranium. Evidence was found for a hard gamma associated with the decay of 54 min. I^{134}. Yield measurements for the gamma ray and absorption studies of the beta radiations of this isotope have been made.

General Nuclear Chemistry - As mentioned in the preceding Quarterly Report, gram quantities of very pure rare earths are now available with the exception of Eu and Gd. Initial steps have been taken in the separation of Eu by ion-exchange from a concentrate of Sm-Eu.

Nuclear chemical studies of the rare earths have continued with further investigation of 129 d Tm^{170}, 7 d Tb^{161}, 225 d Gd^{153} and a probable new nuclide of Dy.

Radio-Organic Chemistry - Preparations of organic intermediates containing C^{14} included: (1) acetylene in 15% yield from barium carbonate and magnesium at 700° C, (2) 91 mc. of high specific activity methanol by the lithium aluminum hydride reduction of CO_2, (3) 7.9 mc. of formaldehyde by the pyrolysis of methyltriphenylmethyl ether, (4) ethyl formate in 96% yield from formic acid, (5) 18 mc. of acetic acid by carbonation of methyl magnesium bromide, (6) malonic ester by the vapor phase decarbonylation of diethyl oxalacetate, and (7) styrene by the dehydration of methylphenylcarbinol produced from acetic acid. The styrene has been polymerized in rod form for transference to Dr. W. G. Brown at Chicago where it will be used for C^{14} counting standards. A preliminary synthesis of "ring-labeled" benzoic acid with inactive materials was successful.

Applied Nuclear Chemistry - The separation of hafnium from zirconium is being investigated making use of the differential extraction of zirconium and hafnium from aqueous solutions into an organic phase such as benzene, containing thenoyl trifluoroacetone (TTA). The distribution ratio (organic over aqueous) has been studied for nitric acid systems and found to have a third power dependence on the hydrogen ion concentration and nearly a fourth power dependence on the TTA concentration.

A procedure has been developed for the complete electrodeposition of ruthenium, as the metal, from solutions of radio-ruthenium. Concentrated sources of Ru^{106}, in the form of needles or plates, are desired for medical therapy. The separation of traces of manganese from large amounts of iron appears possible by preferential electrodeposition of the manganese as MnO_2 from solutions containing sodium nitrilotriacetate.

Laboratory scale investigation of an adsorption process for isolating fission zirconium and columbium from Redox process wastes has continued with emphasis on procurement of the data necessary for design of equipment for operation on a full activity scale in the hot-laboratory. The substitution of nitric acid or ammonium hydroxide solution for the water wash following the adsorption of Zr-Cb on the silica gel adsorbent materially reduced losses. The radiochemical purity of the Zr-Cb after their removal from the adsorbent has been found to be high, based on laboratory experiments.

Physical Chemistry and Chemical Physics - The examination of the spectra of rare earths in solution at the boiling point of nitrogen was extended to europium bromide hexahydrate and thulium bromide hexahydrate.

Molecular beam techniques are being perfected for the study of the kinetics of chemical reactions, starting with the reaction of potassium with bromine as a test of this procedure. By this method direct measurement of the cross-sections of the molecules for scattering and for reaction should be possible.

Design and construction of a calorimeter capable of measuring a heat input of 10^{-7} cal/sec to within 1% are underway, with the ultimate objective of extending the measurements of total energies of beta and gamma disintegrations to less energetic systems and to, possibly, the measurement of the energy of the gamma emitted during the neutron capture process.

Physical Measurements and Instrumentation - A method for determining absolute disintegration rates of X-ray emitters has been developed based upon the measurement of the counting rates of a given sample in the chamber of a beta proportional counter at two pressures of the argon-butane mixture which differ by a factor of two.

The crystal structure of potassium perruthenate has been determined on the basis of copper radiation Debye-Scherrer patterns and rotation and Weissenberg photographs with molybdenum radiations.

Analytical Chemistry - A polarographic method has been developed for analysis of lead in highly radioactive solutions from the radio-barium production process. Adoption of this method will eliminate many of the hazards attendant the current use of the dithizone extraction. A thiourea

colorimetric method for determining palladium was devised in connection with the xenon cross-section experiment.

The decay scheme of Be^{140} has been investigated, with evidence for a new gamma ray. Standards for routine beta and gamma counting were prepared for Laboratory use and, in connection with the radioisotope production program, gamma efficiencies of standard G-M counters were measured using gamma emitters of known decay scheme.

[redacted]

I. Nuclear and Chemical Properties of Heavy Elements

Thorium Complexes in Aqueous Solution
(R. A. Day and R. W. Stoughton)

Using the TTA-benzene solvent extraction method, identical curves of distribution ratios vs. iodate concentration in the aqueous phase were obtained with nitrate and perchlorate media at an ionic strength and a hydrogen ion molarity of 0.5, after correction was made for the known thorium-nitrate complex. The total iodate concentration in this work varied from 2.49×10^{-4} to 2.36×10^{-2} M. The identity of these curves is evidence against the existence of any complexes containing both iodate and nitrate, which would of course change the distribution ratio in favor of the aqueous phase compared to that observed with perchlorate medium.

In a similar study of the thorium-fluoride complexes, the distribution ratios (aqueous/organic) were higher with nitrate medium than with perchlorate medium, after correcting for the nitrate complex, $ThNO_3^{+3}$. Interpreting the difference as due to complexes containing both fluoride and nitrate and assuming only one nitrate on each thorium-fluoride-nitrate complex, the values of the following constants were deduced for a hydrogen ion molarity and an ionic strength of 0.5:

Reaction	k
$Th^{+4} + HF = ThF^{+3} + H^+$	4.3×10^4
$Th^{+4} + 2HF = ThF_2^{+2} + 2H^+$	3.1×10^7
$Th^{+4} + NO_3^- + HF = ThNO_3F^{+2} + H^+$	2.0×10^4
$Th^{+4} + NO_3^- + 2HF = ThNO_3F_2^{+} + 2H^+$	0.8×10^7

The first two constants were obtained from the results in perchlorate medium, and they agree very well with Dodgen's values of 4.5×10^4 and 2.9×10^7 respectively, obtained by another method. The last two constants were obtained from the results in nitrate medium using the values of the first two constants already obtained.

This and previous work on thorium complexes will be issued soon as a progress report.

[redacted]

[redacted]

Chemistry of Uranium (V)

F. Nelson and K. A. Kraus

During the last quarter investigation of the chemistry of uranium (V) was continued, attention being focused on the potential of the uranium couples and on the kinetics of the U(IV)-(V)-(VI) systems.

Most of this work has not yet been completed and only a few fragmentary results will be reported at this time.

a) Potential of U(V)/(VI) Couple

Some of the oxidation-reduction potentials of the U(V)/(VI) couple which have been observed in chloride solutions are summarized in Table 1. Although the results are to be considered of a preliminary nature only, the practical invariance of this potential with chloride concentration is considered noteworthy. The average of the potentials previously determined for 0.1 M Cl^- solutions has been included for comparison.

Table 1

Potential of U(V)/(VI) Couples in Chloride Solutions.

$[U] \times 10^3$	$[H_3O^+] \times 10^3$	Method of Preparation	μ	$E_{obs.}$	$\log \frac{[U(VI)]}{[U(V)]}$	E_{56}
(a)			0.1			-0.062
2.19	1.07	electrolysis	0.5	0.1914	0.053	-0.057
2.12	1.34	"	"	0.1903	0.088	-0.056
1.04	1.08	"	"	0.1997	-0.088	-0.057
1.50	13.3	sol'n of UCl_5	"	0.1552	0.715	-0.054
2.50	12.8	"	"	0.1555	0.680	-0.055
0.743	2.7	"	"	0.2100	-0.257	-0.055
2.27	1.88	electrolysis	1.0	0.1602	0.331	-0.054
1.13	1.13	"	"	0.1895	-0.158	-0.054

(a) From ORNL-188 and ORNL-189

b) Disproportionation of UO_2^+

The second order rate constant for the disproportionation of UO_2^+ (K_1) was found to be strongly dependent on acidity and on ionic strength as shown by the data summarized in Table 2 and Fig. 1.

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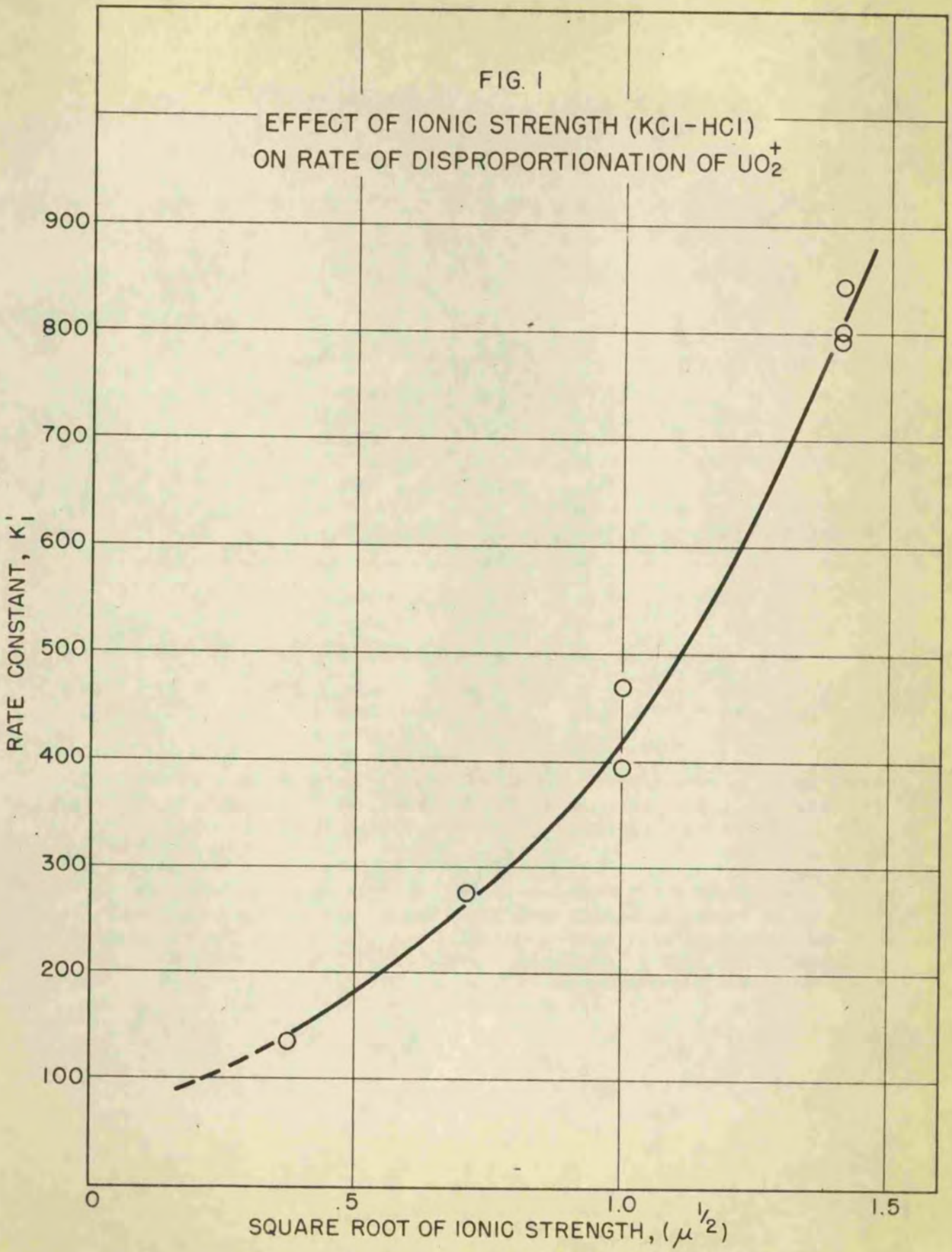

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Table 2

Disproportionation of UO_2^+ in Chloride Solutions at 25 ± 1°C

μ (KCl-HCl)	M HCl (final)	γ_{H^+} (a)	K_1	$K_1' = \frac{K_1}{a_h}$
0.14	0.0390	0.775	4.09	135
0.50	0.00560	0.763	1.173	275
"	0.0225	"	4.75	276
"	0.0236	"	5.10	283
"	0.0288	"	6.32	288
"	0.0298	"	6.16	271
"	0.0495	"	10.3	274
"	0.0820	"	16.3	260
1.00	0.0201	0.853	8.05	469
	0.0332	"	11.15	394
2.00	0.0200	1.056	17.8	843
	0.0202	"	16.9	791
	0.0257	"	21.7	801

(a) Calculated using $\gamma_{\pm}$ for HCl in HCl-KCl mixtures given by Harned and Hamer, J. Am. Chem. Soc 55, 2194 (1933) and $\gamma_{\pm KCl}$ given by Latimer, "Oxidation Potentials", assuming $\gamma_{K^+} = \gamma_{Cl^-}$.

The rate constants (K_1) at ionic strength $\mu = 0.5$ were determined as a function of acidity and it was found that $K_1/a_h = K_1'$, where a_h is the oxonium ion activity and K_1' the acid-independent rate constant. The same relationship was found for perchlorate solutions by Kern and Orlemann (MDDC-1703). Thus in chloride as well as in perchlorate solutions the rate determining step appears to be the reaction

$$UO_2^+ + UO_2H^{++} \longrightarrow [UO_2 \cdot UO_2H]^{+3}$$

[redacted]

[redacted]

c) Catalytic Disproportionation of UO_2^+

When U(IV) in U(IV)-(V)-(VI) mixtures begins to polymerize the disproportionation of UO_2^+ is catalytically accellerated. The mechanism of disproportionation must be different from that described in section (b) and might be either

$$UO_2^+ + P \longrightarrow P.UO_2^+$$

followed by

$$P.UO_2^+ \longrightarrow P.U(IV) + UO_2^{++}$$

where P represents a polymeric particle of U(IV), or it might be due to discharge of UO_2^+ on the polymer surface followed by a collision of a second UO_2^+ ion with the surface when the excess positive charge is picked up to form UO_2^{++}.

The catalysis is demonstrated in Fig. 2 where the molarity of UO_2^+ is plotted as a function of time. The (small) concomitant change in acidity is also shown in this figure. In may be noticed that acid is liberated during the reaction, primarily due to the polymerization of U(IV), whose formula before polymerization is approximately UOH^{+3} under the conditions of the experiment. The average formula of the U(IV) polymer in the solutions at the end of the experiment (t = 80 min.) was calculated from the pH measurements to be $U(OH)_{3.9}^{+0.1}$ in close agreement with the polymer formulas previously found for Pu(IV).

Precision Glass Electrode-pH Measurement with a Vibrating Reed Electrometer
R. W. Holmberg and K. A. Kraus

The vibrating reed electrometer, which can operate with extremely high input resistance, is ideally suited as null-point detector in precision pH measurements with glass electrodes, and following a suggestion by C. J. Borkowski has been put to this use for the last three years in this laboratory.

For pH measurements the instrument is being used in conjunction with a precision potentiometer and Brown Elektronik strip chart recorder. The full-scale sensitivity of the recorder was 10 mg., yielding a reading accuracy of ± 0.01 mv. A block diagram of the circuit is shown in Fig. 1.

In the past, when the instrument was used in a thermostated room, without further special control of the temperature of the solutions and electrodes the voltage measurements appeared to be reliable to a few tenths of a millivolt. This error appeared to be considerably larger than the expected inherent accuracy of the instrument. Considerably more precise results were obtained, if only potential differences were measured of acid solutions before and after

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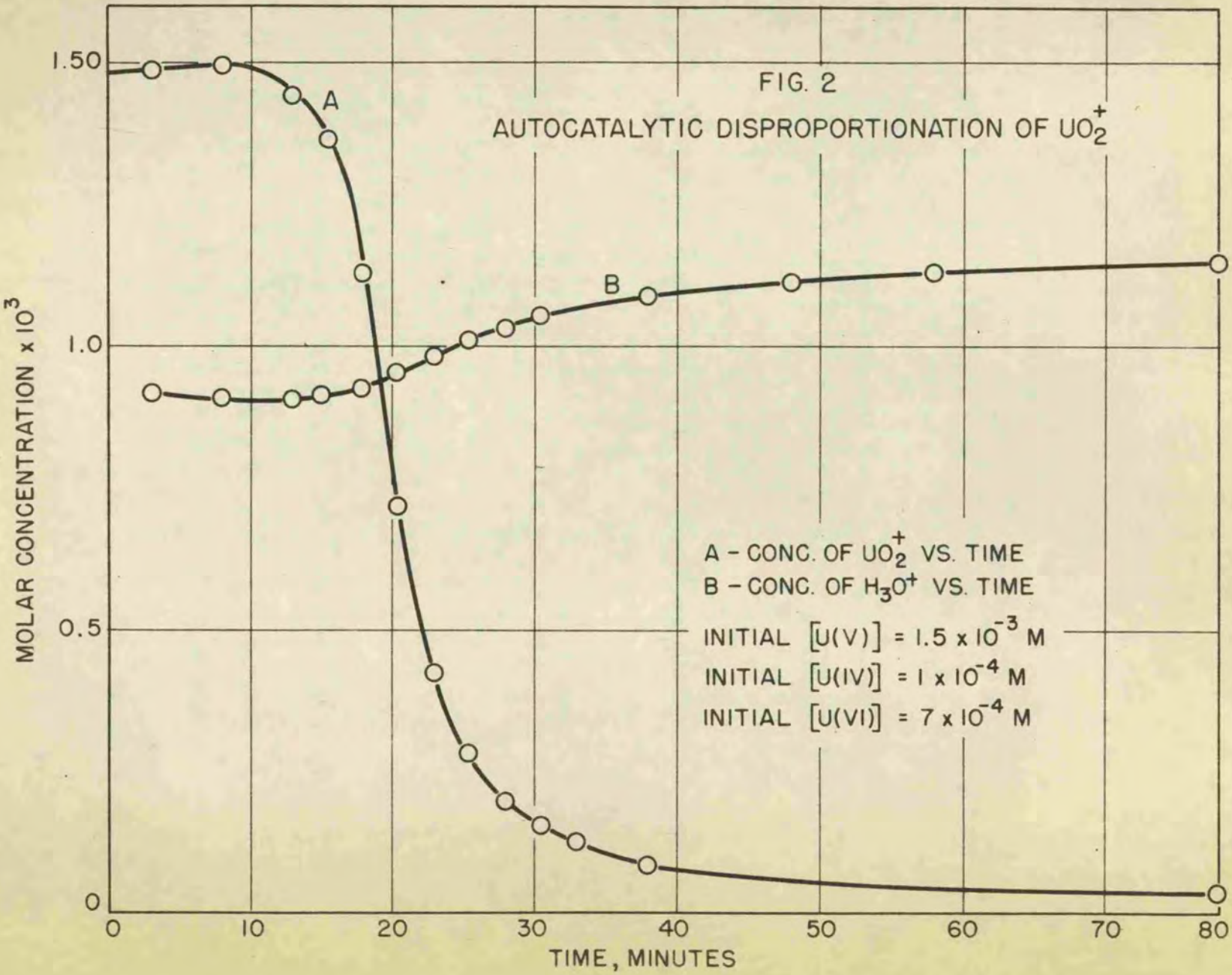
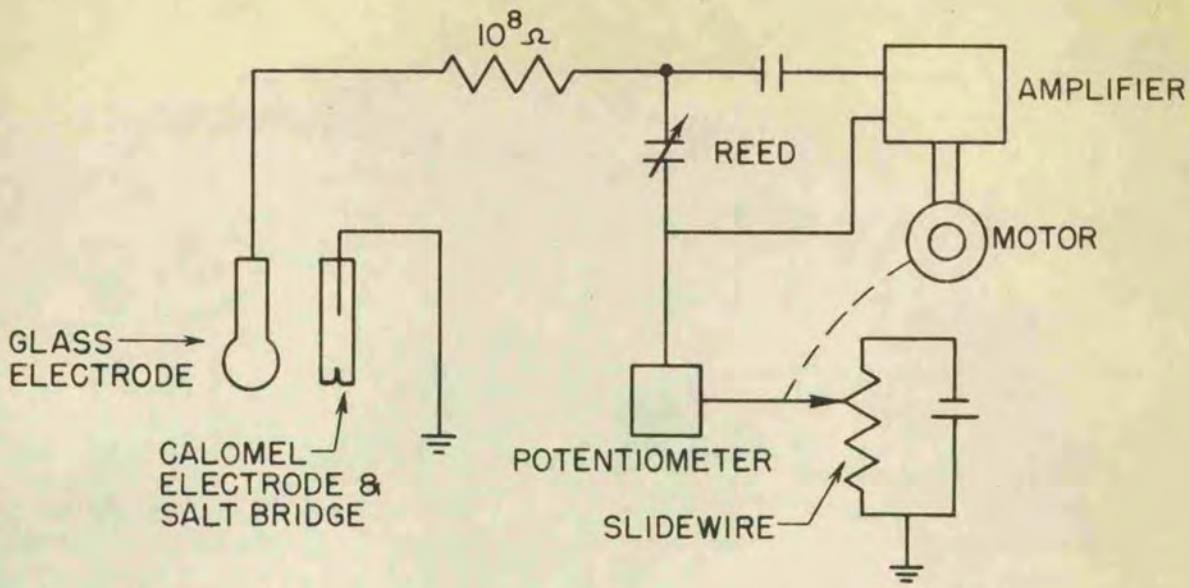


FIG. 2
AUTOCATALYTIC DISPROPORTIONATION OF UO_2^+
A
B
A - CONC. OF UO_2^+ VS. TIME
B - CONC. OF H_3O^+ VS. TIME
INITIAL [U(V)] = 1.5×10^{-3} M
INITIAL [U(IV)] = 1×10^{-4} M
INITIAL [U(VI)] = 7×10^{-4} M
MOLAR CONCENTRATION x 10^3
1.50
1.0
0.5
0
0
10
20
30
40
50
60
70
80
TIME, MINUTES

FIG. 1

VIBRATING REED ELECTROMETER CIRCUIT FOR pH MEASUREMENTS



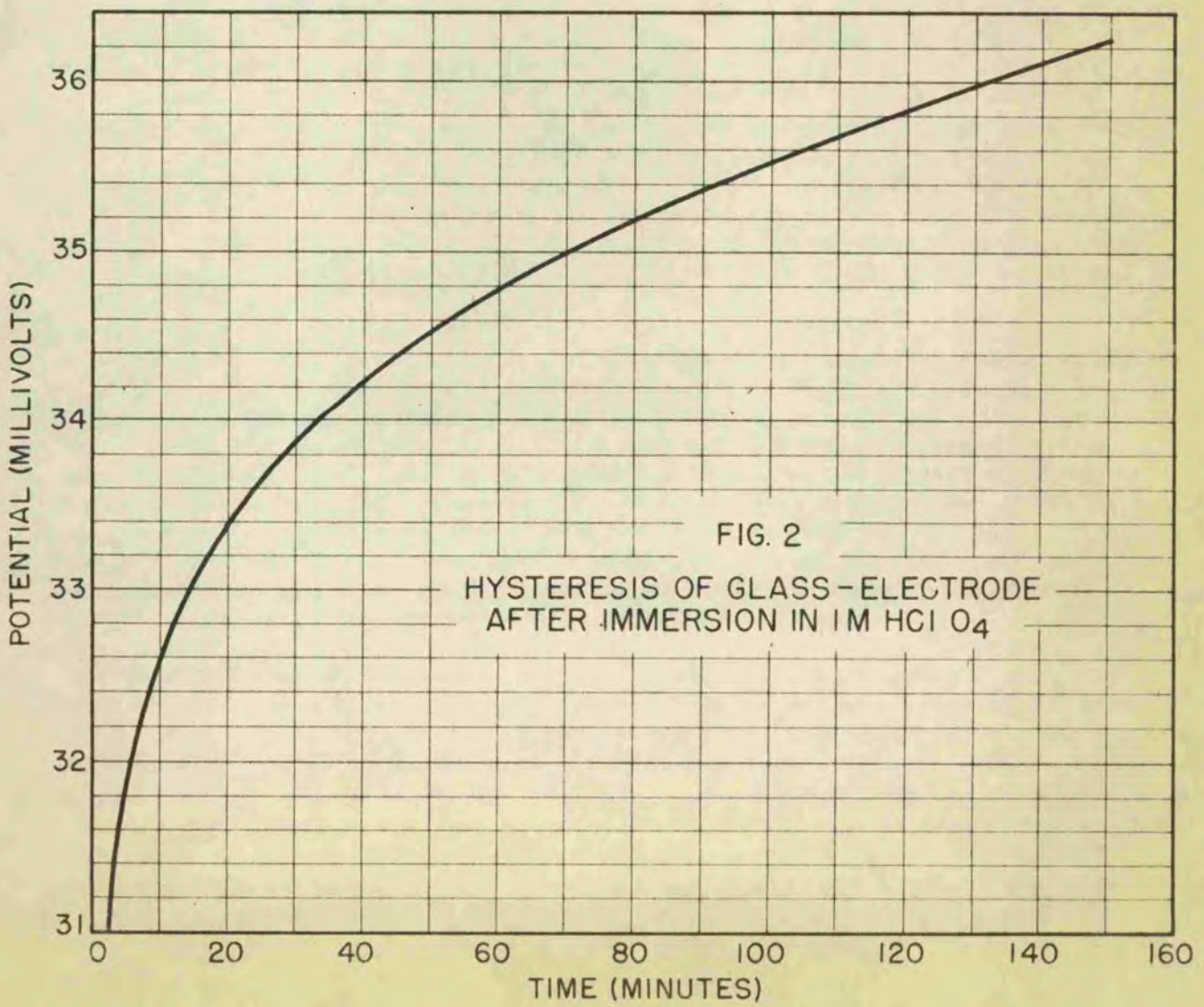


FIG. 2

HYSTERESIS OF GLASS-ELECTRODE AFTER IMMERSION IN 1M HCl O_4

[redacted]

addition of known amounts of acid and if the potential changes were extrapolated back to the time of mixing.

A set of 12 recent experiments performed in an 8 hour period is shown in Table 1. It can be seen that the voltages (E_1) of the cell (glass electrode/0.01013 M HCl//sat'd KCl/HgCl/Hg) fluctuated for different aliquots of the same acid with a standard deviation $\sigma = 0.1$ mv. ($\sigma = \sqrt{\frac{1}{n-1}\sum(x-\mu)^2}$) After addition of 0.4992 ml. of 0.1000 M HCl, without removing the electrodes, the potentials E_f were observed to also have $\sigma = 0.10$ mv. The precision of the measurements of the potential changes, however, was considerably better, ($\sigma = 0.030$ mv.)

Since temperature fluctuations were considered responsible for the changes in cell potentials for different aliquots as well as for the considerably larger day-by-day fluctuations, tests of the instrument under better controlled conditions were carried out. The calomel (reference) electrode containing a sat'd KCl bridge was placed in a Dewar flask, and placed in a 25°C thermostat when not in use. The insulation was sufficient to keep the temperature of the reference electrode at 25 ± 0.05°C for an afternoon if it was used in a thermostated room. The cell containing the solution to be measured and the glass-electrode were placed in a thermostat (25 ± 0.03°C). With this arrangement the cell potentials for various aliquots were considerably more reproducible, and the standard deviation ($\sigma = 0.025$) of the measurements was only slightly larger than the reading accuracy of the instrument, as shown in Table 2. These data were obtained by alternating measurements of 0.01004 M HCl with 0.005025 M HCl solutions. (both of $\mu = 0.5$).

If the glass-electrode behaves like a hydrogen electrode, and if activity coefficients and liquid junction potentials do not change, a voltage change of 59.15 mv. should be observed for a ten-fold change in acidity. Since the experiments, summarized in Table 2, were carried out at constant ionic strength ($\mu = 0.500$) and at HCl concentrations small compared with 0.5 M this slope was expected. Instead a slope of 57.62 ± 0.10 mv. was found with this particular glass-electrode. Other electrodes were tested (Table 3) with the same HCl buffer solutions and their potential - pH slopes were found to vary considerably, although the response of each electrode appeared satisfactory from all other points of view.

Since glass-electrodes are generally considered unreliable at high acidities, experiments are now being carried out to determine the upper limit of the useful acid range. It has been found that immersion of the glass-electrode in 1 M $HClO_4$ causes a very serious hysteresis effect. No such effect was found in 0.1 M $HClO_4$. To avoid errors due to liquid junction changes the measurements were carried out in a cell without liquid junction, using as reference a glass-electrode which had been permitted to age in 0.01 M H_3O^+. The other glass-electrode was immersed in 1 M $HClO_4$ over night, rinsed, and then placed into the 0.01 M H_3O^+ solutions. The change in cell potential with time, due to the hysteresis of the treated electrode is shown in Fig. 2.

[redacted]

[redacted]

Table 1

Voltage of Glass-Calomel (sat'd KCl) Assembly
(millivolts) ($T = 25 \pm 1^{\circ}C$)

E_i - voltage in 0.01013 M HCl

E_f - voltage after add'n of 0.4992 ml 0.1000 M HCl to 15 ml 0.01013 M HCl

	E_i	E_f	ΔE
(1)	332.52	338.97	6.45
(2)	332.36	338.84	6.48
(3)	332.28	338.74	6.46
(4)	332.30	338.72	6.42
(5)	332.35	338.79	6.44
(6)	332.38	338.79	6.41
(7)	332.39	338.86	6.47
(8)	332.30	338.78	6.48
(9)	332.46	338.96	6.50
(10)	332.44	338.90	6.46
(11)	332.51	339.00	6.49
(12)	332.61	339.02	6.41
av.	332.41	338.86	6.456
σ	0.10	0.10	0.030

[redacted]

[redacted]

Table 2

Voltage of Glass-Calomel (sat'd KCl) Assembly
(millivolts) ($T = 24.67 \pm 0.03$ C, 0.500 M Cl^-)

	0.01004 M H_3O^+		0.005025 M H_3O^+	ΔE
(1)	330.74	(2)	313.45	17.29
(3)	330.76	(4)	313.43	17.33
(5)	330.75	(6)	313.43	17.32
(7)	330.75	(8)	313.46	17.29
(9)	330.80	(10)	313.40	17.35
(11)	330.75	(12)	313.40	17.35
(13)	(330.29)	(14)	313.38	-
(15)	330.73	(16)	313.45	17.28
(17)	330.72	(18)	313.43	17.29
(19)	330.76	(20)	313.40	17.36
(21)	330.75	(22)	313.42	17.33
Av.	330.751[a]		313.427	17.319
σ	0.021[a]		0.025	0.030

(a) Average calculated excluding #13.

[redacted]

[redacted]

Table 3

Voltage - pH Slopes for Various Glass-Electrodes

Electrode	E mv. 0.01004 M HCl	0.005025 M HCl	Δ E(mv.)	Slope mv/pH
1	330.77	313.44	17.33	57.6
2	349.28	331.30	17.98	59.6
3	331.05	313.52	17.53	58.3

Chemistry of Americium
G. W. Smith and K. A. Kraus

During the last quarter an additional 5 mg of Am has been purified and studies of the chemistry of Am in aqueous solutions have been started. The studies are centered around the spectrophotometry of Am and its oxidation - reduction behavior. Since the results which have been obtained are still of a preliminary nature, their discussion will be deferred.

Counting of Liquid Samples of α - Emitters.
K. A. Kraus, H. H. Miller

A study on precision counting of liquid samples of α-emitters is under way using variations of the technique previously described (CNL-37, February 1948). The work is almost completed and will soon be issued as a progress report.

[redacted]

[redacted]

Separation of Protactinium from Metal Ions by Anion Exchange Resins in Chloride Solutions. (K. A. Kraus and G. E. Moore)

a) Distribution Coefficients of Pa

The behavior of protactinium and of a number of other metal ions in strong HCl solutions is being investigated with Dowex A-1 anion exchange resins whose functional groups are quaternary amines. Since this resin can adsorb negative ions, it is of interest to see if separation of metallic ions could be carried out under conditions where they form negatively charged complexes.

Since protactinium can apparently form a neutral chloride complex[1]

(1) K. A. Kraus, G. Van Winkle, ORNL-239
K. A. Kraus, A. Garen ORNL-65, ORNL-176

in ca. 3 M HCl, it appeared possible that it can form a negatively charged chloride complex at somewhat higher HCl concentration. The existence of such negatively charged complexes, though not necessarily their concentration, should be readily detectable by distribution coefficient measurements with an anion exchanger.

Experiments were carried out using the β-emitter Pa^{233} ($T_{1/2}$ = 27.4 days) which had been purified by di-isopropyl carbinol extraction from HCl solutions. It was found that the distribution coefficient (K_d) of protactinium on Dowex A-1 (amount of Pa per gram of resin divided by amount of Pa per ml of solution) increases rapidly with increasing HCl concentration between 2 and 8 molar HCl thus clearly indicating the existence of negatively charged complexes. The charge of the ion (or ions) as well as the concentration is in doubt. In view of the fact that chloride ions tend to adsorb reasonably strongly in this resin[2] and are present at extremely high concentration

(2) G. E. Boyd, Private Communication

the charge on the Pa-chloride complex (or complexes) appears to be $\geqslant 2$. (e.g. $PaCl_7^{=}$, $PaCl_8^{=}$ or oxychlorides).

The reproducibility of the experiments was low as shown in Table 1 but the abrupt change of the distribution coefficients with HCl concentrations as well as their large numerical values appears to be sufficiently well established to make the use of this resin in many separation processes very promising.

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The distribution coefficients were determined by agitating for 16-20 hours at room temperature ca. 20 mg of air-dried resin (ca. 10 mg on over-dried basis) with 100 λ of HCl solutions containing approximately 12000 d/m of Pa^{233}. The resin was separated from the solution by centrifugation, an aliquot of the solution assayed for Pa^{233}, the resin deposited on filter paper, dried by blotting, washed on the filter paper with a drop of the HCl solution, transferred to a weighed platinum plate and its weight determined after drying at 110°C. For beta assay, the resin was first heated with concentrated nitric acid and then completely decomposed by careful flaming of the plates.

Table 1

Distribution of Pa between Dowex A-1 and HCl Solutions
(T = ca. 25°C, Solution volume 0.100 ml)

M HCl	mg Resin (oven-dried)	Equilibration hours	c/m Pa per ml solution	c/m Pa per gram resin	K_d (a)
0.9	10.5	15.75	37,300	70,000	1.9
0.9	7.3	15.75	37,900	128,000	3.4
2.7	9.3	15.75	28,600	145,000	5.1
2.7	9.1	15.75	28,200	110,000	3.9
6	8.0	20.5	14,060	338,000	24
6	10.6	20.5	13,300	250,000	19
6	9.4	15.75	15,000	253,000	16.9
8.4	7.0	16.75	9,900	426,000	43
8.4	10.5	16.75	9,900	295,000	30
8.4	11.5	15.75	10,720	213,000	20

(a) K_d = amount of Pa/g resin divided by amount of Pa/ml solution.

b) Separation of Protactinium from Thorium

The separation of thorium from Pa was tested with ca. 15 cm. long adsorption column of Dowex A-1 resin which was constructed of a pyrex tubing (2 mm. i.d.) using 200-230 mesh resin. Before use the resin was washed with a large excess of 8 M HCl.

Pa^{233} (4×10^6 c/m) and thorium (ca. 33 mg $ThCl_4 \cdot 8H_2O$ containing ca. 2.4×10^5 d/m of ionium) in 8 M HCl were added to the column. On washing of

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the column with 8M HCl (flow rate ca. 0.2 ml/cm^2 column area) the ionium activity appeared in the detector in a very sharp band and so soon as to suggest that it was not appreciably adsorbed. On the other hand, protactinium was found by probing of the column with a beta-probe to be still in a narrow band at the top of the column, even after washing with ca. 15 column volumes of 8M HCl (column volume was estimated to be ca. 0.3 ml, assuming a void space of 30%). The Pa was finally removed from the column by elution with 1 M HCl and it was found to come off the column in a sharp band. The separation is illustrated in Fig. 1. From this experiment it appears that thorium does not tend to form a negative charged chloride complex and furthermore that the separation of protactinium from thorium by this method could be achieved with a very short column and with very high efficiency.

c) Separation of Zirconium and Columbium from Protactinium

An 8M HCl solution containing ca. 4 x 10^7 d/m of Zr^{95} and $columbium^{95}$ and ca. 8 x 10^6 d/m Pa^{233} was added to the column described in (b) after it was equilibrated with 8 M HCl.

Both zirconium and columbium could be rapidly eluted with 8 M HCl (flowrate:0.2 ml/cm^2) and they came off the columns in a sharp band. The band showed a slight asymmetry suggesting that a partial Zr-cb separation occurred. This point is now being checked under more carefully controlled conditions.

To remove the protactinium from the column, elution with 4 M HCl was carried out. A sharp elution band was obtained. The separation is illustrated in Fig. 2.

It appears that Pa(V) apparently forms considerably stronger chloride complexes than Cb(V) which might be due to the fact that protactinium, which almost certainly is considerably larger than columbium, can also be more readily polarized and thus form more stable chloride complexes in analogy to similar trends among the transition elements.

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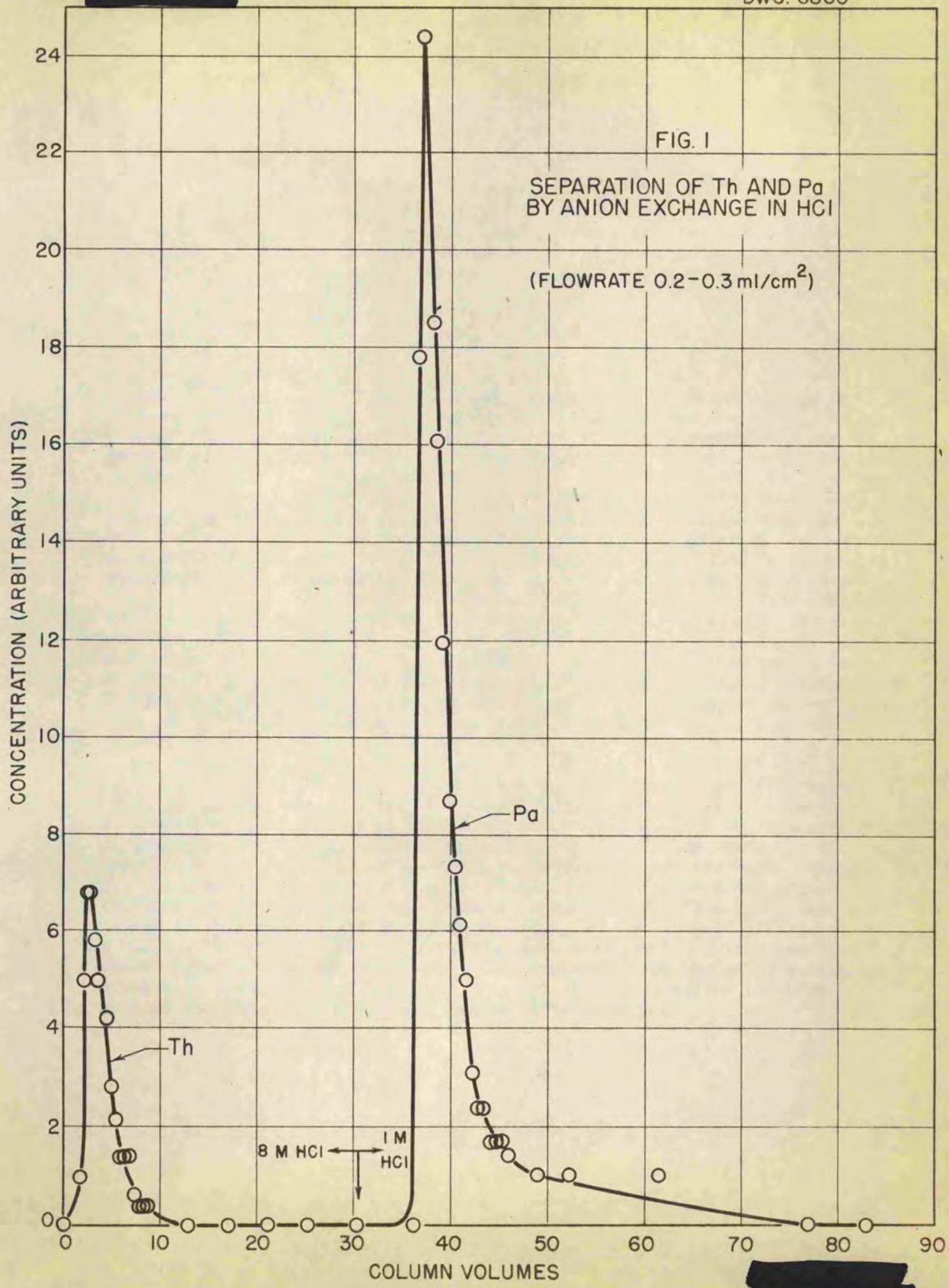

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The System Uranyl Sulfate - Water: (C. H. Secoy)

The phase study of this system has been completed from the trihydrate - ice eutectic to 374° C. with the exception of the determination of the vapor composition in the two-liquid phase region and the measurement of the vapor pressure of the solid-saturated solutions. Previously reported data for the composition of the saturated liquid phases were based on the overall composition of the system and should be corrected for the loss of H_2O to the vapor phase. In order to make this correction the vapor pressure and vapor phase volume must be determined as functions of temperature.

Considerable time has been spent in devising a reasonably accurate method of measuring the vapor pressure. A number of experimental difficulties have been encountered. However, it is believed at this time that a good method has been devised and that the data will be completed soon. Details of the experimental method will be given when the work is completed.

The volume coefficient of expansion of a 34.9% uranyl sulfate solution in a closed system under its own equilibrium vapor pressure has been measured. The method consisted of following the position of the meniscus in a sealed silica capillary. The capillary was not of uniform bore, and, therefore, it was necessary to determine its diameter at a series of points along its length and interpolate graphically for intermediate points. Major sources of error were due to the non-uniformity of the capillary as well as estimates of the tube ends. Suitable corrections for the expansion of quartz were made. A concentration in the neighborhood of 30% was selected since this is approximately the critical composition for the two-liquid phase region. The fraction of the total volume occupied by the liquid phase at 22° was 0.34. This is approximately the same as was used in the solubility measurement (0.33 to 0.35).

The data are tabulated in Table I. Mean expansion coefficients, β, in cubic centimeters per degree per cubic centimeter were calculated for each temperature interval except for one containing 294° C., the critical solution temperature, at which a discontinuity is to be expected. In Figure I, the calculated values of β are plotted against temperature. Below 294° C., (the one liquid phase region) β varies only slightly and probably nearly linearly with temperature. On the assumption that the variation is linear in this region, the empirical equation, $\beta = 5.097 \times 10^{-7}\,T + 4.004 \times 10^{-4}$, was obtained by least squares. Above 294° C., (the two-liquid phase region) β increases rapidly with temperature. By use of this data, along with the results of the vapor pressure study, values for the true compositions of the liquid phases can be calculated.

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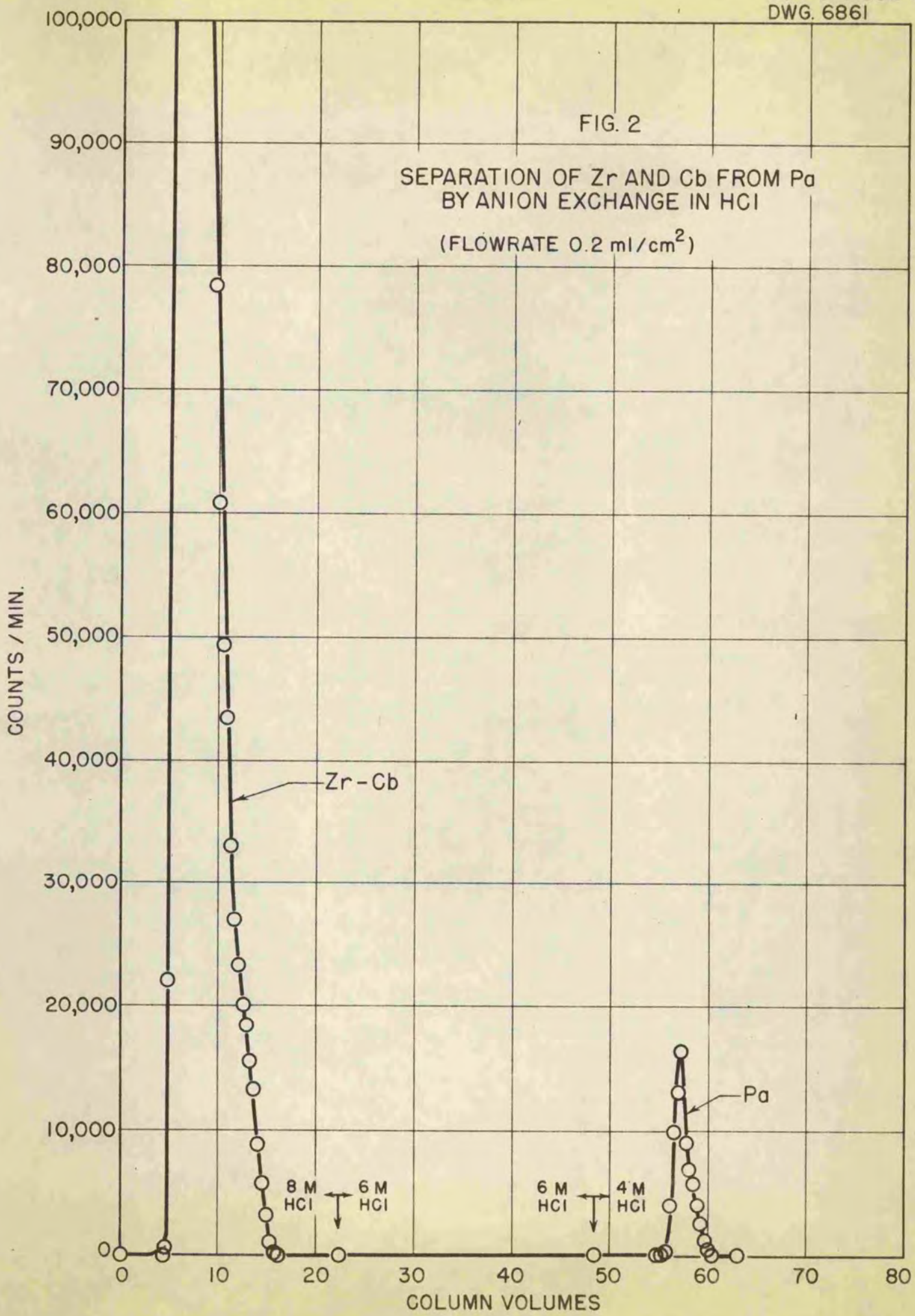

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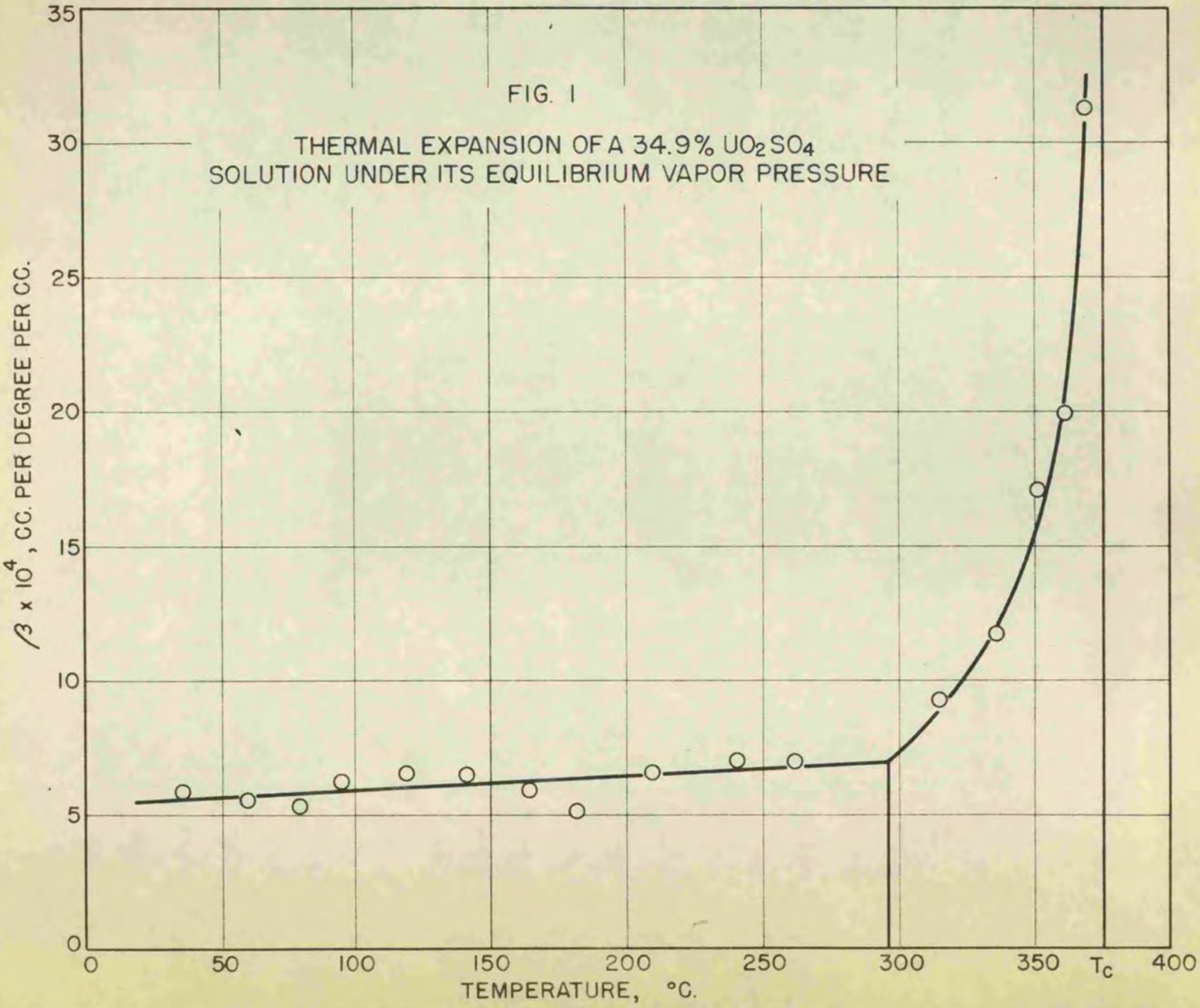

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Table I

Volume Expansion of Uranyl Sulfate Solution

34.9% UO_2SO_4

Total Volume of Tube = 0.4130 cc.

T, °C.	V, cc.	$\beta = \frac{\Delta V}{V_m \cdot \Delta T}$	T_m, °C.
22.3	0.1413		
		5.83 x 10^{-4}	35.5
48.8	0.1435		
		5.56 "	59.4
70.0	0.1452		
		5.33 "	79.0
88.0	0.1466		
		6.19 "	94.4
108.8	0.1485		
		6.56 "	119.0
129.2	0.1505		
		6.48 "	140.9
152.6	0.1528		
		5.91 "	164.1
175.7	0.1549		
		5.13 "	181.3
187.0	0.1558		
		6.51 "	209.3
231.7	0.1604		
		7.00 "	240.5
249.4	0.1624		
		6.95 "	261.7
274.0	0.1652		
303.8	0.1695		
		9.29 "	314.8
325.8	0.1730		
		11.71 "	335.8
345.8	0.1771		
		17.05 "	351.5
356.3	0.1803		
		19.91 "	361.4
366.5	0.1840		
		31.27 "	369.0
371.5	0.1869		

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II. Nuclear and Chemical Properties of Elements in the Fission Product Region

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Xenon Cross-Sections as a Function of Energy (A. R. Brosi, S. Freed, G. M. Hebert, G. W. Parker, G. E. Creek, H. Zeldes of the Chemistry Division, S. Bernstein, J. Dial, T. Stephenson and C. P. Stanford of the Physics Division, and Dan Jones of the Engineering Division)

The greater part of the work on this problem is now considered finished, and it is planned to give a comprehensive report on methods and results in several months.

A memorandum to A. M. Weinberg dated January 1, 1949 gives preliminary analyses of the data for runs 3, 5 and 6. Since then, runs 7, 8, 9 and 10 have been carried out.

Absolute assays of the amount of xenon have been made on runs 3 and 7, and the relative values are in good agreement with those obtained from spectrometer measurements. In general it may be said that the average total cross-section is about equal to the capture cross-section previously determined in the pile. The maximum cross-section is 3.5×10^6 barns.

A great deal of computational work has been performed for us by the Mathematical Panel. The following table gives the values of the parameters in the Breit-Wigner relationship for different sets of runs. E_0 in electron volts is the peak energy of the resonance curve, Γ in electron volts is the half width of the resonance, and σ_0 is the maximum total cross-section relative to that at 0.03 electron volts.

Runs	E_0	Γ	σ_0
7, 8, 9	0.0831	0.1137	1.148
7, 8, 9, 10	.0849	.1137	1.164
3, 5, 7, 8, 9, 10	.0865	.1067	1.24
3, 5, 6, 7, 8, 9, 10	.0890	.1206	1.183

The chemical processing has become fairly well standardized. One added step is now being carried out and was used in runs 7, 8, 9, and 10. Its purpose is to remove hydrogenous materials such as alcohol or ether used in washing the PdI_2 precipitate free of water. A small amount of hydrogenous material, because of its appreciable scattering power for neutrons, has constituted much of the dead material in the neutron beam. At present as the last wash, perfluoro triethylamine is passed through the precipitate under vacuum, and it seems satisfactory in every way.

Six X-10 slugs irradiated in the Hanford pile were shipped here by plane. The liaison and cooperation with Hanford was carried out by the Division of Research of the Oak Ridge Operations Office of the Atomic Energy Commission, in particular by John Ruch. The elaborate operation, called

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"Operation Very Green" was so smooth that the slugs were being processed here in less than two half-lives, twice 6.7 hours, after they were taken from the Hanford pile.

The activity through the shielding of the cell was less than from slugs radiated here, but the active gases and particles blown up the roof stack of 706-C and swept back into the operating space of the 706-C building were far above previous experience.

Steps have been taken with the cooperation of the Radiation Hazards Committee to reduce this activity materially.

The content of I^{135} in the slugs was roughly three times our previous maximum. All the chemical operations gave good yields. However, for some reason at present still unknown, the greater portion of the iodide precipitate adhered to the funnel, an experience not met with in any of the previous runs.

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Final Scale Operation of the ($I-Xe^{135}$) Process: (G. W. Parker, G. E. Creek, C. M. Hebert, P. M. Lantz)

Introduction and Summary.

Since the appearance of the last Quarterly Report ORNL-229 (pp. 21-29) summarizing the results of the intermediate level I^{135} separations, full scale operation has been engaged and continued at a rate of about one run per week or approximately as often as possible with limitations existing in the 3-5 day transmission counting period at the spectrometer and in the clean-up and recovery time necessary in the chemical equipment.

The preparations and mountings generally have been satisfactory although improvements have occurred gradually in terms of maximum yield and in transmission quality. Only variations in operation technique as an effort to circumvent speculative radiation effects have been introduced, with the exception of the much more emphasized necessity for complete dehydration of the PdI_2. It has not been possible to evaluate any radiation effects in terms of yield of iodine.

It is believed that with a few additional samples the usefulness of the operation will have been exhausted at the Clinton level of total Xe^{135}. It is hoped that at least one higher level sample will be available from Hanford.

Yield and Character of the First Nine Active Samples of PdI_2 Prepared for Transmission Study.

Note that Runs No. 1 and 2 were not full scale: (six slugs); and that No. 1 is described as Intermediate Run No. 3 in the previous Quarterly Report ORNL-229.

TABLE I

	Relative Strength in Xenon as Reported by the Physicists	Strength in Curies as Determined with Ion Chamber by Brosi	H_2O Content* and Range of Transmission Reported by the Physicists
1 (slug, 1 hr.)	--	0.25	--
2 (4 slugs, 3hrs.)	1.8	1.8	OK
3 (6 slugs, 20-22 hrs.)	4.2	4.5	OK
4 (6 slugs, 20-22 hrs.)	Not Used(1)	--	Incompletely Dried
5 (6 slugs, 20-22 hrs.)	3.2	--	OK
6 (6 slugs, 20-22 hrs.)	8.0(2)	--	Poor (16-33%)
7 (6 slugs, 20-22 hrs.)	8.3	9.8	OK (41-85+%)
8 (6 slugs, 20-22 hrs.)	4.7(3)	--	OK (62-96%)
9 (6 slugs, 20-22 hrs.)	8.5	(to be measured)	OK (44-85+%)

*The larger limit of the transmission range is a measure of the background attributed to scattering caused by presence of materials such as hydrogen in water or solvents.

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(1) Run No. 4, was not satisfactory for transmission study because of incomplete solvent removal, made particularly difficult by a flocculent precipitate and additional carrier iodine. However, the yield was fairly high, probably equal to No. 6. Considerable gas formation in the capillary by radiation-induced solvent decomposition further complicated drying efforts.

(2) Run No. 6, due to a mechanical failure of the vacuum drying system was assumed to be incompletely dried and freed of solvents. The very poor transmission data eventually confirmed this idea.

(3) Run No. 8, was also affected by mechanical difficulties, in this case, by the abrupt failure of two of the four quartz heating elements which in turn resulted in an incomplete iodine distillation.

Attempts to Further Improve the Yield of Iodine.

The limiting factors discussed in the Quarterly Report ORNL-229 and assumed to determine the yield of I^{135} have apparently been verified by the consistent preparation of about 8-10 curies. An unusual yield of about 13 curies may eventually result from a combination of circumstances such as slight advantages from a maximum bombardment time, slightly improved flux, a $\frac{1}{2}$ to 1-hour reduction in processing time, and a nearly perfect mechanical transfer. The use of small amounts of reducing agents to combat the formation and deleterious effects of H_2O_2 and the exclusion of air by flooding with inert gas has been practiced, but there has been no opportunity to compare yields without this provisiion.

Consideration is being given the possibility of seeking a yield of perhaps 50% increase by delaying the precipitation of one 6-slug run long enough to obtain the product from a second 6-slug distillation. Obviously, a considerable loss must be overridden from the decay of the first batch; however, it is conceivable that this lag period will be not more than 4 hours which would still leave about 50% of the 6 hour iodine for addition to the yield of the second batch. If this doubling is attempted, it will extend the total operating time to about 12 hours.

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Decay of 8 Day Iodine^{131} to a Metastable State of Xenon^{131} (A. R. Brosi, T. W. DeWitt and H. Zeldes)

In the calibration of an ionization chamber with respect to the disintegration rate of I^{135} the absolute disintegration rate of daughter Xe^{135}, determined by coincidence counting methods, has been used as a primary standard. When the I^{135} is prepared by rapid separation of fission product iodine from uranium which has received a short neutron bombardment, about 98% of the iodine disintegrations are those of I^{135} at the optimum time. After a 12 hr. growth period the Xe activity is mostly 9.2 hr. Xe^{135}. In precise work, however, it is necessary to follow the decay and correct for the presence of 5.3 d. Xe^{133}.

In an attempt to assay the I^{135} in an iodine sample obtained from a long uranium bombardment by this method it was found that the residual activity after 9.2 hr. Xe^{135} had decayed was not pure 5.3 d. Xe^{133}, but contained another component with a longer half-life and different radiations. The work done to characterize this component is reported below.

Gaseous activity was removed from a sample of 8 d. I immediately after it was isolated from fission products by the Operations Division. This gas had about the expected amount of 5.3 d. Xe activity and in addition had another component with a longer half-life and different radiation characteristics.

Several succeeding samples of gas were taken from this I sample after 17 hr. growth periods. When the 22 hr. I^{133} had decayed, the gas obtained had a half-life of about 11 days. The yields of this 11 day gaseous activity in succeeding samples decreased with a half-life of 8 days. A similar experiment was done using 8 d. I isolated from pile bombarded Te by the Operations Division. The character of the radiations and the yields were the same as those obtained from fission product iodine. The yields of gaseous activity as a function of the age of the iodine sample are shown in Figure 1.

The fact that the activity does not react with calcium vapor indicates that it is associated with a noble gas. A sample of gas which gave 87,200 cts/min. before calcium treatment gave 85,200 cts/min. afterward. In another case, reaction with calcium vapor reduced the counting rate from 57,300 cts/min. to 53,200 cts/min. In both cases, a 0.35 MeV gamma ray component was removed by this treatment whereas a soft component was unaffected.

The lead absorption curve of the radiations from this 11 day rare gas activity had two components. One with a half thickness of 23 mgs/cm^2 indicates an X-ray energy of about 30 KeV and another with a half thickness of 325 mgs/cm^2 could be either 85 or 170 KeV gamma rays. Since lead absorption curves do not give a unique value in this energy region, the half-thickness in tantalum was measured and found to be 400 mgs/cm^2. This gives a gamma ray energy of 165 KeV.

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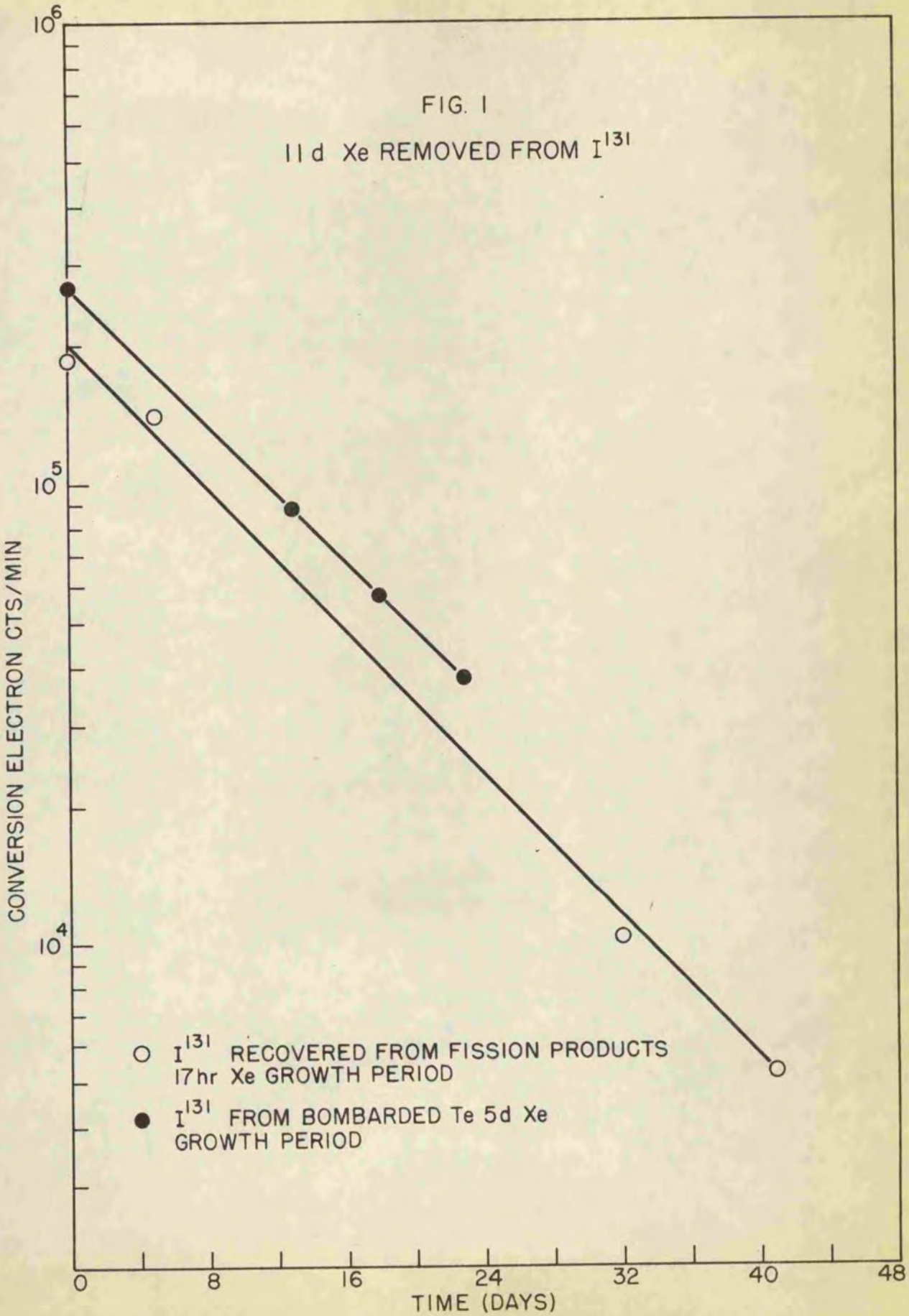

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Since X-rays with an energy of about 30 KeV could be those of I, Xe or Cs, critical absorption measurements were made to identify the element. The K X-rays of Xe should be critically absorbed by tin with a half-thickness of about 15 mgs/cm^2. In antimony only the K_β X-rays of Xe are critically absorbed, whereas the higher intensity K_α X-rays should have a half-thickness of about 85 mgs/cm^2. Absorption curves of the 11 d. rare gas activity are shown in Figure 2. These curves show that the X-rays are those of Xe. Since the activity is associated with a rare gas and since the X-rays are those of xenon, this evidence indicates that the 11 d. activity results from an isomeric transition in Xe. This is further supported by the fact that a lead absorption curve taken with a coincidence counter showed X-rays but not gamma rays to be coincident with electrons. Since the parent is an 8 d. I, it is highly probable that the 11 d. isomer is a metastable state of Xe^{131}.

An aluminum absorption curve is shown in Figure 3. This curve has been interpreted on the assumption that monoenergetic electrons were being counted. On this basis the curve can be broken down into two components, one with a range of 20 mgs/cm^2 and another with a range of 29 mgs/cm^2. This gives energies of 130 and 160 KeV which differ from the observed gamma ray energy by the K and L binding energies of Xe. The above interpretation was further verified by coincidence counting which showed only the 130 KeV component to be in coincidence with the Xe K X-rays.

An estimate of the fraction of I^{131} atoms which decay to the 11 d. isomer of Xe^{131} was made from the coincidence data. In order to do this the electron and coincidence rates were extrapolated to zero total absorber. Since both the functional form and the distance of the extrapolation are somewhat uncertain, no great accuracy is claimed for the result. On the assumption that the gamma radiation was all internally converted, it was found that the number of conversion electrons was 0.8% of the number expected had all of the 8 d. I decayed to 11 d. Xe. A rough calibration of the gamma counter for counting efficiency of 165 KeV gamma rays gave an internal conversion coefficient, N_e/N_q, of approximately 20. This would give 0.85% for the percent of 8 d. I^{131} decaying to 11 d. Xe^{131}. It is expected that this result is within a factor of two of the correct value.

The 11 d. Xe^{131} isomer reported here is probably the same one that Camac(1) obtained by fast neutron bombardment of Xe. It may also be the same as the approximately 14 day Xe activity found in 0.03% fission yield by Chackett(2). Neither Camac nor Chackett made a mass assignment or drew conclusions about the radiations. Camac gave an aluminum absorption curve similar to the one given here.

In a beta ray spectrometer study of 8 day iodine^{131}, Owens, Moe and Cook(3) found conversion electrons with an energy of 128 KeV which were

(1) M. Camac, CC-2409 (1944).
(2) W. J. Arrol, K. F. Chackett and S. Epstein, CRC-297 (1947).
(3) G. E. Owen, D. Moe and C. S. Cook, Phys. Rev. 74, 1879 (1948).

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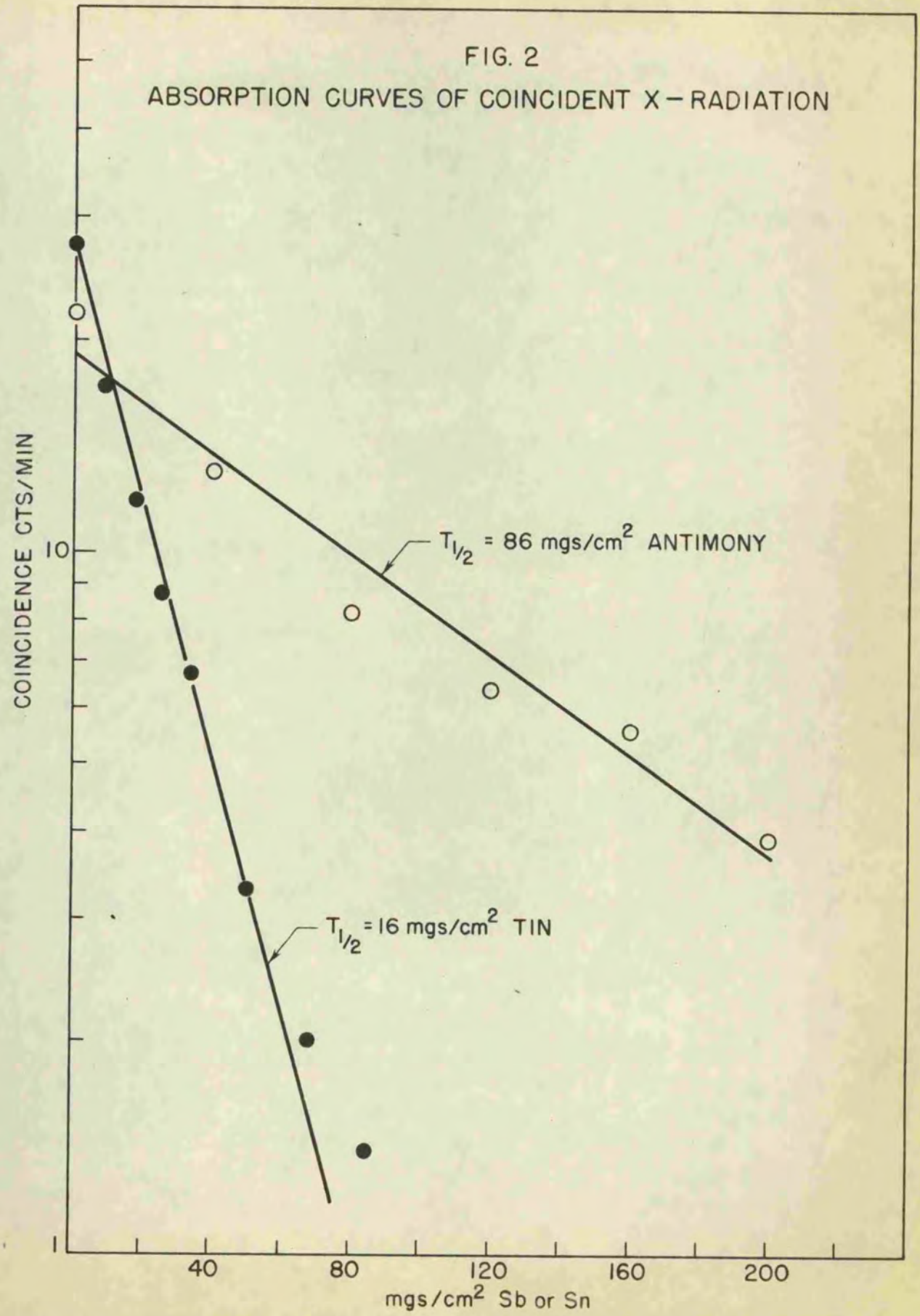

FIG. 2
ABSORPTION CURVES OF COINCIDENT X-RADIATION

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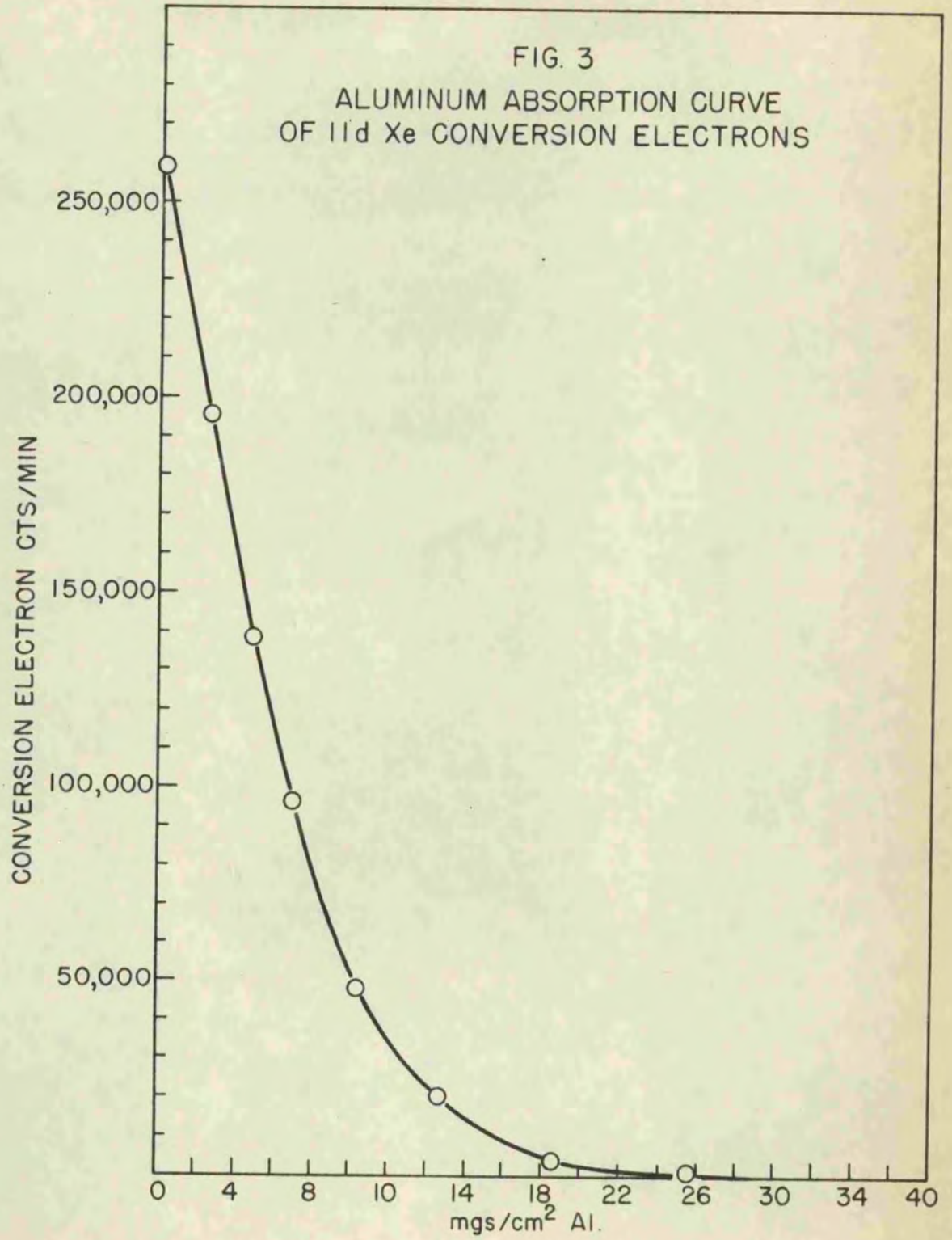

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not found by Metzger and Deutch[4]. It is believed that these electrons were from the 11 day xenon daughter trapped in their source. The results reported here lend support to the suggestion of Owen, Moe and Cook that a small fraction of the 8 day iodine^{131} atoms which decay with a 600 KeV beta ray emit a 286 KeV gamma ray followed by a 165 KeV gamma ray.

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(4) F. Metzger and M. Deutch, Phys. Rev. 74, 1640 (1948).

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165
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Search for Short-lived Activities Formed by the Neutron Irradiation of Zirconium in Connection with the Zr^{93} Problem (Q. V. Larson, G. E. Boyd)

An examination of the neutron induced activities in Zr has been conducted by way of a continuation of the search for the radiations of Zr^{93} reported upon earlier. [See: ORNL-229, p. 31]. Since previous work had indicated that possibly a 2.0 m period could be formed in good yield, a series of short pile irradiations of the calutron separated zirconium isotopes was made. Aliquots weighing between 2.2 and 2.7 mg of each ZrO_2 preparation were bombarded for exactly two minutes and then counted within one minute afterwards. Small quantities of several short lived activities, including the 29 s O^{19}, were observed but none of the unidentified periods was present in sufficient abundance to be attributed to Zr. In the case of $Zr^{92}O_2$, using the pile oscillator value of H. Pomerance of $\sigma_a = 0.2b$, an activity of $\sim 10^7$ c/m at 27.8% counting geometry should have been observed if the radionuclide Zr^{93} possessed a 2 m half-life. Actually, a total counting rate of only 7180 c/m was observed for the entire sample after 1.5 m decay. Since the absorption cross-sections of the other stable zirconium isotopes vary between 0.15 and 1.5b, it is concluded that probably no radionuclides of this element exist in the mass range 90-98 with half-lives between 10 s and 17 h. The irradiation of the $Zr^{96}O_2$ preparation gave the 17 h Zr^{96} activity in very good yield, the decay curve also showing the growth of the 70 m Cb^{97} daughter quite nicely.

Tc and Mo Activities Produced by Pile Irradiation of the Calutron Separated Stable Molybdenum Isotopes (G. E. Boyd, Q. V. Larson)

In our previous cyclotron work with E. E. Motta [See ORNL-176, p. 39] a 2.7 h positron emitting technetium activity formed in the deuteron irradiation of Mo^{92} was assigned to $Tc^{93,92}$ on the basis of yield considerations. If the 2.7 h Tc activity belongs at mass 93 it might be expected to decay to form the 6.7 h Mo^{93}. Accordingly, a "milking" for the presumed molybdenum daughter was attempted and met with negative results in three successive deuteron irradiations of Mo^{92}. Either, therefore, the 2.7 h activity must belong to Tc^{92} or else the reported 6.7 h Mo^{93} is incorrect. A four hour pile irradiation of a 5.0 mg aliquot of calutron produced $Mo^{92}O_3$ was conducted to test the latter alternative. The entire sample was mounted in the "positron" position on a small permanent magnet of ca. 1000 gauss field strength, and the decay was followed continuously for several days. Resolution of the decay curve showed small amounts of the well-known 67 h Mo^{99} and 14 m Mo^{101} activities, (mainly from the electromagnetic radiations of these radionuclides), but no 6.7 h period could be seen. A simple computation based on the presumed 6 mb absorption cross-section indicates that a large counting rate should have been found. Either the value of σ_{ac} is far lower than now believed, or perhaps Mo^{93} possesses quite different characteristics from those attributed to the 6.7 h period. Further work is planned.

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It is of interest to note that Seren, Friedlander and Turkel [Phys. Rev., 72, 888 (1947)] likewise did not observe the seven hour Mo activity upon irradiation with slow neutrons and consequently give σ_{ac} as <.001b.

Earlier cyclotron deuteron bombardments had indicated an 80 s period in Tc formed either by a (d,2n) or a (d,n) reaction with calutron prepared Mo^{100}. In order to determine if the latter possibility were correct, the Mo^{100} was subjected to a neutron irradiation to form the previously known 14.6 m Mo^{101}. Conceivably the decay of this activity could lead to an 80 s Tc^{101} period existing as an independent isomer in addition to the known 15 m Tc^{101}. However, a series of "milkings" of the 14.6 m Mo^{101} by means of a rapid distillation procedure failed to reveal any activity other than the 15 m Tc^{101}. Probably, therefore, the 80 s period belongs at Tc^{100}. The failure to produce the 80 s Tc activity by means of fast neutrons on Rh according to $Rh^{103}(n,\alpha)Tc^{100}$ at the cyclotron remains unexplained, however, unless this short period belongs to some other volatile radionuclide than Tc.

The Occurrence of Tc Activities in U^{235} Fission (Q. V. Larson, G. E. Boyd)

A series of preliminary pile irradiations of UNH and rapid chemical separations of the Tc fraction has indicated the formation of a new 10 m and a 22 m period in addition to the known 6.0 h Tc^{99} and 15 m Tc^{101}.

The Radionuclides of Tin: (C. M. Nelson, G. E. Boyd)

A further clarification of the status of the radioactive isotopes of tin beyond that reported previously (ORNL-229, p. 33) has been attempted using the calutron enriched stable Sn isotopes. A series of pile irradiations for periods varying from ten minutes up to one week has given rise to a variety of activities. Certain information about these may be reported at this time, although it is to be recognized that only a preliminary characterization is presented:

1) Sn^{125} - A 9.5 ± 0.1 m negative beta emitting period was produced in maximum yield in the pile irradiation of the Sn^{124} preparation. Absorption isochrones in Be, Al and Pb indicate β^- with ca. 0.6 and 2.06 MeV and γ-radiation of 0.38 and 1.86 MeV. The beta energies were estimated by Feather comparisons with 2.7 y Tl^{204} (0.80 MeV β^-) and 14.3 d P^{32} (1.712 MeV β^-), respectively. A previous characterization of these radiations by Sullivan and Wyatt (Mon N-243, January 1947) gave $\beta^- \sim 2.2$ MeV by absorption in Al and $\gamma \sim 0.74$ MeV by absorption in Pb. The Bohr-Wheeler disintegration energy for this nuclide is 2.5 MeV suggesting that beta branching may occur as follows: (0.6 MeV β^- + 1.86 MeV γ) and (2.06 MeV β^- + 0.38 MeV γ).

A 3 h and a 2 d period also were observed to be formed in the pile irradiation of the Sn^{124} preparation.

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2) Sn^{123} - A 41 m negative beta emitting period was formed in good abundance in the pile bombardment of the Sn^{122} preparation. Absorption isochrones taken with Al and Pb gave energies of 1.1 and 0.76 Me$^-$, respectively, for the β^- and γ radiations. In addition a hard component in the aluminum absorption curve, possibly due to Sb K_α X-rays, was noted and will be studied further. The apparent $\sim$15 m Sb daughter of the 41 m Sn^{123} mentioned in ORNL-229 has not been confirmed. Evidently the growth of activity observed must be attributed to a highly non-linear response in the particular G.M. tube used in that experiment. In addition to the short period, an 18 h activity distinguished by its intense hard γ radiations was observed to be formed in good yield. The occurrence of the previously known 130 d activity in mass 123 is strongly suggested by the high relative yield of very long half-life produced by a one-week pile irradiation of the Sn^{122}. However, the course of the decay is such after 40 days that it may be said that probably there is no 9-10 d period in Sn^{123}. It is quite possible that our 41 m Sn^{123} may be the same as the 39 m activity observed recently by A. S. Newton [UCRL 267, p. 6, December 1948].

3) Sn^{121} - The 27.5 h period previously assigned to Sn^{121} by Lindner and Perlman [Phys. Rev., 73, 1124 (1948)] was observed to be formed in maximum yield in the pile irradiation of the Sn^{120} preparation. In addition to the $\sim$0.4 MeV β^- radiations a 0.7 MeV γ in low abundance together with a softer quantum radiation of 90-100 mg Pb/cm^2 half-thickness were observed. The shape of the decay curve after 40 days indicates that the 130 d period does not belong to Sn^{121}.

A 36 m period assigned to Sn^{121} by Newton, loc. cit., was not observed in the pile irradiation of the Sn^{120} preparation, although an as yet uncharacterized 80 m period may belong at mass 121.

4) Sn^{120} - Pile neutron irradiation of the Sn^{119} preparation did not give rise to any new periods. The 41 m, 18 h and 2 d activities were formed in much lower yield than in the Sn^{122} and Sn^{124} preparations, respectively. Possibly there are no isomeric states of relatively long half-life in stable Sn^{120}.

5) Sn^{119} - An 80 m and a $\sim$17 d period were observed to be produced in the Sn^{118} preparation. It is not clear as yet, however, that either activity belongs to mass 119.

6) Sn^{118} - Good quantities of $\sim$17 d period decaying with e$^-$ of about 3 mg Al/cm^2 half-thickness and γ-radiations wereproduced by the irradiation of the Sn^{117} preparation. The half-life and radiation characteristics are such as to suggest that this period may be the same as the 14 d Sn^{119m} reported by Lindner and Perlman [Rev. Modern Phys. 20, 614 (1948)].

7) Sn^{117} - The above mentioned $\sim$17 d activity was produced in the Sn^{116} in roughly the same yields as with the Sn^{117} preparation.

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[redacted]

In addition to the foregoing, 33 m and 3 h activities were produced in the $Sn^{117,118}$ preparationsin yields such as to suggest that these periods belong to Sn^{113} and Sn^{115}, respectively.

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Characterization of Long-Lived Palladium Activity in Fission: (G. W. Parker, G. E. Creek, G. M. Hebert, P. M. Lantz)

Previous Work.

Speculation upon and search for a long-lived palladium activity at mass 107 among the fission products have generally concluded that it was only necessary to await a further increase in total activity level until its identification was assured. Probably the most recently established lower limits of the half life of this activity were due to the work of Lincoln and Sullivan (H-CN 3449) in October, 1945 and of Glendenin (PRR Vol. 9B 7.22.2 (1946). Both assumed it had detectable radiations and established a lower limit on this basis of about 10^8 years. Actually, however, these investigations were seriously limited to the detection of beta particles or electrons of not much below 0.1 mev.

It has been largely possible in the present instance to detect a new activity (Fig. 1) because of the very significant advantages of the Proportional Beta Counter developed by C. J. Borkowski for counting very soft particles.

New Source in High-Level Fission Product Concentrate.

The fission product sulfide concentrates available here as a by-product of the large-scale separation of 43^{99} (CNL-1) have been recognized as a possible fruitful source of this and other low-yield or long-lived activities still incompletely characterized. The highest nvt metal available from Hanford, having a two-year cooling period, has been obtained. From this sulfides in platinum carrier have been precipitated in 2-3N hydrochloric acid. Palladium as well as element 43 are carried well under these conditions along with the highly active ruthenium and some zirconium and columbium. The 43 is distilled with sulfuric acid from the dissolved sulfides. This is followed by a distillation of the ruthenium activity with permanganate in sulfuric acid. After a second distillation of ruthenium with carrier, the sulfide residues become much less radioactive and can be handled outside of the cell.

For the most rapid reduction in background radiation and separation from bulk MnO_2, the still residues were treated with an excess of NH_4OH and filtered once in the shielded cell. The filtrate was then removed to a hood and treated as in Table I.

TABLE I

Chemical Purification of Palladium from Fission

1.	NH_4OH Filtrate from still residue:	Boil off NH_3. Add excess aqua regia to decompose NH_4^+ salts. Evaporate excess HNO_3. Adjust acidity to 3N HCl. Precipitate sulfides. Filter. Discard filtrate.
2.	Residue: Pt, Pd, Mo, etc., sulfides.	Dissolve in NH_4OH and H_2O_2. Boil off NH_3. Dissolve in 0.3N HCl. Add excess of dimethylglyoxime in ethyl alcohol. Filter. Discard filtrate.

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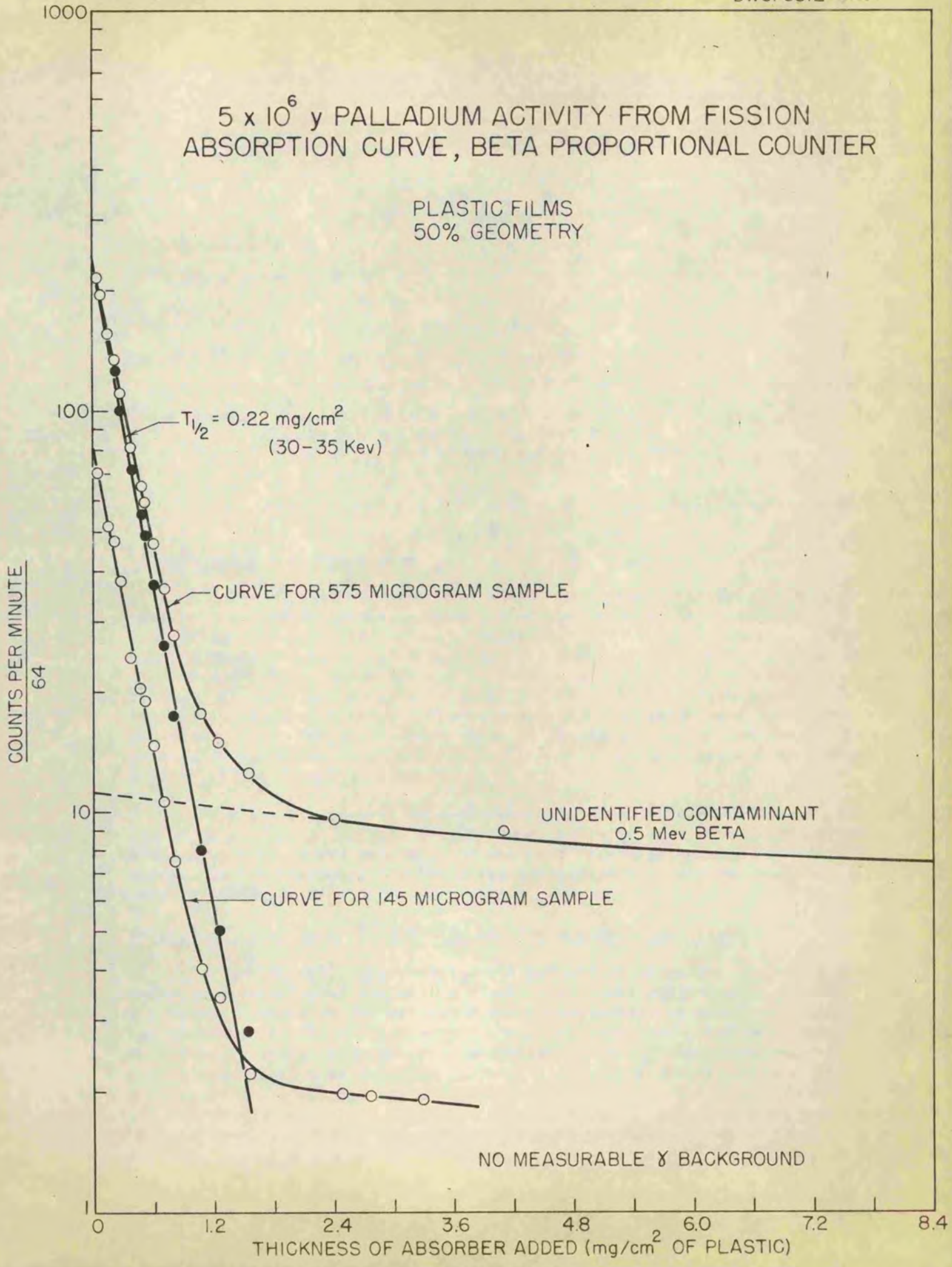

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3. Residue: Pd-dimethylglyoxime. Dissolve in aqua regia. Boil off HNO_3. Take up in 0.3N HCl and repeat dimethylglyoxime cycle until filtrate is inactive. Count aliquot of filtrate for later comparison.

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4. Residue: Pd-dimethylglyoxime. Add carrier, Mo, Ru, Re (for 43), Ag, Cd, As, Sn, Sb, I and Fe. Make alkaline with excess NH_4OH and centrifuge. Discard precipitate.

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5. Centrifugate: $Pd(NH_3)_4^{++}$. Boil off NH_3. Take up in 0.3N HCl. Add excess dimethylglyoxime. Filter.

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6. Residue: Pd-dimethylglyoxime. Dissolve in aqua regia and filter.

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7. Filtrate: Pd. Boil off HNO_3. Take up in 0.3N HCl. Repeat dimethylglyoxime precipitation. Dissolve in aqua regia. Boil off HNO_3. Take up in 0.3N HCl. Electro-deposit aliquot for counting and weighing.

Estimation of the Beta Energy.

Since it was thought likely that only very soft radiations might be observed from this isotope, almost all of the counting has been done on the Proportional Beta Counter. The presence of a very soft component (~35 kev) was immediately seen as was also a harder component (0.5 Mev) which has since been observed to be diminished by further purification. A soft gamma (0.1 Mev) was also present in the crude material and was thought possibly related to the 30 sec. isomer of Ag^{107}. The existence of this gamma associated with palladium is now very improbable since it can no longer be detected in the purer product. The actual identity of the soft particle has not been determined; however, it is probably a beta.

From the apparent half-thickness in plastic films, (Fig. 1), and an approximation factor of 8-10 to determine its range in aluminum, we estimate a maximum of 30-35 Kev according to standard reference curves of range and energy for monoenergetic electrons and nuclear beta particles (Nucleonics, January, 1948, p. 26).

Determination of Specific Activity and the Apparent Half Life.

In Table II, the results of a comparison of weight vs. count of three different quantities of the electro deposited palladium on platinum disks are given in terms of the values of the extrapolated absorption curves. It can be seen that the total count is not quite linear with the mass deposited. This non-linearity is principally accountable as self absorption and is partly taken into consideration in calculating the corrected count. The plating was done in slightly ammoniacal, dilute NaCl solution at about 3 volts and 3-5 ma according to a technique used by A. R. Brosi. The plated deposits have not been accurately analyzed for percent palladium; however, a previous analysis (colorometric by R. F. Thomason) agrees well with the amount observed.

The expected isotopic percentage according to the theoretical mass-yield curve is somewhat less than the 20% which is used as a maximum. We

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expect direct measurements from M. G. Inghram will be somewhat lower perhaps because of the presence of palladium in the chemical platinum carrier used in the original precipitation. The following Table (II) describes the treatment of the counting data for determining the specific activity. The theoretical isotopic percentage (~20%) is used here in lieu of experimental data which will be available later. The calculate half-life on this basis would probably represent a maximum value.

TABLE II

Specific Activity of Fission Palladium

No.	Observed Wt. in Micrograms Total	107 (20%)	Total Counts Per Second: 50% Geometry	Self Absorption Correction for 50% of Mass Area (2.5 cm^2) Corr'td. Counts/Sec.	Subtracted Back Scatter Correction for Platinum Mounting(50%) Corr'td. Counts/Sec.	Corrected Counts/ Sec./ Microgram Pd 107
1	145	29	86	+10% = 93.5	62	2.1
2	575	115	255	+30% = 331	220	1.9
3	905	181	287	+50% = 431	287	1.6

TABLE III

Estimation of the Half-Life of Palladium 107

Sample No.	Specific Activity d/s/ug	$T\frac{1}{2}$, Years
1	4.2	6.6×10^6
2	3.8	7.3×10^6
3	3.2	8.5×10^6

Discussion of Results.

Since time has not permitted enough direct observations, it has been necessary to assume that sufficient proof has been obtained in the purification scheme to allow a reasonable conclusion that this is a long-lived palladium activity. The limited number of disintegrations and the probable radiochemical contamination make it impossible to say that there is only a single radiation; however, this appears likely. Self absorption and other counting difficulties, together with the probable stable isotopic contamination, suggest that most weight be given the lowest of the half-life estimates.

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Hard Gamma Emitters in Fission:- 54-Minute Iodine[134]: (H. A. Levy, M. H. Feldman)

General: In a continuation of studies[1] to identify the γ-activities in uranium fission of sufficient energy (> 2.17 Mev) to eject photo-neutrons from deuterium, an iodine fraction from pile-bombarded uranium was examined. A low-yield activity of half-life about 1 hour was found, suggesting that a hard γ-ray is associated with the decay of 54-minute[2] $I^{(134)}$. An approximate yield measurement of the hard gamma, and an absorption study of the β-radiations of 54-minute iodine have been carried out.

Hard gamma measurement: For the isolation of short-lived fission iodine, the versatile remote control chemical apparatus previously described was used. A 5 to 10 gram sample of $UO_2(NO_3)_2 \cdot 6H_2O$ or of UO_3 was irradiated for 1 hour in the pneumatic tube, allowed to cool 1/2 to 1 hour, introduced into the apparatus, and dissolved in 1 N HNO_3 (10 ml per 5 g UNH). Following a well-established procedure for the separation of iodine[3], the solution was neutralized with 2% Na_2CO_3 (10 ml or more), KI + KIO_3 carrier was added, followed by 4 ml of 2.5% $NaClO_4$ and slow acidification with HNO_3. The iodine was then reduced to I_2 with 1 M hydroxylamine hydrochloride (3 to 6 ml), and extracted into 20 ml of CCl_4. This solution was delivered outside the remote control apparatus and extracted into H_2O with dilute $NaHSO_3$, after which the iodine was put through a second similar cycle for purification.

For hard gamma measurement, an aqueous iodine fraction from 10 g of UNH was placed at the center of a tank of D_2O equipped with a fission-type neutron counter previously described[1] and counted for a succession of 5-minute intervals, starting 40 minutes after the end of irradiation. The circles in Fig. 1 show the averages of 5 successive counts, while the triangles show the same data corrected for instrument background. While the statistics are poor, owing to the low counting rate, the data are satisfactorily represented by a 55-minute half-life.

A .01% aliquot of a similar sample giving 34 hard gamma counts per 5 min. interval was mounted as AgI and counted under an end-window G-M tube. Resolution of the 54-minute component was difficult, owing to the multiplicity of I activities; however, the 54-minute activity was estimated at 5.6×10^5 d/m corrected to the start of the hard γ-counting. Taking the efficiency of γ-counting as $\sim 10^{-7}$, the fraction of $I^{(134)}$ disintegrations giving hard γ-counts is estimated to be 10^{-2} to within an order of magnitude.

Study of β-Radiations: For a study of the β-radiation of $I^{(134)}$, an iodine fraction isolated directly from fission contains too many periods (54 m, 2.4 h, 6.7 h, 22 h, and 8 d). However, the 6.7 h activity can be eliminated if a Te fraction is first isolated, and the 2.4 h period can be minimized to negligible levels if irradiation times are kept short. The applicable chain relations are as follows:

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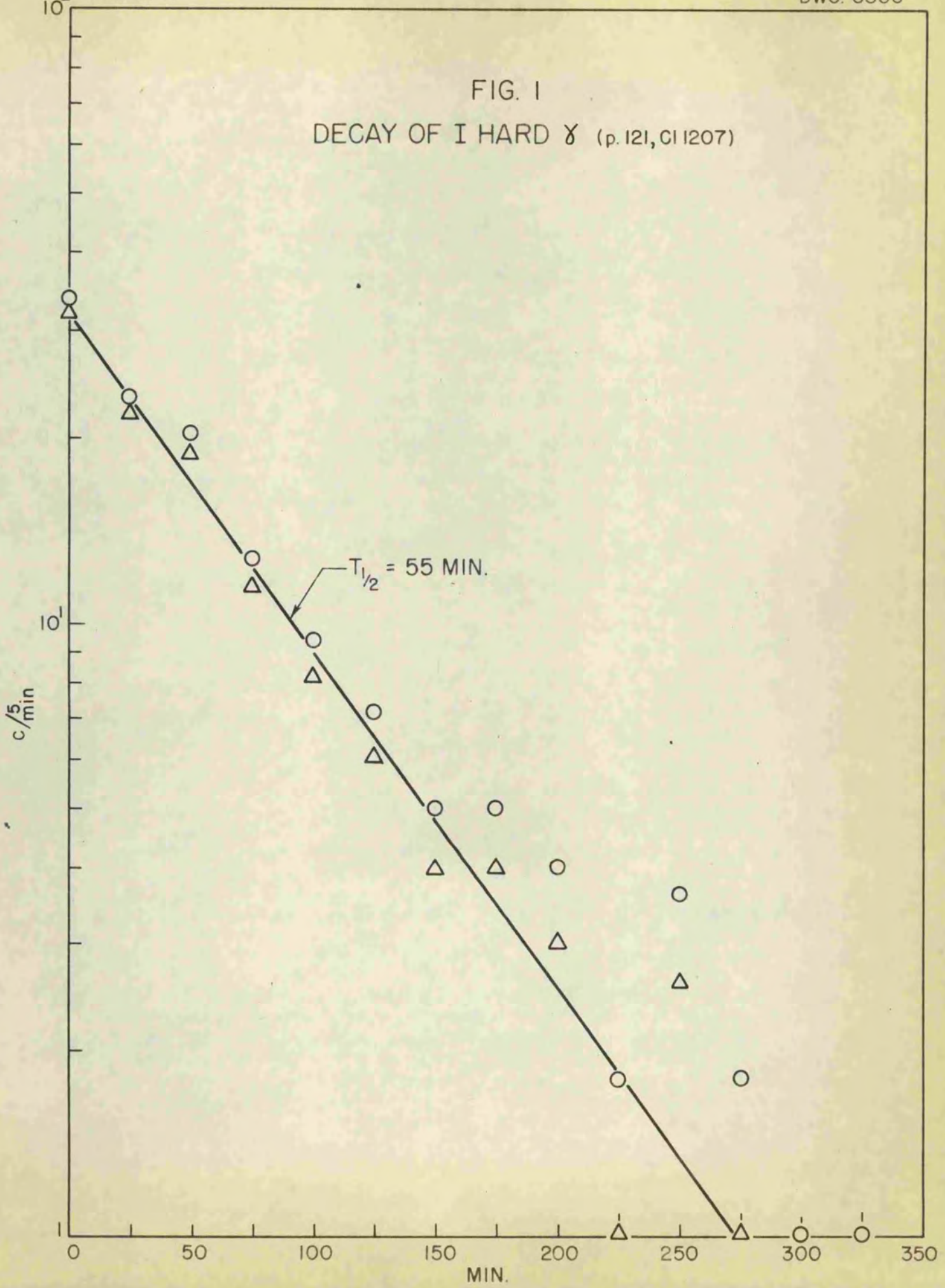

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$$43\ m\ Te \longrightarrow 54\ m\ I^{(134)}$$

$$77\ h\ Te \longrightarrow 2.4\ h\ I^{(132)}$$

$$< 2\ m\ Te \longrightarrow 6.7\ h\ I^{(135)} \longrightarrow 9.2\ h\ Xe^{(135)}$$

$$60\ m\ Te \longrightarrow 22\ h\ I^{(133)} \longrightarrow 5\ d\ Xe^{(133)}$$

$$30\ h \longrightarrow 25\ m\ Te \longrightarrow 8\ d\ I^{(131)}$$

One to 2 g samples of UNH were irradiated for 2 minutes, cooled ~20 minutes to insure complete Te^{135} decay, and processed to isolate Te, according to the standard analytical procedure[3], by precipitation of Te metal with SO_2 from a hot 3 N HCl solution containing iodine hold-back carrier as iodide and iodate. About 25 minutes later, the Te was dissolved in HNO_3, and iodine was separated and deposited as NaI on a polystyrene film by evaporation of a Na_2CO_3 solution at pH 10. This material has been shown not to retain Xe daughter. The timing of a typical experiment was as follows:

Exp. Ip 131 CL 1207 - February 15, 1949

8:55 - 8:57 AM	Irradiation in pile
9:20 - 9:22	Te precipitated and centrifuged
9:30	Second Te precipitation
9:55	Final I_2 separation
10:00 - 10:30	Evaporation
10:30	Counting begun

The decay of the iodine was observed through a succession of Al absorbers with an end-window G-M counter.

Figure 2 shows the decay without added absorber and is typical of all the curves taken. The resolution into a 54 m and a 22 h component without intermediate period is quite clean. The 22 h decay was actually followed for about 2 1/2 days. Extrapolation of the various decay curves to an arbitrary zero time gave absorption curves shown in Figure 3a. Data from two samples are shown; points B from a sample 20-fold larger, were normalized by means of the two points recorded as dotted circles (representing absorber thicknesses used with both samples) so that all data are represented in Curve A. Subtraction of the γ-component gave the function defined by the triangles.

It is seen that the β-absorption curve suggests a complex spectrum. The analysis into components is necessarily uncertain; however, curves C and D represent limiting estimations of a harder β-component, for which Feather analysis gives a range between 1560 and 1900 mg/cm^2, corresponding to an energy of 3.2 to 4.1 Mev. Two estimates of the softer components, obtained by subtracting curves C and D, are shown in Figure 3b. For these, Feather analysis gives a range between 750 and 950 mg/cm^2, corresponding to an energy of 1.6 to 2.0 Mev. The ratio of soft to hard component is roughly 5 to 1, with no correction for window or air absorption. The β to γ ratio is roughly 50 to 1.

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1. ORNL-65, p. 101; MON-432, p. 100
2. P. H. Abelson, Phys. Rev. 56, 1 (1939)
3. CN-2815, p. 45

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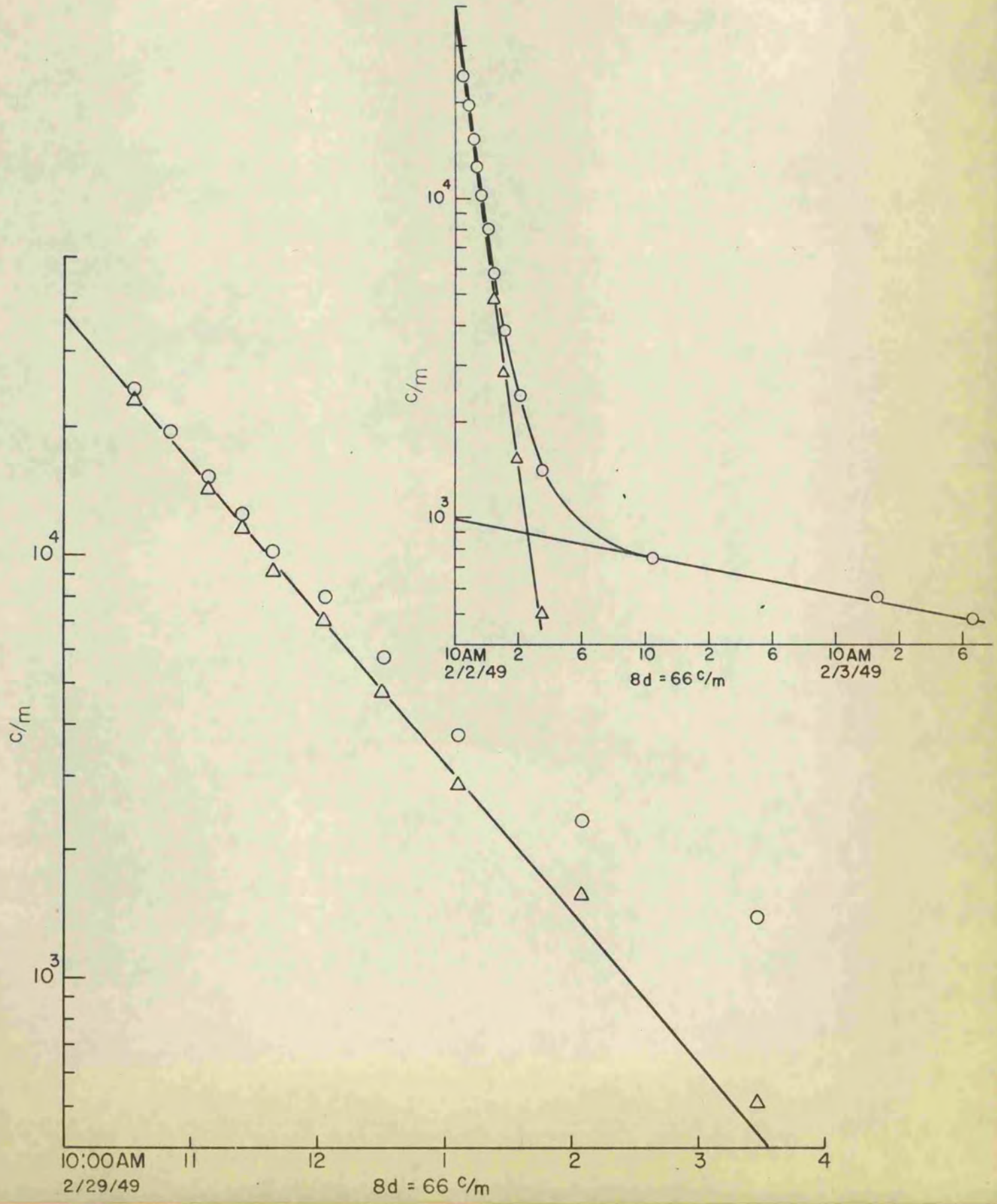
FIG. 2

DECAY THROUGH ZERO ABSORBER



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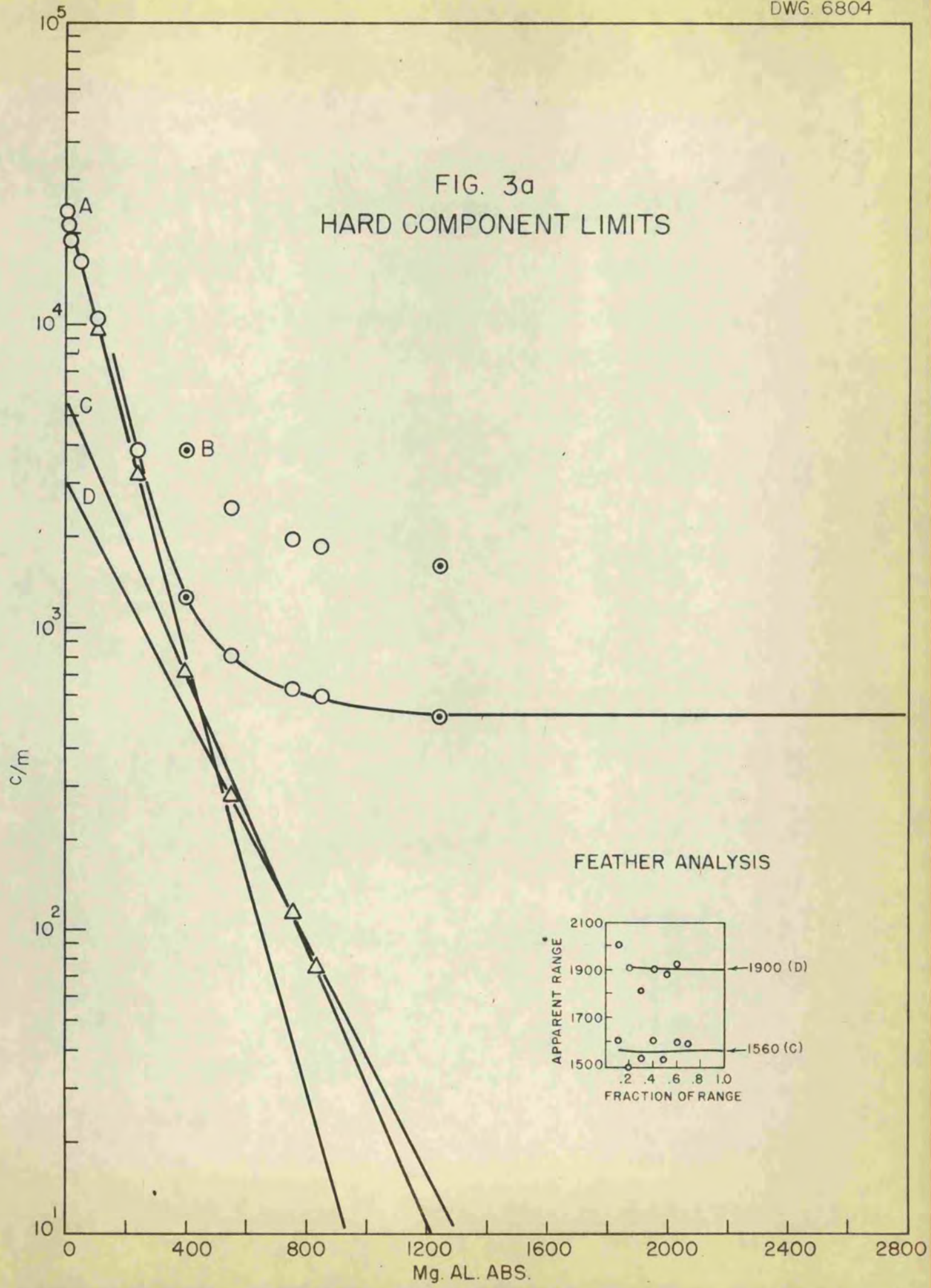

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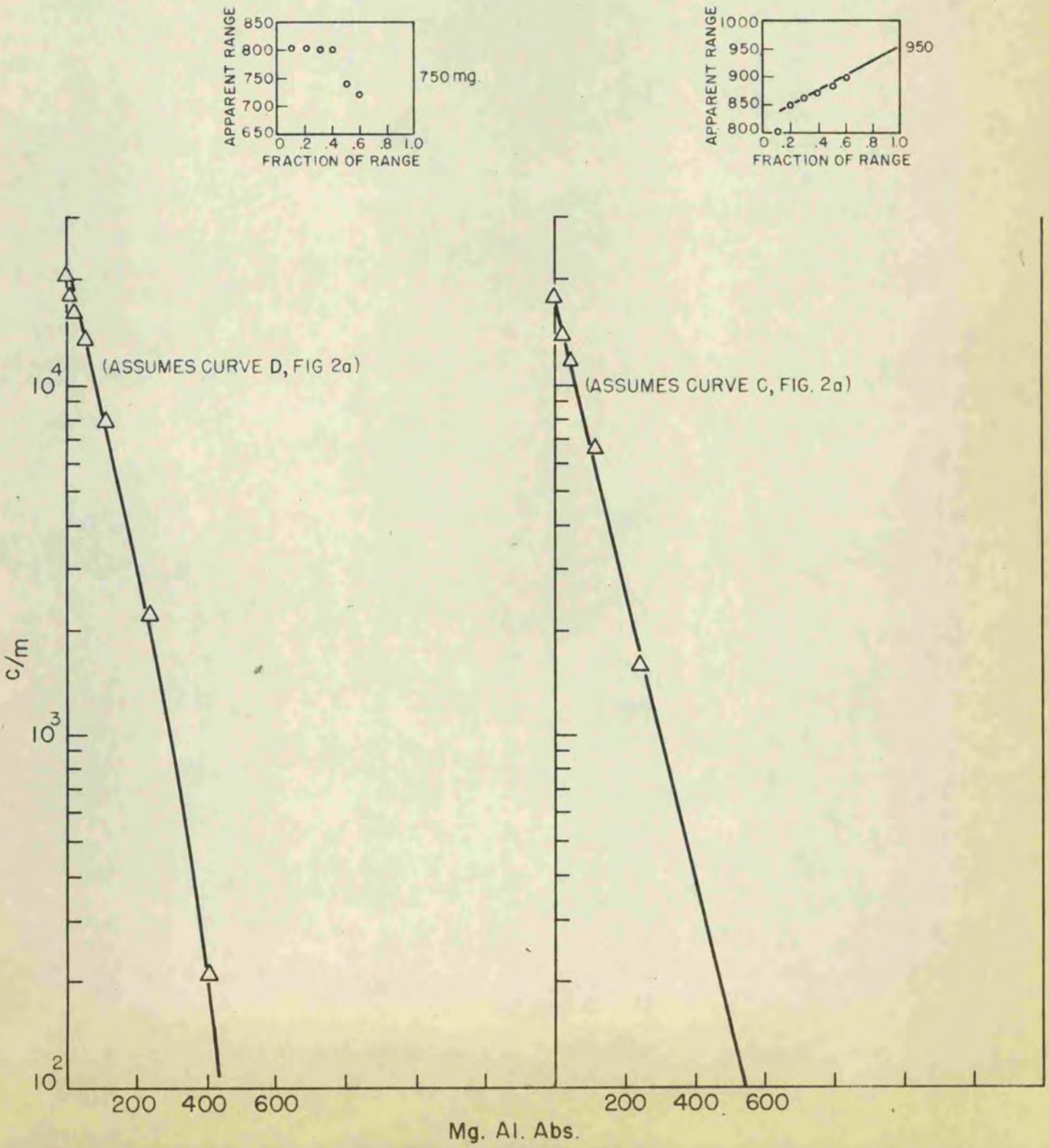
FIG. 3b

β ABSORPTION CURVE OF SOFT COMPONENT



III. General Nuclear Chemistry

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Nuclear Chemical Studies on the Rare Earths (G. E. Boyd)

The Radiations of 129 d Tm^{170} (B. H. Ketelle)

We have previously reported this isotope to emit beta radiation with a maximum energy of 0.98 ± 0.02 MeV[1], gamma rays of 83 KeV[2] and K X-rays of 50 KeV following internal conversion. Coincidence counting of beta rays and conversion electrons indicated that the gamma ray was not delayed by as much as one micro second.

A study of beta-gamma coincidence and of beta X-ray coincidences using proportional beta counters in collaboration with A. R. Brosi has been made. Coincidence counts were taken with sufficient beryllium between the source and the gamma counter to absorb all beta rays and lead absorption curve of the X-rays and γ rays was obtained. The lead absorption curve of coincidence counts as well as of gamma counts was resolved into two components of half thickness 83 mg Pb/cm^2 and 336 mg Pb/cm^2. The photon energies corresponding to these half thicknesses are 51 KeV and 85 KeV respectively and are in excellent agreement with the spectrometer data. Coincidence counts using aluminum absorbers in front of the beta counter indicate that only a very small fraction of the beta disintegrations go to the excited level of the daughter nucleus. Because of the low energy difference between the two beta components this fraction cannot be accurately determined from these data. Furthermore, it makes difficult the resolution of the spectrometer data into two components with any precision. A crude estimate would be that 90% or more of the beta disintegrations go to the ground state of the product nucleus.

Further Characterization of 7 d Tb^{161} (B. H. Ketelle)

The assignment of activities to isotopes of Gd and Tb was discussed in ORNL-229, p. 34, and a preliminary discussion was given of an experiment using several milligrams of irradiated pure Gd. The Gd and Tb were completely separated on an ion-exchange column and the decay of each element was followed. It has been observed that only about 10% of the total beta activity in the terbium sample at the end of the bombardment was due to the 72.5 d Tb^{160} activity. After subtraction of this component, the remainder of the activity decayed with a half-life of 7 days. After correction for the longer lived activity in the original Tb, the maximum beta energy remains at 0.5 MeV as was previously reported. The aluminum absorption curve also indicated that the 7 d activity has a photon of about 30 KeV. The lead absorption curve gave a value of about 45 KeV for the photon energy. Even though there was a rather small amount of longer lived activity the resolution of the two components introduced considerable uncertainty into the energy of the short lived activity.

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(1) ORNL-65, p. 96
(2) ORNL-229, p. 36

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The Radiations of 225 d Gd^{153} (B. H. Ketelle)

The activity of the 225 d Gd (see: ORNL 65, p. 95) separated in the above described experiment was studied on the thin lens spectrometer. Conversion lines of energy 50 KeV and 88 KeV were obtained. In order to establish for certain that these were K and L conversion lines, absorption curves of the activity were obtained using absorbers of Ta and Cu. The Cu curve gave two components: 43 KeV and 103 KeV. The Ta curve gave energies of 40 KeV and 110 KeV. Therefore, it is felt that the spectrometer lines were K and L lines of a gamma ray of 100 KeV (K value) and 96 KeV (L value). The absorption curves gave the correct K-X-ray energy for Eu. The coincidence study of this isotope will be accomplished upon the completion of a new coincidence counter now being constructed.

A Possible 85 h Period in Dysprosium (B. H. Ketelle)

Four different pile bombardments and exchange column separations of rare earth mixtures in the Gd region have given a period of 85 $\pm$ 10 h in the dysprosium fraction in addition to the well-established 145 m Dy^{165}. The 85 h period decays with electrons of about 2 MeV energy and in addition there is an indication of e^- and about 0.5% of quantum radiation. A further study of this apparent Dy activity is planned.

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Electrodeposition of Manganese: (J. C. Griess and J. A. Swartout)

I. Introduction

The purpose of the present investigation is to study the electrolytic deposition of manganese both as the metal and as the dioxide with special emphasis on a possible electrolytic separation of micro amounts of manganese from macro amounts of iron.

Very little has been published concerning the complete electrodeposition of manganese from aqueous solutions. In most analytical textbooks it is usually stated that manganese is deposited along with all metals below aluminum in the electromotive series during the process of a mercury-cathode electrolysis. However, the deposition is never complete and a trace of manganese remains in solution. As far as could be found, no investigations have been made of the complete electrolytic removal of manganese from solutions as the dioxide. Manganese dioxide does deposit on the anode under certain conditions but no complete study concerning these conditions has been reported.

Since manganese will be the trace constituent in the systems involved in our studies, it is desirable to deposit the manganese and leave the iron in solution. However, in non-complexing media iron deposits at a lower potential than manganese. In order to reverse the order of deposition it is necessary to use a complexing agent which complexes iron to a greater extent than manganese. Therefore, to predict whether a separation is possible, the decomposition potentials of the two elements in the given solution must be known. As pointed out by Lingane[1], the polarograph is a useful instrument for the determination of this information. By a correct interpretation of a given polarographic wave, it is possible to predict the potential necessary to obtain complete deposition of that metal from the given solution.

Polarographically it has been shown that a number of anions complex ferrous iron but there is little information concerning the reduction of manganese under the same conditions. The experimental work reported here has been concerned with the determination of half-wave potentials of iron and manganese in several different complexing media. In cases where no reduction wave was obtained before a hydrogen or sodium wave, the decomposition potential was obtained by a controlled cathode potential electrolysis.

II. Experimental

The procedure used in the polarographic work was the same as that described in ORNL-91. The polarizable electrode was a dropping mercury electrode and the anode a saturated calomel electrode connected to the

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1 Lingane, J.J., Ind. and Eng. Chem., Anal. Ed., 16, 147 (1944).

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cell by means of an agar bridge saturated with potassium chloride. The dissolved oxygen was removed from solution before the polarogram was prepared by passing oxygen-free nitrogen through the solution for ten minutes. An automatic recording Sargent Model XX polarograph was used.

Some data obtained for the half-wave potentials of manganese in some common complexing agents are given in Table I. The half-wave potentials of the $Fe^0 \rightleftharpoons Fe^{+2} + 2e^-$ reaction are given for comparative purposes.

Table I

Half-Wave Potentials of Iron and Manganese in Four Common Complexing Agents

Supporting Electrolyte	Molar conc.	pH	$E_{\frac{1}{2}}$ vs. S.C.E.	
			$Mn^0 \rightleftharpoons Mn^{+2} + 2e^-$	$Fe^0 \rightleftharpoons Fe^{+2} + 2e$
Sodium Oxalate	0.2	5.3	None	None[1]
Sodium Citrate	0.5	5.6	None	None[1]
Sodium Tartrate	0.5	6.8	-1.54	-1.68[1]
Sodium Fluoride	0.5	5.0	-1.55[2]	None[2]

Although most of the data presented in the above table is of a negative nature, it is interesting to note that manganese was deposited before iron when the complexing agent was either fluoride or tartrate. In the case of the tartrate complex the iron wave followed the manganese wave too closely to allow a separation. When a tartrate solution containing equimolar amounts of iron and manganese was polarographed, only one wave was obtained and the height of the wave was approximately twice that of the manganese wave alone. The fluoride complex had the disadvantage that both ferric and ferrous fluoride were rather insoluble in 0.5M sodium fluoride. Even when the iron concentration was millimolar, a precipitate formed. The formation of this precipitate would undoubtedly carry most of the trace of manganese and hence would be of little value in the proposed separation.

Since neither manganese nor iron gave a reduction wave in a citrate solution, it was necessary to carry out a controlled cathode potential electrolysis to determine the minimum potential required to obtain essentially complete deposition of the manganese. By using a mercury cathode it has been shown that very nearly all of the manganese (99%) can be plated from a citrate

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[1] Values reported by Lingane, J.Am.Chem.Soc. 68, 2448 (1946).
[2] Values reported by West, Dean and Breda, Collection Czech.Chem.Commun., 13, 1 (1948).

[redacted]

[redacted]

or oxalate solution at a cathode potential of -1.75V vs. S.C.E. when the initial manganese concentration is as low as 10^{-5}M. At present the behavior of iron solutions under the same conditions has not been investigated.

Both sodium ethylenediaminetetraacetate and sodium nitrilotriacetate are known to complex iron. Since there were limited data in the literature concerning these two reagents and none involving their use in polarography, the half-wave potentials and diffusion currents of iron and manganese waves were investigated at different pH values. Thus far the nitrilotriacetate complexes have been investigated. The concentration of sodium nitrolotriacetate was arbitrarily selected at 0.1M and the desired pH was obtained by the addition of dilute hydrochloric acid. In the case of iron the only reduction wave obtained was due to the reduction of ferric to ferrous; there was no evidence for reduction to the metal. The results are given in Table II.

Table II

The Half-Wave Potentials of Manganese and Iron in 0.1M Sodium Nitrilotriacetate at Different Acidities

pH	Reducible Ion Conc.	Manganese		Iron	
		$E_{\frac{1}{2}}$	i_d	$E_{\frac{1}{2}}$	i_d
4.0	$1x10^{-3}$M	-1.51	4.0	-0.05	3.6
4.0	$2x10^{-3}$M	-1.50	9.8	Not taken	Not taken
4.6	$1x10^{-3}$M	-1.50	2.4	Not taken	3.6
4.6	$2x10^{-3}$M	-1.50	4.3	-0.13	7.2
6.0	$1x10^{-3}$M	None	None	-0.17	3.6
6.0	$2x10^{-3}$M	-1.56	0.8	-0.18	7.5
9.8	$1x10^{-3}$M	None	None	-0.30	Not taken

From the standpoint of the present research the most interesting feature of the above table is the fact that manganese was reduced at lower potential than iron. At the acidities employed, iron was not reduced to the metal before the reduction of sodium ions. That the one wave obtained in iron solutions was due to the reduction of ferric to ferrous was shown by the fact that a plot of log $\frac{i}{i_{d-i}}$ vs. potential gave a straight line with a slope of 63 mv. This agreed well with the theoretical value of 59 mv. for a one electron change.

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The ferric-ferrous wave shifted to a more negative position when the pH was increased. This indicated that the stability of the ferric complex increased with decreased acidity.

The diffusion currents of the iron waves were independent of pH and were linear with concentration. Since no special precautions were taken in measuring the diffusion currents, the degree of reproducibility and linearity was remarkable. There is a good possibility that a satisfactory polarographic method could be worked out for the determination of iron using sodium nitrilotriacetate as a complexing agent.

The diffusion currents obtained for the manganese reduction were not linear with concentration nor were they independent of pH. Since the diffusion current became smaller with decreasing acidity, it appeared that manganese began to precipitate at pH levels higher than 4. The fact that the manganese half-wave potential was approximately the same in sodium nitrilotriacetate as in potassium chloride ($E_{\frac{1}{2}} = -1.51$) indicated little or no complexing. It should be mentioned that the measurement of both the half-wave potential and diffusion current of the manganese wave was complicated by the presence of the hydrogen wave which was only a few millivolts more positive than the manganese wave. As a result the half-wave potential and especially the diffusion current were difficult to measure accurately.

From the data it appears that a separation of manganese from iron may be possible in a sodium nitrilotriacetate solution.

The Complete Electrodeposition of Ruthenium from Dilute Solutions: (J.C. Griess and J. A. Swartout)

The purpose of this investigation was to find a method for the complete electrodeposition of ruthenium when the initial ruthenium concentration was low.

Ru^{106} is one of the isotopes produced in the process of uranium fission and is offered for sale by the Isotopes Division of the Atomic Energy Commission. Before Ru^{106} is separated from other fission products, a small amount of natural ruthenium is added. As a result the present supply of radio-ruthenium is not carrier-free but exists as a hydrochloric acid solution containing approximately 40 ppm. ruthenium. It is this ruthenium for which a method of deposition was sought.

The experimental studies have been nearly completed and a report will be issued in the near future. An abstract of the method is given below:

The solution containing the ruthenium to be deposited is evaporated to dryness to remove the excess hydrochloric or nitric acid. After dissolving the residue in a minimum amount of water, 1 ml. of red fuming nitric acid (sp. gr. = 1.6) is added. The solution is evaporated to dryness

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under an infrared bulb and the residue dissolved in either 0.3N sulfuric or hydrochloric acid. The resulting solution is electrolyzed at a cathode potential of -0.4 to -0.6V vs. S.C.E. (current density = 1 to 3 amps/dm^2). In order to prevent loss of ruthenium at the anode, the anode is placed in an outside container and connected to the electrolysis cell by a bridge containing 6N sulfuric or hydrochloric acid. From the above solution it is possible to obtain essentially complete deposition (> 99%). The deposit is dark but has a polished appearance and is very adherent.

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IV. Radio-Organic Chemistry

Experimental Use of C^{14} (C. J. Collins, J. G. Burr, H. Heller, D. N. Hess, A. R. Jones, R. G. Mansfield, O. K. Neville, G. A. Ropp, W. J. Skraba

Summary

Attempts to prepare amorphous carbon by the high temperature interaction of magnesium and carbon dioxide showed little promise.

Acetylene has been prepared in 15% yield from the product of the reaction of barium carbonate and magnesium at 700°.

By means of the lithium aluminum hydride reduction of carbon dioxide-C^{14}, 91.4 millicuries of methanol-C^{14} of high specific activity has been prepared.

The production of formaldehyde-C^{14} by the pyrolysis of methyl triphenylmethyl ether has given erratic results, yields of 22.6% and 42.7% being obtained on pyrolysis of methyltriphenylmethyl ether-C^{14}. Using this method, 7.9 millicuries of formaldehyde-C^{14} of high specific activity has been prepared.

Formic acid prepared by the reduction of carbon dioxide with lithium borohydride was converted to pure ethyl formate in 96% yield.

The isolation of acetic acid produced by the carbonation of methyl magnesium bromide has been satisfactorily accomplished, and 18 millicuries of acetic acid-1-C^{14} with a specific activity of 1.2 millicuries per gram has been prepared. In addition approximately 100 millicuries of sodium acetate-1-C^{14} of high specific activity (radioactive assay not complete) has been prepared.

The preparation of malonic ester by the vapor phase decarbonylation of diethyl oxalacetate has been successful, but attempts to convert the latter to diethyl acetylenedicarboxylate have failed.

The carbonation of pentamethylene bis-magnesium bromide failed to give a good yield of cyclohexanone.

Methylphenylcarbinol-C^{14} (12 millicuries, 24.1 g.) has been produced in 67% yield from acetic acid-1-C^{14}. Approximately 0.05 millicurie of methylphenylcarbinol-C^{14} was dehydrated to styrene-C^{14}, which was diluted to a total weight of eight grams with non-radioactive styrene. This material was thermally polymerized.

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A synthesis for "ring-labeled" benzoic acid has been completed with inactive materials. Intermediates in this synthesis will include 2-methyl-1,4-naphthoquinone-8-C^{14} (synthetic vitamin K) and phthalic acid-3-C^{14}.

The Synthesis of Low Molecular Weight Intermediates Containing C^{14}

Amorphous Carbon (H. Heller)

Discussion

Magnesium and carbon dioxide reacted slowly at 1,000 degrees, more rapidly at 1,100-1,300 degrees Centigrade, to form magnesium oxide, magnesium carbide, carbon and possibly a small amount of carbon monoxide. Unreacted magnesium and carbon dioxide were also present. The quartz tubes used for the reactions were badly attacked, preventing the determination of the carbon by weight difference following acid treatment of the product.

Experimental

In a quartz tube attached to a vacuum line was placed 0.958 g. (39.4 mg. atoms) magnesium turnings. The vessel was evacuated to a pressure of 10^{-5} mm. and temporarily isolated from the system.

Tank carbon dioxide was collected in a calibrated vessel of 181 ml. capacity attached to another portion of the line. The gas was frozen in a trap cooled with liquid nitrogen and a small amount of non-condensible material was pumped off. On warming and expanding into the calibrated vessel, the gas exhibited a pressure of 225 mm. of mercury at 26°C. (2.20 mmols).

An electrically-heated furnace was placed around the tube containing the magnesium turnings. At a furnace temperature of 900°C., the metal began to sublime. At this point the gas was allowed to contact the heated metal. On expansion to fill both the calibrated vessel and the reaction tube, the gas showed a pressure of 88 mm. When the furnace temperature reached 1000°C., the pressure began to decrease until a final pressure of 3 mm. was obtained. Since a part of this pressure was due to non-condensible gas, presumably carbon monoxide, it was not possible to collect it in the calibrated vessel. However, an estimate was made of the pressure that this amount of gas would exhibit in the calibrated vessel by assuming the validity of the proportion $P/3 = 225/88$, where P was the final pressure the gas would exhibit if compressed to the calibrated vessel, 3 was the observed final pressure of the gas in both calibrated vessel and reaction tube, 225 was the initial CO_2 pressure in the calibrated vessel alone, and 88 was the initial CO_2 pressure in the calibrated vessel plus the reaction tube. The value thus estimated was 12 mm. The final pressure of condensible gas was found to be 2 mm. at 25° or about 1% of the original gas pressure. The estimated value for the non-condensible gas was therefore

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10 mm. or 5% of the original pressure. Assuming that the only gases present were carbon dioxide and carbon monoxide, and that the partial pressures of these were proportional to the numbers of mols of each present, the material balance on CO_2 was

1%	unreacted
5%	converted to CO
94%	converted to non volatile products (C and Mg_2C)
100%	

The experiment was repeated several times with similar results.

Acetylene (G. A. Ropp)

Discussion

The reaction of barium carbonate with magnesium at 700°C. to give barium carbide has been carried out. The dark solid products obtained, when heated with water, gave a maximum yield of acetylene of 15% based on barium carbonate.

Attempts to cause reaction of barium with excess carbon dioxide at 700°C. have been unsuccessful, although manometric measurements showed some decrease of the carbon dioxide pressure. Addition of water to the reaction product caused the evolution of a gas which gave only a faint test for acetylene.

Good results were obtained in the determination of acetylene by precipitation from neutral silver nitrate solution and back-titration of excess silver ion in the filtrate with standardized potassium thiocyanate solution.

Experimental

Powdered magnesium, 1.00 g., and barium carbonate, 1.00 g. (0.0051 mol), were mixed thoroughly in a 10 ml. alundum cup which was placed in a large quartz test tube attached to a vacuum line. After evacuation, dry helium was allowed to flow into the system until a pressure of one atmosphere was reached. The tube was maintained at 700°C. for ten minutes with a tubular furnace. After six minutes a slight flash threw some powder out of the cup. The tube was disconnected from the vacuum line. 20 ml. of water was run in slowly, and the contents of the tube were heated to boiling. Issuing gases were bubbled through three wash bottles in series; each containing 100 ml. 0.1 N silver nitrate solution. The precipitated silver acetylide was filtered and washed with water. Silver ion in the filtrate was determined by titration with standard potassium thiocyanate solution. The amount of silver precipitated was equivalent to 0.00038 mol of acetylene or 15% yield based on barium carbonate.

Preparation of Formaldehyde-C^{14} (W. J. Skraba with A. R. Van Dyken)

Formaldehyde-C^{14} containing 7.9 millicuries C^{14} was prepared by the pyrolysis of methyl-C^{14} triphenylmethyl ether.

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The scheme for the preparation was as follows:

1. $(C_6H_5)_3CCl + C^{14}H_3OH \longrightarrow (C_6H_5)_3COC^{14}H_3 + HCl$

2. Chromatographic purification of $(C_6H_5)_3COC^{14}H_3$

3. $(C_6H_5)_3COC^{14}H_3 \xrightarrow[400^oC.]{\Delta} C^{14}H_2O + C^{14}H_3OH + C^{14}O$

The purified methyl-C^{14}-triphenylmethyl ether was divided into two portions and these were pyrolyzed individually. During the pyrolysis considerable polymerization of formaldehyde-C^{14} occurred in the cooler portions of the apparatus. In order to minimize this loss infra-red lamps were placed along the glass train. The yields were lower than were obtained in the tracer run.

Experimental

Preparation and Purification of Methyl-C^{14}-Triphenylmethyl Ether - In a 50 ml. round-bottom flask containing 25 ml. of anhydrous benzene and equipped with a magnetic stirrer bar was placed 4.04 g. (14.6 mmols) of $(C_6H_5)_3CCl$ and 2 ml. of pyridine. The flask was attached to a vacuum line, frozen in a liquid nitrogen, and evacuated. Methanol-C^{14} (13.16 mmols) containing 31.3 millicuries C^{14} was vacuum distilled into the flask, which was then isolated from the system.

The contents were warmed to room temperature, and the reaction mixture was stirred for twenty-four hours.

The volatile constituents, consisting of benzene, pyridine, and unreacted methanol-C^{14}, were removed by vacuum distillation. Water, 10 ml., followed by 15 ml. of benzene were added and the mixture was stirred. The benzene layer, containing the ether, was separated in a Brown extractor and passed through a column of activated alumina. The product was eluted with 50 ml. of benzene. Vacuum distillation of the filtrate gave 2.865 g. $(C_6H_5)_3COC^{14}H_3$ (79.5%).

Pyrolysis -- The material obtained above was pyrolyzed in two separate portions. The first portion containing 1.479 g. (5.40 mmols, 12.87 millicuries C^{14}) was placed in a long-neck 50 ml.-round-bottom flask. This was attached to a glass train consisting of a water absorber, copper oxide combustion-apparatus and two $Ba(OH)_2$ bubblers. The temperature of the copper oxide furnace was adjusted to 800°C. and the flask containing the $(C_6H_5)_3COC^{14}H_3$ was immersed in a salt-mixture bath maintained at 400°C. A stream of nitrogen gas was slowly passed through a side arm of the flask and the evolved decomposition gases consisting of $C^{14}H_2O$, $C^{14}H_3OH$ and $C^{14}O$ were swept through the train. The water bubbler absorbed the formaldehyde and methanol. Carbon monoxide, after oxidation in the furnace, was removed as $BaCO_3$ in the $Ba(OH)_2$ bubblers. Radiochemical analysis of the methone-formaldehyde derivative, quantitatively prepared from the water solution, showed 2.3 millicuries (a yield of 22.6% $C^{14}H_2O$).

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The pyrolysis was repeated with the second portion of $(C_6H_5)_3COC^{14}H_3$ containing 1.340 g. (4.90 mmols, 11.68 millicuries C^{14}). The absorber solution from the first pyrolysis was re-used. Radiochemical analysis of the methone-formaldehyde derivative quantitatively prepared from this solution showed 7.9 millicuries (42.7% yield from the second pyrolysis). The final product solution consisted of 3.32 mmols $C^{14}H_2O$ containing 7.9 millicuries C^{14} and 2 mmols $C^{14}H_3OH$ containing 4.9 millicuries C^{14} in 21.60 g. of water solution.

All radiochemical determinations were made by ion current measurements of the $C^{14}O_2$ from the combustion of the methone derivative of $C^{14}H_2O$.

Formic Acid (J. G. Burr, Jr.)

Discussion

Work on the preparation of formic acid by the lithium borohydride reduction of carbon dioxide in ethyl ether solution has progressed along two lines: 1) purification of formic acid and its derivatives; and 2) identification of by-products of the reaction.

Boric acid, which is formed in the work-up of the reaction products, was removed by high-vacuum distillation of the aqueous formic acid. The distillate was neutralized with sodium hydroxide, and again distilled to dryness under high vacuum. The residue of sodium formate containing traces of alkali and phenolphthalein was converted to ethyl formate in 96% yield by reaction with diethyl sulfate.

Diborane has been identified in the exit gases from the reaction by conversion to trimethylamineborine. Data from tracer runs performed with the aim of detecting other by-products of the reaction are incomplete.

Experimental

Isolation of Aqueous Formic Acid -- A solution prepared from 0.260 g. (5.0 mmols) of lithium formate, 5 ml. of water and 1 ml. of 85% phosphoric acid was distilled at 10^{-3} mm. The distillate contained 4.9 mmols of acid by titration with base. It gave a faint phosphomolybdate test for phosphate ion. The distillates from similar solutions containing boric acid were free from boric acid as determined by the turmeric test.

Conversion of Sodium Formate to Ethyl Formate -- A mixture of 1.00 g. sodium formate (C.P. anhydrous) and 5.0 ml. of diethyl sulfate, b.p. 90-95° (12 mm.), was heated at 160-180° for ten minutes. The ester was distilled under high vacuum at room temperature. The distillate was redistilled at 10 mm. pressure. The liquid product weighed 1.05 g. (96%). The refractive index at 25° and the vapor pressure at 0° were respectively 1.3562 and 78 mm. as compared with 1.3567 and 73 mm. for distilled commercial ethyl formate, b.p. 54.5-55°.

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Acetic Acid (D. N. Hess)

Discussion

As a further step in the development of a method for the routine production of acetic acid-1-C^{14}, a synthesis at tracer level has been carried out in order to determine the maximum over-all yield.

The carbonation of the methyl Grignard solution and the recovery of aqueous sodium acetate were carried out as previously described(1). The water was removed from the sodium acetate under high vacuum, and a known amount of non-radioactive acetic acid was allowed to exchange with the radioactive sodium acetate. Equilibration was allowed to take place overnight. The acetic acid was pumped off and assayed for C^{14} by dry combustion and ion chamber determination of the radioactive CO_2. Titration of the acetic acid prior to exchange indicated a 93% yield. The over-all radiochemical yield was 75%.

By this method 18 millicuries of acetic acid (specific activity: 1.2 millicuries per gram) has been prepared for conversion to polystyrene. In addition, two 50 millicurie preparations of sodium acetate of high specific activity have been completed.

Further work on the recovery of anhydrous acetic acid from sodium acetate has resulted in the development of a method of considerable promise. A mixture of dry sodium acetate and 70% phosphoric acid saturated with phosphorus pentoxide were distilled at 100°C. under high vacuum. An excellent recovery of acetic acid with a very slight phosphate contamination was obtained. Further investigation of the method is in progress.

Experimental

Acetic Acid (Tracer Level) -- By the method previously reported(1), 15 mmols of 0.3 M methyl Grignard ether solution was carbonated with 10.13 mmols $C^{14}O_2$ (specific activity: 4.28 μc./mmol) during one hour). The solution was hydrolyzed with aqueous phosphoric acid. The bromide ion was precipitated with Ag_2CO_3, and the ether was removed by distillation. After thirty-one hours of "equilibrium distillation"(1) into a solution containing 10.00 mmols of sodium hydroxide, back-titration of the solution with standard acid indicated 7.81 mmols of sodium acetate (93.2% of the theoretical yield based on unrecovered $BaCO_3$). The aqueous solution, containing a slight excess of base was evaporated, and then taken to dryness on a vacuum line by heating at 65°C. for six hours at 10^{-5} mm. pressure. The flask was removed from the line and 2 ml. glacial acetic acid was added. The stoppered flask was heated to 65°C. for fifteen minutes and then allowed to stand overnight to allow exchange to take place. The acetic acid was distilled under high vacuum, and a sample was burned to carbon dioxide. Radiochemical analysis showed a yield of 75.0%, based on 8.39 mmols $C^{14}O_2$. The recovered $BaCO_3$ amounted to 1.74 mmols (17.2%).

(1) ORNL-229, Progress Report, Sept., Oct., Nov., 1948, p. 47-8.

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Conversion of Sodium Acetate to Dry Acetic Acid -- A mixture of 5 ml. of 70% H_3PO_4 saturated with P_2O_5 and 0.7759 g. anhydrous sodium acetate was heated at 100°C. and 10^{-5} mm. pressure. The distillate was collected in a trap cooled in liquid nitrogen and weighed 0.6086 g. The yield, calculated on the basis of these figures is greater than 100%. This discrepancy has not been explained, although the presence of water in the "anhydrous" sodium acetate has not been ruled out. The refractive index of the distillate was $nD_{22.9^o} = 1.3752$ as compared to $nD_{22.9^o} = 1.3718$ for commercial glacial acetic acid. A qualitative phosphomolybdate test gave a lemon yellow color indicating some phosphate contamination.

Diethylmalonate and Diethyl Acetylenedicarboxylate (G. A. Kopp)

Discussion

Experiments with diethyloxalacetate have indicated that this ester cannot be decarbonylated in good yield by heating with powdered soft glass. Vapor phase decarbonylation of the ester at 300-320°C. has given approximately 50% yields; however, optimum conditions have not yet been determined.

Diethyloxalacetate has been catalytically reduced in 72% yield to diethylmalate. Attempts to cause reaction of diethylmalate with anhydrous hydrogen bromide have failed.

Attempts to prepare α, α-dichlorodiethylsuccinate, a possible intermediate in the synthesis of acetylenedicarboxylic ester, by reaction of diethyloxalacetate and phosphorus pentachloride, have failed.

Cyclohexanone (A. R. Jones)

Discussion

An apparatus for the small scale carbonation of pentamethylene bis-magnesium bromide has been found useful for the carbonation with radioactive carbon dioxide of other Grignard reagents. The following notes apply to Figure 1.

Barium carbonate in flask 1 was acidified with dilute acid. The carbon dioxide was swept with dry nitrogen through the Drierite traps and into the reaction vessel 2. The condenser 3 filled with powdered Dry-Ice and acetone prevented all but traces of ether from escaping. These traces were trapped in 4, also cooled with Dry-Ice and acetone. The sweep gas was bubbled through half-saturated barium hydroxide solution in the bubblers 5.

Whenever the products of the Grignard reaction were insoluble in ether, pure dry mercury was added to the reagent solution just before carbonation. This prevented the magnetic stirrer bar from sticking.

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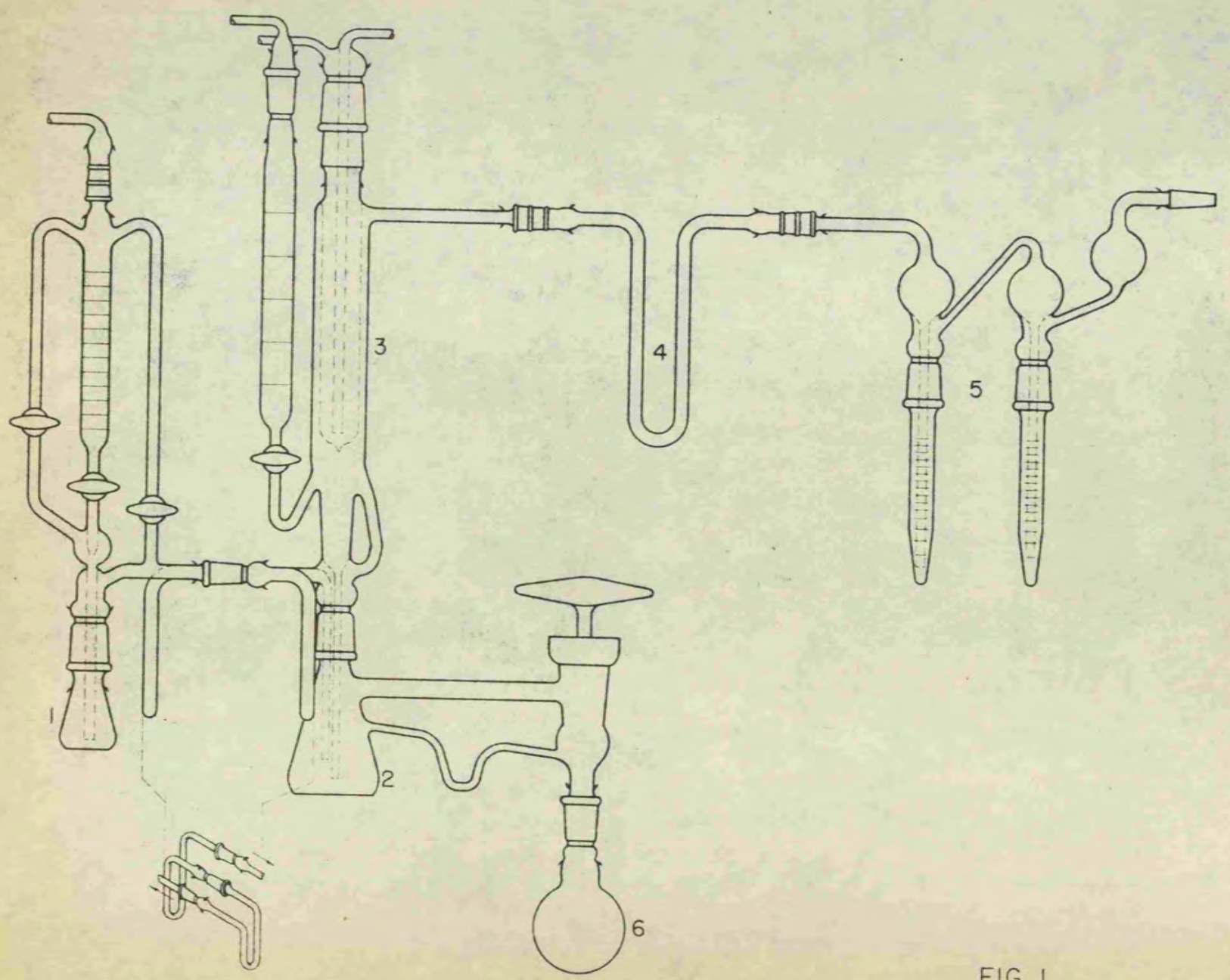

FIG. 1
GRIGNARD CARBONATION APPARATUS

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After hydrolysis of the reaction mixture, the nitrogen sweep was discontinued; the condenser was equipped for water cooling; the large stopcock was opened and the pure dry ether in flask 6 was heated to boiling. The ether extraction was carried out in this way without contamination of the atmosphere.

The Synthesis of High Molecular Weight Intermediates Containing C^{14}

Styrene (O. K. Neville)

Twelve millicuries (24.1 g.) of methyl phenylcarbinol-C^{14} has been prepared in sixty-seven percent yield by a three-step process from carboxyl-labeled acetic acid. The procedure involved the conversion of acetic acid to acetyl chloride with phthalyl chloride; the Friedel-Crafts condensation of the acid chloride with benzene in the presence of aluminum chloride; and the reduction of the resulting acetophenone to methylphenylcarbinol with lithium aluminum hydride. The conversion of acetic acid to the acid chloride was necessitated by the failure of the direct condensation of acetic acid with benzene (which had given good results on a smaller scale) to provide satisfactory yields with larger quantities of materials.

A portion of the methylphenyl-carbinol containing 0.05 mc. of carbon-14 was dehydrated to styrene-C^{14} by treatment with sulfanilic acid at 200°C. The distilled styrene, diluted 500 times with inactive material, was thermally polymerized at 125°C. in a 1.5 mm. (i.d.) sealed tube. The total weight of polystyrene was 8 grams.

Experimental

Acetyl Chloride-C^{14} -- To 13.5 g. (18 mc.) acetic acid-1-C^{14} in a 200 ml. flask was added 100 g. of phthalyl chloride. The acetyl chloride was distilled through a short column and collected in a Dry-Ice cooled receiver which also served as an addition funnel for the next step. Due to the extreme volatility of the product, the yield was not determined. However, in a previous non-radioactive run the yield was over 95%.

Methylphenyl-Carbinol-C^{14}

To a 500 ml. flask equipped with a condenser, connection for the addition funnel, a magnetic stirrer bar, and a horizontal outlet (capped) for later ether extraction, was added 40 g. of anhydrous aluminum chloride and 125 g. of anhydrous thiophene-free benzene. The contents were cooled with a Dry-Ice bath until about one-half of the benzene was solidified. The acetyl chloride-C^{14} was added to the stirred suspension in one portion and washed in with 25 ml. of dry benzene. The reaction, which proceeded very slowly at this temperature, was allowed to take place over a period of about one hour, during which time the slow melting of the benzene maintained a low reaction temperature. After the mixture was stirred for an additional hour, the light yellow solution was hydrolyzed with 30% hydrochloric acid. The acetophenone and benzene were transferred by con-

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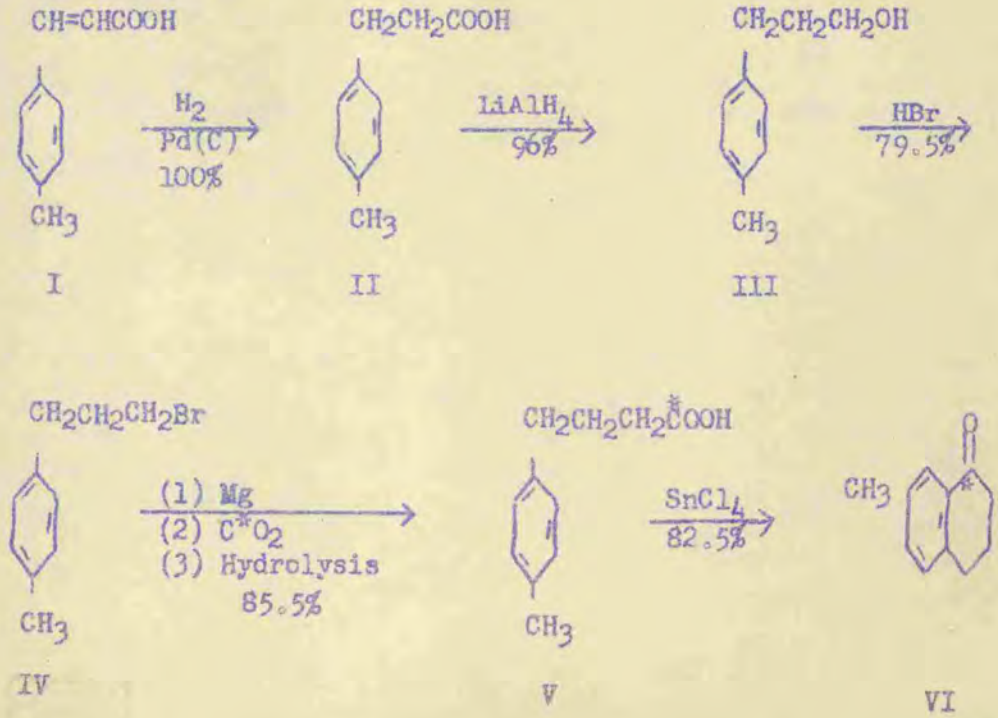
timuous ether extraction through the horizontal outlet tube to a receiver flask equipped with a nipple closed with a stopcock. The ether and part of the benzene were distilled through a short column in order to remove water carried over during ether extraction. The benzene solution of the crude acetophenone was added dropwise to a magnetically stirred solution of 4.5 g. of lithium aluminum hydride in 200 ml. of dry ether in a 500 ml. flask equipped, with a condenser, an inlet for the addition tube, and a horizontal outlet for later ether extraction. After completion of the addition, the solution was hydrolyzed with water followed by sufficient conc. hydrochloric acid to dissolve the inorganic precipitate. The resulting methylphenyl-carbinol-C^{14} was extracted with ether. The ether and benzene were removed through an 18 inch tantalum-spiral column and the product, b.p. 55-56°(2 mm.) was distilled through the same column. After nearly all of the product had been distilled, a 5.00 g. portion of inactive carbinol was added as carrier for radioactive product held up in the column and flask. The distillation was then continued to completion. In this way was obtained 19.08 g. (corrected for the added 5.00 g.)(69% yield based on acetic acid).

Carbon^{14} assay of a diluted aliquot of the material by dry combustion and ion current determination showed the presence of 11.8 millicuries of radioactivity in the product (radiochemical yield: 67% of theoretical).

Ring-labeled Benzoic Acid and Intermediates (C. J. Collins)

The following reaction scheme to be used in the preparation of ring-labeled benzoic acid has been carried out with non-radioactive materials. Yields are shown below the arrows, but do not necessarily represent optimum conditions:



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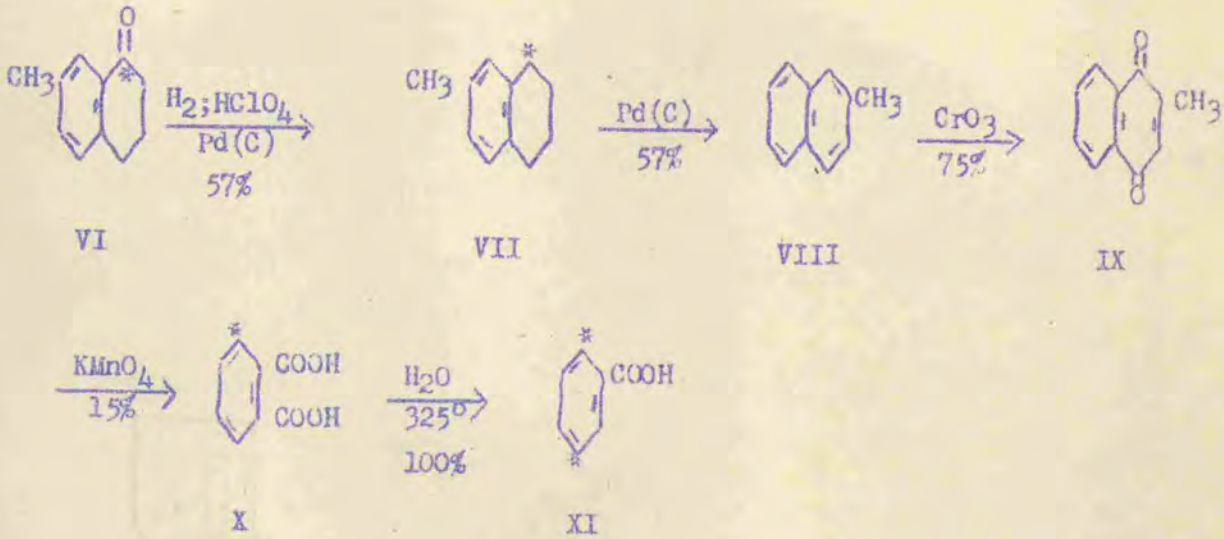

The lithium aluminum hydride reduction of p-methylcinnamic acid (I), produced an unsaturated alcohol, probably p-methylcinnamyl alcohol. This behavior of p-methylcinnamic acid is surprising in view of the observation[2] that hydrocinnamyl alcohol is obtained when cinnamic acid is similarly treated. p-Tolylpropionic acid (II) was prepared by the catalytic hydrogenation of I before conversion to the alcohol (III) with lithium aluminum hydride. Preparation of the bromide (IV) and the carbonation of the Grignard to yield 4-(p-tolyl)-butyric acid (V) proceeded smoothly. Ring closure of the acid (V) and hydrogenation of the methyl tetralone (VI) in the presence of 5% palladium-on-carbon catalyst and a trace of perchloric acid[3] yielded 7-methyl-1,2,3,4-tetrahydronaphthalene (VII). Dehydrogenation in the presence of 30% palladium-on-carbon catalyst gave 2-methylnaphthalene (VIII) which was oxidized with CrO_3 to 2-methyl-1,4-naphthoquinone (IX). Phthalic acid was obtained in 15% yield by the permanganate oxidation of IX. Further work is in progress on this oxidation. Decarboxylation of phthalic acid in aqueous solution at 325°C., according to the procedure of Sultanov[4] yielded pure benzoic acid quantitatively.

Experimental

3-(p-Tolyl)-propionic Acid (II) -- In a typical run, 200.0 mg. p-methylcinnamic acid, 125 mg. of 5% palladium-on-carbon catalyst, and 10 ml. of glacial acetic acid were stirred in a hydrogen atmosphere until 31.6 ml. of hydrogen was absorbed (30.5 ml. was the theoretical volume at 21.5°C. and 744.6 mm. pressure). The mixture was filtered through talc, concentrated and desiccated yielding 203 mg. (100%) of crude product, m.p.

(2) Nystrom and Brown, J. Am. Chem. Soc. 69, 2548 (1947).
(3) Kindler and Dschi-yin Kwok, Ann. 554, 9 (1943).
(4) Sultanov, J. Gen. Chem. (USSR) 16, 1835-44 (1946); Chem. Abstracts 41, 6223 (1947).

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110-115°. Recrystallization yielded crystals melting at 117-118°[5]. Larger runs gave similar results.

3-(p-Tolyl)-propyl Alcohol (III) -- The procedure of Nystrom and Brown[2] for ether-insoluble acids was employed. Thus 10.5 g. acid (II) yielded 9.13 g. of carbinol (96.2%), after distillation in vacuo.

3-(p-Tolyl)-propyl Bromide (IV) -- The procedure employed was analogous to that described for n-dodecyl bromide[6]; 8.72 g. alcohol yielding 9.90 g. of 3-(p-tolyl)-propyl bromide (IV) (79.5%) after distillation under high vacuum.

4-(p-Tolyl)-butyric Acid (V) -- The carbonation apparatus shown in Figure 2 was used for this reaction. In flask 5 was placed 0.90 g. of magnesium turnings, 25 ml. of dry ether, and 5.0 ml. (6.37 g.) of 3-(p-tolyl)-propylbromide (IV). A $CHCl_3$-CCl_4 mixture was added to powdered Dry-Ice in the reflux condenser 7. Dry-Ice baths surrounded traps 3 and 8. Trap 4 contained Drierite. A half-concentrated barium hydroxide solution was contained in the chamber attached by a ball-joint to the medium-frit sintered-glass funnel 9. Into flask 1, 6.00 g. of barium carbonate and 5 ml. of distilled water had previously been measured. The length of the capillary inlet tube was so adjusted that it did not at this time extend below the surface of the aqueous suspension. The entire apparatus was swept with dry helium gas, which was introduced through the top of funnel 2, and a positive pressure of helium was maintained throughout the experiment. A hot-water bath was then raised about flask 5, and the Grignard reaction started immediately. It was vigorously agitated with refluxing for 1 hour, at which time the hot water bath was replaced with a Dry-Ice-chloroform bath adjusted to a temperature of -40 to -45°C. (Below this temperature the Grignard reagent precipitated.) The barium carbonate in flask 1 was slowly decomposed (one-half hour) with 5 M perchloric acid, and the mixture was agitated with a magnetic stirring bar. The carbon-dioxide-addition product began to precipitate almost immediately. (During one experiment, the temperature of the bath surrounding flask 5 was allowed to rise momentarily to -20°C., at which temperature the precipitate completely dissolved; in this run the yield was less than 50%.) Carbon dioxide not absorbed by the Grignard solution was trapped in the barium hydroxide bubbler. After the barium carbonate was completely decomposed, the sweep was continued an additional five minutes, with the mechanical stirrer still in operation, and 50 ml. of an aqueous solution containing 7 ml. concentrated phosphoric acid was slowly added through the funnel 6. The Dry-Ice bath surrounding flask 5 was removed to prevent freezing of the water. The mixture was allowed to warm to room temperature, and the helium sweep was continued 1 hour, during which time a considerable amount of carbon dioxide was recovered from the hydrolysis mixture. The mercury seal stirrer was removed, and replaced with a male joint ring-sealed to a tube which extended to the bottom of flask 5, and the two layers were forced under

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(5) Miller and Rhode, Ber. 23, 1897 (1896) gave a m.p. of 116°.
(6) Reid, Ruhoff and Burnett, Organic Syntheses, Coll. Vol. II, p. 246 (John Wiley and Sons, 1943).

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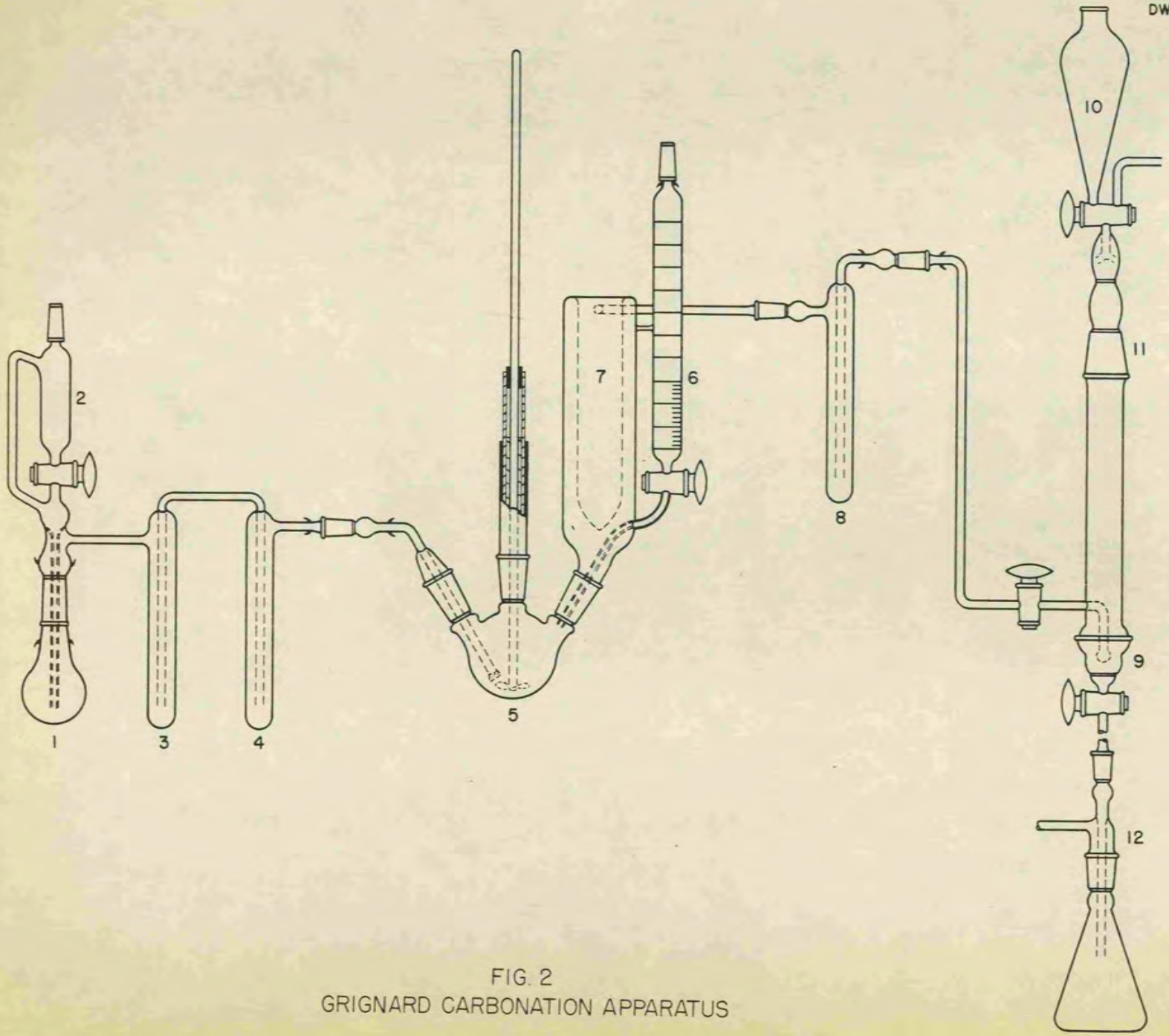

FIG. 2
GRIGNARD CARBONATION APPARATUS

helium pressure into a continuous extractor, and ether-extracted for eight hours. The ether solution was concentrated to a colorless oil which solidified on standing. To this solid was added 75 ml. of saturated sodium bicarbonate solution, and the mixture was stirred with a magnetic stirring bar for 1 hour. The aqueous solution was washed with 3 - 5 ml. portions of ether using the extractor described previously[7]. The bicarbonate layer was acidified with 20 ml. concentrated hydrochloric acid, and the white precipitate was removed by continuous ether extraction. Concentration and desiccation yielded 3.63 g. of crude 4-(p-tolyl)-butyric acid, m.p. 54-55° (softening 51°), (85.5% based on unrecovered barium carbonate).

Recrystallization of 2.09 g. acid from petroleum ether gave 1.31 g. acid, m. p. 57.5 - 59°.

7-Methyl-1,2,3,4-Tetrahydronaphthenone (VI) -- To 504 mg of a cold solution of 4-(p-tolyl)-butyric acid, m.p. 57.5-59.0° in 6.0 ml. dry benzene was added 620 mg. phosphorous pentachloride. The mixture was allowed to stand one and one-half hours at room temperature, and then cooled once again, and treated with 1.2 ml. of a solution prepared from 5 ml. $SnCl_4$ and 10 ml. dry benzene. Almost immediately a cream-colored precipitate appeared. The suspension was allowed to stand fifteen minutes and then treated with 6 N hydrochloric acid. The benzene layer was washed several times with dilute hydrochloric acid, concentrated, and the resulting oil was distilled several times into successive traps on a high vacuum line. The product crystallized on standing, and had a melting point of about 30°C. In this way 373 mg. of 7-methyltetralone (VI) was obtained (82.5% yield). The semicarbazone melted at 223-225°[8].

7-Methyl-1,2,3,4-Tetrahydronaphthalene (VII) -- Using high vacuum technique, 271 mg. of VI was distilled into a flask to which was added 150 mg. palladium-on-carbon (5%) catalyst, 5.0 ml. glacial acetic acid, and 0.10 ml. of 70% perchloric acid. The mixture absorbed 90% of the theoretical amount of hydrogen. It was filtered through a talc pad on a sintered glass disc, and washed through with 10 ml. glacial acetic acid. The solution and washings were combined, neutralized with aqueous sodium bicarbonate solution, and continuously extracted for eight hours with 50 ml. of ether. The ether fraction was concentrated and distilled under high vacuum yielding 141 mg. (57%) of 7-methyl-1,2,3,4-tetrahydronaphthalene (VII).

2-Methylnaphthalene (VIII) -- Dehydrogenation of 2-methyl-1,2,3,4-tetrahydronaphthalene (VII) was effected by placing 141 mg. of VII, and 30 mg. of 30% palladium-on-carbon catalyst[9] in the bottom of a test tube fitted with a "cold finger" condenser. The mixture was maintained at 215-225°C. for 22 hours[10] by immersion in a Woods metal bath. The contents of the flask were washed with four 3 ml. portions of ether, and the

(7) Collins, J. Am. Chem. Soc. 70, 2419 (1948).
(8) Krollpfeiffer and Schafer, Ber., 56, 620 (1923), give 224-225°.
(9) Zelinski and Turowa-Pollak, Ber. 58, 1295 (1935).
(10) Linstead and Thomas, J. Chem. Soc. 1127 (1940).

ether solution was filtered and concentrated yielding 78.3 mg. (57%) of crude 2-methylnaphthalene, solid up to 30°C. The picrate melted at 115-117.5°. Passage of the alcoholic picrate solution through a column of alumina yielded white crystals of 2-methylnaphthalene (VIII), m.p. 32-33°C.

2-Methyl-1,4-naphthoquinone (IX) -- To 5.00 g. of 2-methylnaphthalene (VIII) in 50 ml. of glacial acetic acid was added 7.80 g. of CrO_3 dissolved in 5 ml. of water and 25 ml. of glacial acetic acid. The temperature was maintained at 20-25° during the ten minutes required for the addition of the chromic acid solution. The mixture was allowed to stand overnight, then poured into an excess of water and continuously extracted with ether for twenty-four hours. The yellow ether-acetic acid solution was treated dropwise with saturated sodium bicarbonate solution until no more carbon dioxide was evolved. The mixture was continuously extracted with ether for eight hours. The ether solution was filtered after treatment with Norit, and concentrated, yielding 4.53 g. of 1,4-naphthoquinone (75%).

Phthalic Acid (X) -- 2-Methyl-1,4-naphthoquinone (IX), 1.31 g. was suspended in 20 ml. of water containing 1 g. of sodium hydroxide. A solution of 8.5 g. of potassium permanganate in 75 ml. of water was then gradually added, while the mixture in the reaction flask was boiled and vigorously stirred. All of the permanganate had been added in twenty minutes. The mixture was then heated an additional forty-five minutes, and 5 ml. of alcohol was added to decompose the excess permanganate. The mixture was passed through a talc pad on a glass funnel. The precipitate was suspended in dilute sodium hydroxide solution, stirred well, and once again filtered. The two filtrates were combined, acidified with concentrated hydrochloric acid, and subjected to continuous extraction with ether for three hours. On concentration, a red liquid was obtained possessing the odor of acetic acid. This was concentrated and desiccated, yielding 1.28 g. of white solid. This solid was dissolved in bicarbonate, the solution was washed with ether, acidified, and extracted with ether. The ether was evaporated and the white solid so obtained was triturated with ether, leaving 138 mg. of phthalic acid, melting with decomposition at 185-210°C. The p-nitrobenzyl ester was prepared and purified. It melted at 157.5-159° (Lit. 155.5°).

Benzoic Acid (XI) -- A pyrex tube containing 200 mg. of phthalic acid and 4.0 ml. of distilled water was sealed under high vacuum, the tube contents being frozen in liquid nitrogen. The tube was heated at 325° for 12 hours[4]. The tube was then cut open and the colorless solution was drained into a continuous extractor. The tube was washed with two 5 ml. portions of water and the washings and solution combined and extracted with ether. The ether was evaporated and the residue desiccated. Benzoic acid, m.p. 119-120°, without crystallization was obtained in quantitative yield.

[redacted]

V. Applied Nuclear Chemistry

Zirconium-Hafnium Separation
(J. P. McBride)

The extraction of Hf tracer from HNO_3 solution into benzene containing thenoyl trifluoroacetone (TTA) has been studied over the range of 0.5 to 3.5 molar H^+ and 0.005 to 0.1 molar TTA. A report, ORNL-303, has been completed and is being readied for publication.

The distribution ratio, organic over aqueous, was found to have a 3rd power dependence on hydrogen ion activity and a nearly 4th power dependence on TTA activity. The deviation from 4th power TTA dependence was explained by assuming the formation of an aqueous soluble Hf-TTA complex. The important reactions involved in the extraction have been postulated to be:

$$Hf(OH)_A^{+3} + 4HT_B \rightleftharpoons HfT_{4B} + 3H_A^+ + H_2O$$

and

$$Hf(OH)_A^{+3} + HT_B \rightleftharpoons HfT_A^{+3} + H_2O$$

where HT stands for TTA and the subscripts indicate the phases in which the various species appear (i.e., A-aqueous; B-benzene).

The following equation expresses the distribution ratio, organic/aqueous, in terms of HT and H^+ concentrations

$$D.R.\ (B/A) = \frac{4.0\,(1 + 15.5\,[HT]_B)\,[HT]_B^4}{[H^+]^3} \times 10^7$$

where $[HT]$ is the TTA activity in the benzene phase and $[H^+]$ is calculated using a semi-empirical value for the hydrogen ion activity coefficient read from a figure included in the report (ORNL-303).

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[redacted]

Recovery of Zirconium and Columbium from Separations Process Wastes:

(W. H. Baldwin, J. M. Ruth, A. W. Smith, and R. E. Wacker)

Summary and Conclusions.

Continued testing of various adsorbents has revealed nothing that will replace silica gel for the removal of Zr-Cb from Redox Process wastes. The reducing agents tested to prevent adsorption of dichromate did not greatly reduce the adsorption of gross gamma activity on silica gel. Variations in samples of silica gel and the temperature of adsorption did not change the equilibrium adsorption but did affect the rate (more finely divided samples and higher temperatures gave higher rates). The use of different samples of tracer changed the equilibrium values, this may be due to the relative amounts of Zr-Cb in the tracers.

For column operation, the washing of the silica gel may be accomplished with nitric acid or ammonium hydroxide with a lower loss of Zr-Cb than occurs in a water wash. Eluting agents tested in addition to oxalic acid included H_3PO_4, HF and H_2SO_3; these may be tested further.

Column runs indicated a relatively high radiochemical purity for the Zr-Cb product. The yield can be increased by minimizing losses during the washing step. A volume reduction greater than 14 was obtained. The silica gel retained a small portion (less than 3%) of the gross gamma activity.

Program.

Plans are being made to attempt column runs with Redox pilot plant waste 1AW in a hot cell. Preparation will require several weeks longer.

It is still planned to investigate the separation of Zr-Cb from UNH solutions.

Introduction.

Earlier tests were reported on the recovery of Zr-Cb from Redox waste solutions in ORNL-229. Silica gel was selected as an adsorbing material to be tested further.

Equilibration Tests.

Scouting tests have been continued in the search for other adsorbers. The tests recorded in Table 1 indicate two new samples of charcoal to be good adsorbents for gross gamma activity. It is to be noted too, that reagent MnO_2 removed 51% of the gross gamma activity from solution. It is planned to determine specific fission products adsorbed by this process to determine if any separation has been made.

[redacted]

[redacted]

TABLE 1

Equilibrium Studies

Scouting for new adsorbers: 0.5g agent (except where noted) and 10 ml synthetic waste spiked with 1AW from redox pilot plant were equilibrated in end over end agitator at 25° C. for 2 hours.

Adsorber	Gross Gamma Activity Remaining in Solution %
Pyrex glass wool	87
Darco (charcoal)	28
EZ-152-A (charcoal)	47
Kieselguhr	86
Talc	91
Silica gel (0.2g 60-200 mesh)	38
Do. plus 0.1g Na_2SiO_3	38
0.1g Na_2SiO_3	97
Hyflo supercel (Filter aid)	93,93
Celite 521 (Filter aid)	94,94
MnO_2 (Reagent)	49,49
Fe_2O_3 (Reagent)	71,71

During the adsorption of Zr-Cb on silica gel, dichromate which is present in the Redox raffinate is also adsorbed. Attempted elution of Zr-Cb by oxalic acid before removal of the dichromate led to the expected formation of bubbles with consequent interference with flow during column operations. A reducing agent for dichromate might be used in the feed solution or might be used to wash dichromate from the column after adsorption and before elution. Consequently, adsorption tests were made with various reducing agents added to the feed. Hydroxylamine sulfate seemed to prevent the adsorption of gross gamma activity on silica gel, but a similar effect was noted with potassium sulfate. Hydrazine sulfate, sodium nitrite and sodium bisulfite had little effect upon adsorption (see Table 2).

TABLE 2

Equilibrium Studies with Silica Gel (34)

0.5g Silica gel (60-200 mesh).
10 ml synthetic feed spiked with 1AW from run 4R, 1g. reagent added.

Added Reagent	Gross Gamma Activity (%) Left in Solution
None	32
Potassium sulfate	44
Hydrazine sulfate	32
Hydroxylamine sulfate	46
Sodium nitrite	30
Sodium bisulfite	31

[redacted]

[redacted]

Variables affecting the adsorption of gamma activity on silica gel have been studied and are summarized in Table 3. The equilibrium distribution was relatively little affected by the sample of silica gel used (compare tests 1 and 2, 4 and 7). The data indicate more Zr adsorbed by the finer gel. Rate of approach to equilibrium does differ; however, the 60-200 mesh sample was essentially at equilibrium after 1-3 hours at 26° C. while the 6-16 mesh required over 3 hours.

At higher temperatures the equilibrium distribution is the same as at lower, but the rate of approach has been increased (tests 2 and 3; 4, 5 and 6; 7 and 8). Here too there is an indication that more Zr might be adsorbed at higher temperatures but more tests would be needed to establish this fact.

The feed used in the equilibration studies caused relatively large differences in the amount of gross gamma activity adsorbed (tests 2, 7 and 9, Table 3). Relatively little difference was noted; however, in the amount of Zr and Cb adsorbed.

TABLE 3

Equilibrium Studies

Adsorption of Zr-Cb on silica gel approximately 0.55g silica gel. 10 ml synthetic feed agitated by tumbling end over end for 24 hours.

Test No.	Gel Size (mesh)	Temp. (°C.)	Feed	Gamma Activity Left in Solution		
				Gross	Zr	Cb
1	6-16*	26	A	23,23	20,18	8,9
2	60-200*	26	A	22,22	7,7	10,9
3	60-200	70	A	24	7	10
4	6-16	26	B	45,45	37,35	9,11
5	6-16	50	B	50	9	4
6	6-16	70	B	46	14	6
7	60-200	26	B	38,38	18,1	1,4
8	60-200	70	B	43	7	8
9	60-200	26	C	50,50, 50,50	7,5,6, 4	8,8, 8,9

* Referred to as coarse silica gel in ORNL-229, p. 60 ff.
**Referred to as fine silica gel in ORNL-229, p. 60 ff.

Feed A: 0.8M HNO_3, 0.74M $Al(NO_3)_3$, 0.05M $Na_2Cr_2O_7$ spiked with 1AW, run 4R.

Feed B: 0.74M $Al(NO_3)_3$, 0.05M $Na_2Cr_2O_7$ spiked with 1AW, run 8R pH 2.6.

Feed C: 0.8M HNO_3, 0.74M $Al(NO_3)_3$, 0.05M $Na_2Cr_2O_7$ spiked with 1AW, run 8R.

[redacted]

[redacted]

Water washing has been used to assist the removal of dichromate from the silica gel. This washing with water has been shown to remove varying amounts of the gross gamma activity, Zr and Cb from the silica gel (Table 4). This observation has not yet been accounted for.

The eluting agents that have been tested (Table 4) include, ammonium silicofluoride and HCl that appear to remove Zr selectively; phosphoric acid, hydrofluoric acid, and sulfuric acid; and nitric acid and ammonium hydroxide that removed less than 1% of the gross gamma activity. It is believed that ammonium hydroxide or nitric acid will be useful in washing the silica gel to remove dichromate before elution with oxalic acid.

TABLE 4

Equilibrium Studies

Washing and Elution from Silica Gel

Adsorption: App. 0.55g silica gel 60-200 mesh was equilibrated at 26° C. with 10 ml synthetic 1AW; centrifuged.

Washing: Silica gel was washed with 10 ml distilled water. Centrifuged.

Elution: Silica gel was equilibrated with 10 ml eluting agent at 26° C. for 10 hours, although equilibrium was nearly attained in 3 hours.

Gamma Loss (%)* in Water Wash			Eluting Agent	Gamma Activity (%)* Eluted		
Gross	Zr	Cb		Gross	Zr	Cb
			5.5M HCl	16,12	67,90	1,11
			0.06M $(NH_4)_2SiF_6$	26,12	82,93	7,12
16,17,5,5, 5,4	13,17	2,8	0.4M oxalic acid	31,31,37, 37,39,40	71,73, 69,64, 76,67	30,25, 61,73, 68,71
5,6	0.1,0.1	0.1,0.1	1.4M NH_4OH	0.3,0.3		
6.5	3.5	0.1,0.1	0.8M HNO_3	0.5,0.5		
			1M H_2SO_4	18,18	59,33	20,18
			0.5M HF	31,31		
			0.5M H_3PO_4	35,35		

*Percent of total gamma activity in the 10 ml of synthetic 1AW.

Additional column studies have been made during this period (Table 5 and 6). In column run 41 (Table 5) the samples were analyzed for Pu, Zr and Cb in addition to gross gamma. While the material balances are not good, it was felt that losses in waste solutions were not excessive. The Zr in the water wash was undesirably high, but it is felt that washing with NH_4OH or HNO_3 (Table 4) would remove dichromate without removing so much Zr. The product obtained from this run contained very little of the radioactive impurities for which tests were made (less than 0.4% of the total beta activity was determined as Ru, Ce and Ba; Pu was not detected).

[redacted]

[redacted]

TABLE 5

Column Run 41

Flow rate 1 ml per sq. cm. per min.

Feed Solution: 0.8M HNO_3
0.74M $Al(NO_3)_3$
0.05M $Na_2Cr_2O_7$
spiked with 1AW from run 8R.

Column: 3.5 cm., i.d., packed to 25 cm. with 6-16 mesh silica gel.

Sample	Volume ml.	Pu Alpha %	Gamma Activity(%) in Solution Gross %	Zr %	Cb %
Effluent	600	28	5	0.3	1.2
"	600	11	8	0.7	4.6
"	800	6	10	2.6	7.4
"	170	5	2	0.3	0.7
Water wash	2000	4	6	20	0.6
0.4M oxalic acid	650	N.D.*	96	44	131
Material Balance		54	127	67.9	145.5

In the 0.4M oxalic acid solution
Zr gamma was 13.1% and
Cb gamma was 84.8% of the gross gamma

Ru beta was 0.04%
Cr beta was 0.3%
Ba beta was 0.02% of the gross beta

*N. D. not detectable.

Run 42 (Table 6) was made using the same column and the same silica gel that had been used in run 41. Here 9 liters of effluent from the column contained 35% of the gross gamma activity and 615 ml of 5% oxalic acid elute contained 81% of the gross gamma activity. A volume reduction over 14 was thus demonstrated, and although the loss of gross gamma was increasing toward the end of the run, the major portion of the activity that was detectable with a probe was located on the top third of the column. The silica gel, after washing and drying, was measured and found to contain 2.6% of the gross gamma activity. It is to be noted that this silica gel had been used for at least two previous column runs.

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[redacted]

TABLE 6

Column Run 42

Feed solution and column were the same as used in Run 41, Table 5.

Sample	Volume ml.	Total	Percent of Total Gamma Activity Employed	Total
Effluent	430		0.8	
"	660		1.4	
"	530		1.2	
"	1000		3.0	
"	500		1.7	
"	1100		2.9	
"	1000		3.6	
"	1000		5.5	
"	600		3.6	
"	130		5.1	
"	2000	8,950	6.3	35.1
Water wash	2000		0.8	
Fore-run	90	2,090	0.05	0.9
0.4M oxalic acid	95		50	
	100		21	
	110		6.9	
	310	615	3.4	81.3
Water wash	310		0.5	
Water and alcohol wash	1500		0.2	
Silica gel	--		2.6	

Volume reduction 14

[redacted]

[redacted]

Separation of Fission Rare Earths: (C. E. Higgins, W. H. Baldwin)

Introduction and Summary.

Work has been continued on the development of a process for the separation of the fission rare earths (Y, Eu, and Sm) by ion exchange. (ORNL-229). Distribution data have been obtained for Eu and Y between resin and buffer at 26° C. and 50° C. which indicate that the higher temperature should aid separation since the distribution curves are more divergent at 50° C.

Distribution Data.

Distribution coefficients for Y between unscreened Dowex 50 resin and 0.238 M citrate were obtained at a temperature of 26° C., and were compared with those obtained and previously reported for Eu at the same temperature. These values for Y are shown in Table I and are plotted in Figure 1 together with the corresponding data for Eu. Practically no difference between the two curves can be noted except toward the higher pH's.

Similarly, tests were made at a temperature of 50° C. The values for Eu and Y are shown in Tables II and III respectively and are plotted in Figure 2. It can be seen from the graphs that increasing the temperature has separated the curves. At 26° C. the K_D for both Eu and Y was not significantly different from 20 at pH 3.02, but at 50° C. when K_D for Y was 20 at pH 3.1 the corresponding K_D for Eu was 34.

Further distribution tests are planned to be run at a temperature of 75° C.

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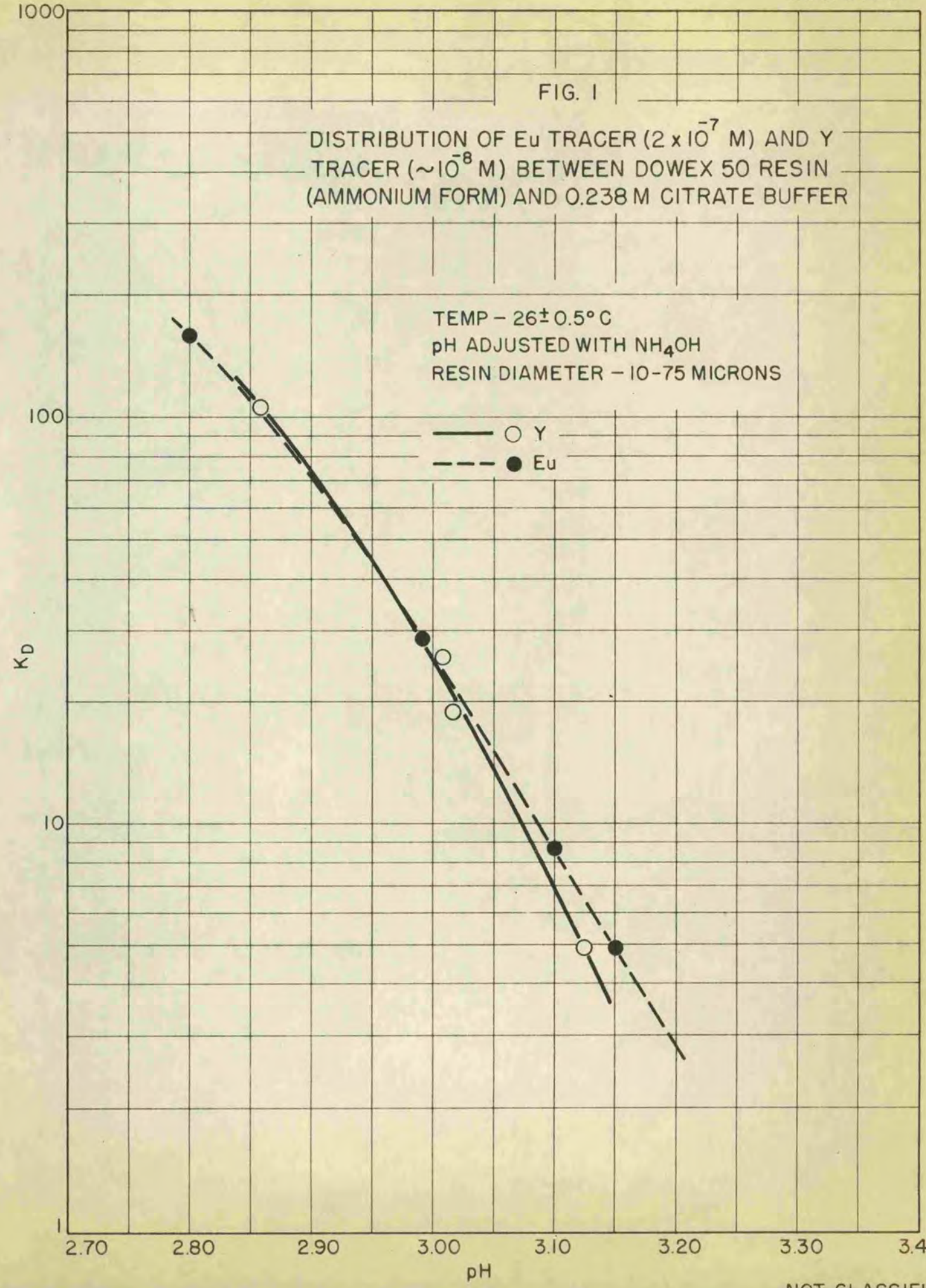

FIG. 1

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

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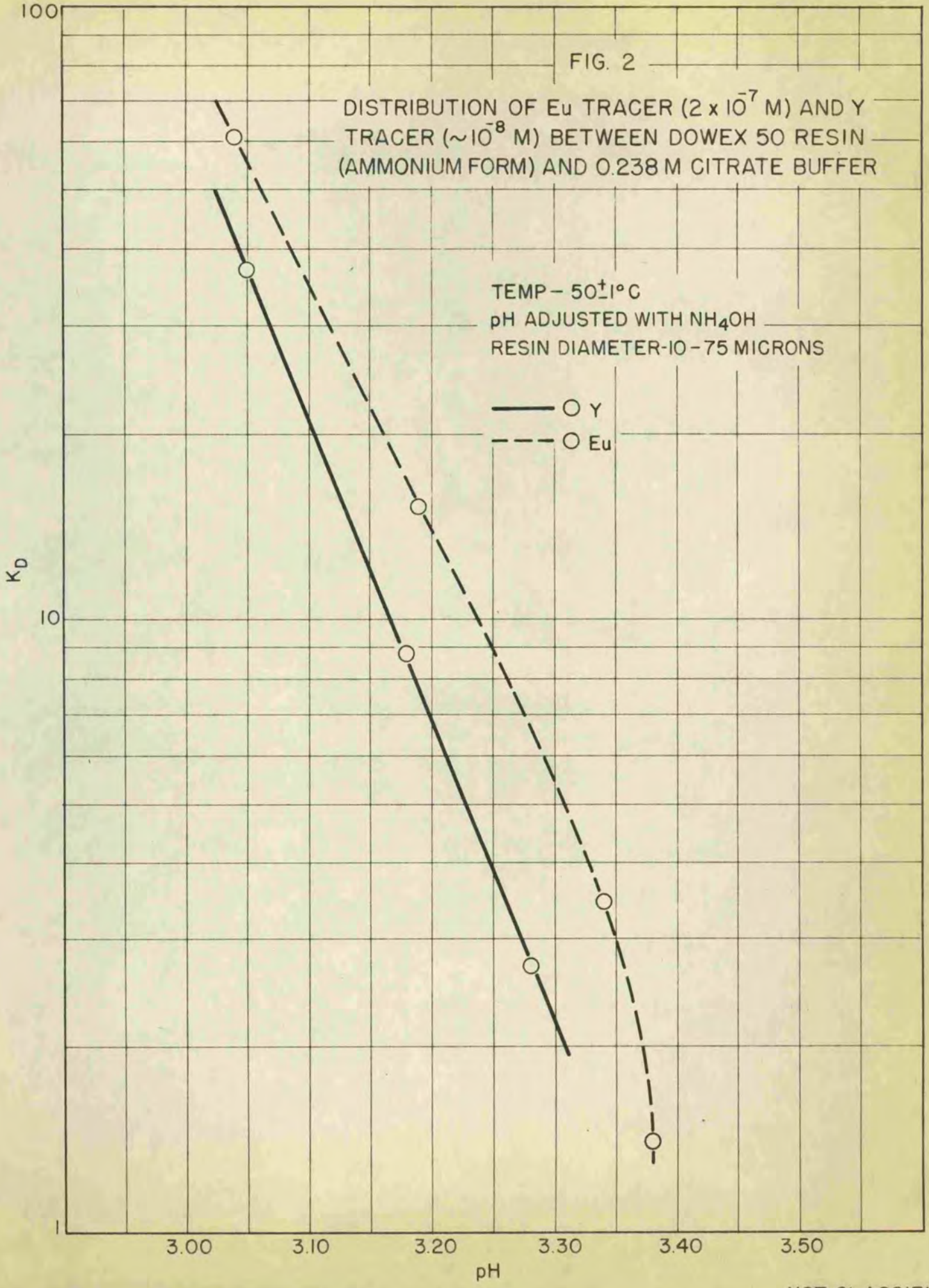

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TABLE I

Y Distribution Coefficients* at 26 ± 0.5 C.

Solution - 15 ml. 0.238 M citrate, ~ 10^{-8} M Y**, pH as tabulated, NH_4OH used to adjust pH.

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

pH	2.86		3.01		3.02		3.13	
Weight Resin (Grams)	0.1384	0.1542	0.6144	0.5888	2.0272	2.3170	5.2756	4.5232
Original Buffer pH	2.91	2.91	3.03	3.03	3.04	3.04	3.22	3.22
pH After 1st Equilibration	2.85	2.85	3.01	3.00	3.02	3.01	3.13	3.13
pH After 2nd Equilibration	2.86	2.86	3.02	3.01	3.02	3.03	3.13	3.13
K_D - 1st Equilibration	99.5	104	26.5	25.2	18.3	20.5	4.5	4.5
K_D - 2nd Equilibration	106	108	26.1	25.7	20.3	16.1	4.5	4.6
K_D - Resin Strip	106	102	25.4	24.9	17.8	20.0	5.5	5.8
Average	104	107	26.0	25.3	18.8	18.9	4.8	5.0
% Material Balance	99.8	97.1	98.8	98.5	91.2	104	113	116
Average Y K_D	106		25.6		18.8		4.9	

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

**Beta Activity in Buffer (Original) = 68,000 c/m/ml at 10% geometry with no absorber.

[redacted]

[redacted]

TABLE II

Eu Distribution Coefficients* at 50±1° C.

Solution - 15 ml. 0.238 M citrate, 2 x 10^{-7} M Eu^{**}, pH as tabulated, NH_4OH used to adjust pH.

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

pH	3.04		3.19		3.34		3.38	
Weight Resin (Grams)	0.2515	0.2113	0.7575	0.7510	2.5500	2.9377	4.5406	4.4355
Original Buffer pH	3.04	3.04	3.17	3.17	3.35	3.35	3.50	3.50
pH After 1st Equilibration	3.02	3.04	3.19	3.20	3.34	3.32	3.37	3.37
pH After 2nd Equilibration	3.04	3.06	3.18	3.19	3.36	3.33	3.38	3.38
K_D - 1st Equilibration	50.9	61.6	15.0	14.6	3.09	3.48	1.00	1.14
K_D - 2nd Equilibration	66.7	58.7	14.1	16.1	3.07	3.11	1.09	1.22
K_D - Resin Strip	65.8	63.2	15.9	18.0	4.06	3.80	2.04	2.06
Average	61.1	61.2	15.0	16.2	3.41	3.46	1.38	1.47
% Material Balance	99	104	105	106	111	108	121	118
Average Eu K_D	61.2		15.6		3.44		1.42	

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

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

[redacted]

TABLE III

Y Distribution Coefficients* at 50±1° C.

Solution - 15 ml. 0.238 M citrate, ~ 10^{-8} M Y**, pH as tabulated NH_4OH used to adjust pH.

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

pH	3.05		3.18		3.28		3.23	
Weight Resin (Grams)	0.2075	0.2476	0.7050	0.7415	2.6065	2.7122	5.7265	4.8177
Original Buffer pH	3.03	3.03	3.18	3.18	3.33	3.33	3.48	3.48
pH After 1st Equilibration	3.05	3.06	3.17	3.19	3.27	3.28	3.24	3.23
pH After 2nd Equilibration	3.04	3.04	3.18	3.17	3.28	3.27	3.23	3.23
K_D - 1st Equilibration	34.8	35.1	7.45	8.94	2.13	2.60	2.52	2.72
K_D - 2nd Equilibration	40.6	35.4	8.57	9.27	2.21	2.48	2.36	2.53
K_D - Resin Strip	38.6	38.7	9.73	9.97	3.28	3.52	3.09	3.62
Average	38.0	36.4	8.58	9.06	2.54	2.87	2.66	2.96
% Material Balance	99	103	104	102	114	113	115	119
Average Y K_D	37.2		8.82		2.70		2.81	

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

**Beta Activity in Buffer (Original) = 42,000 c/m/ml at 10% geometry and no absorber.

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Ion-exchange Separations: Production of Spectrochemically Pure Rare Earths for Research Purposes: (D. H. Harris, G. E. Boyd)

The inventory of spectrochemically pure rare earth preparations has been both added to because of new separations of Nd, Sm, Gd and Tb, and depleted by the meeting of various requests. The amounts presently on hand are:

Sc_2O_3	0.150 g.	Gd	15.000 g.
Y_2O_3	7.050	Tb_4O_7	0.801
La_2O_3	----	Dy_2O_3	1.399
CeO_2	----	Ho_2O_3	0.686
Pr_6O_{11}	----	Er_2O_3	6.262
Nd_2O_3	1.614	Tm_2O_3	0.649
Sm_2O_3	146.0*	Yb_2O_3	0.100
	2.338**	Lu_2O_3	0.131
Eu	----		

*Crystallized, contains $<0.1\%$ Eu
**By exchange column

Currently an ion-exchange column separation of a mixture containing 2.0-2.5 g. each of Sm, Nd, Pr, Ce and La is being conducted using a 15 cm^2 x 100 cm bed and an ammonium citrate buffer at pH = 3.10.

Recently several experiments have indicated the feasibility of attempting to effect a quantitative separation of europium from the Sm-Eu concentrate mentioned in ORNL-229 by means of an ion-exchange column. Accordingly, after one additional chemical concentration operation the Sm-Eu mixture will be put onto a large bed and separated.

Altogether during this past quarter 25 separate shipments have been made to seven A.E.C. research groups.

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Production of C-14: (A. J. Weinberger, W. H. Baldwin)

Most of this period has been devoted to the preparation of a report on the development of a process for obtaining C-14 from bombarded beryllium nitride. Some time has been spent preparing for the continuation of this program. The isotope production group is testing further the proposed process on 100 gram batches of beryllium nitride and assistance will be given to them when needed. It is expected that a certain amount of routine testing of the pressure build-up in bombarded beryllium nitride will be done to help predict the conditions to be encountered on long bombardment at high-flux. Targets in addition to beryllium nitride (such as aluminum nitride, calcium nitrate, potassium nitrate, magnesium nitride and calcium nitride) will be tested for C-14 production where necessary, including pressure development during bombardment. Methods will be sought for the reversal of chemical changes that may occur during bombardment.

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VI. Physical Chemistry and Chemical Physics

Spectra of the Heavy Elements and Rare Earths in Crystals and Solutions: S. Freed, C. J. Hochanadel

It was our aim to obtain solutions of salts and chelate compounds of the transuranic elements and of the rare earths having rather low viscosity at the temperature of liquid nitrogen in the hope that enough transformability would be left among the various species so that one or only a few would survive and be measured. Trivalent europium ion, Eu^{+++}, seems to be the only one* whose spectra from its salts in solution are so sharp at room temperature that the usual bands in the spectrum of the solution are resolvable into lines which may be counted. Since it is the number of lines within a group which is determined by the quantum character of the transition and the symmetry of the fields about the ions, a more general study of ions and transitions required a search for solutions exhibiting discrete spectra. It was natural to turn to solutions at low temperatures.

In the past, efforts to obtain solvents fluid at low temperatures were usually directed toward mixing substances liquid at room temperature but of low freezing points which together had a "freezing point" lower than any of the single or pairs, etc., of the component liquids. Solvent properties had, of course, to be kept in mind. For example, G. N. Lewis and his associates** employed a mixture of ether, isopentane, and ethanol to keep substances such as dyes and leuco-bases in solution near the temperature of liquid air. The solutions became rigid, however, at the temperature of liquid air.

To synthesize our solutions, the first step was to dissolve the salt under more or less normal conditions rather than at low temperatures so that the rate of solution would not be excessively slow; further dilution with solvents of low melting points could take place quickly at much lower temperatures than that of the initial solution of the salt. In our experiments thus far, normal propyl and normal butyl alcohol of high purity served as the solvent for the first step, and for the second, pairs of the following hydrocarbons in various proportions were employed - methane, propane, propene, butene-1, and isopentane.

The apparatus consisted of a dewar flask containing a mixing vessel of Pyrex glass which was connected with a capillary optical tube provided at its ends with windows of corex D glass. The salt was placed in the mixing vessel, and the dried alcohol was condensed on it from a vacuum system integral with the vessel. It turned out to be convenient to have the solution of the salt take place at about -20° C. The temperature was then further reduced, to about that of solid carbon dioxide, and the hydrocarbons were bubbled through the alcoholic solution and condensed there. The final solution was then siphoned into the optical tube.

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*For a short review of previous work - Simon Freed, Rev. Mod. Phys. 14, 105 (1942).

**G. N. Lewis, T. T. Magel, and D. Lipkin, J. Am. Chem. Soc. 62, 2973 (1940).

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We shall illustrate with an example. 20 mg. neodymium bromide hexahydrate ($NdBr_3 \cdot 6H_2O$) were covered with about 0.8 ml. normal propyl alcohol which had been introduced by condensation. The temperature was reduced to about 190° K, and 4 ml. propane and 4 ml. propene were then bubbled through the liquid and condensed. The resulting solution, about 0.005 M, was siphoned into the optical tube at the temperature of liquid nitrogen. At times, helium gas was used to transfer the liquid from one tube to another. However, its solubility in the liquid at these temperatures led to complications in some measurements.

Evidence that some transformations occur rather quickly at these temperatures came from an attempt to dissolve about 38 mg. rather than 20 mg. terbium bromide hexahydrate in the same volume of the solvent. (The relatively low absorption coefficient of terbium ion would require more ions in the light-path.) Between the time the solution was siphoned and that required for aligning the dewar flask in the optical path, less than an hour elapsed, and in that time, terbium salt precipitated out of solution. On the other hand, the less concentrated solutions of the neodymium salt remained transparent and unchanged for more than a week at the low temperature. It was found that the solvent remained fluid at the freezing point of nitrogen.

In the beginning, the absorption spectra were taken with a Bausch and Lomb quartz spectrograph, but the spectra from the solutions at low temperatures seemed so sharp that all subsequent spectra were taken on a twenty-one feet Jarrel-Ash grating spectrograph in Wadsworth mounting having a dispersion of 5 A/mm. in the first order.

The spectra of solutions of neodymium nitrate hexahydrate and of neodymium bromide hexahydrate at 77° K consisted of groups of lines, in some instances as sharp as 1 A, but for the most part, they varied from 2A to 6A. At 193° K, the lines were broader, and some regions were diffuse and faint. These were gathered up into lines at the lower temperature, and thus the general change which the lower temperature brought about was an increase in the number of lines.

Neodymium bromide hexahydrate in solution had groups in the same wave-length regions as the nitrate, but the structures of the groups were strikingly different. Even when the numbers of component lines within a group were the same, the intensity distribution and the spacings were widely different. The following table is an illustration of differences in the spectra of solutions of neodymium nitrate hexahydrate and of neodymium bromide hexahydrate.

Spectral Region	Temperature	Solution	Number of Lines	Spread in A
5200 A	193° K	Nitrate	4 diffuse	60
	77° K	Nitrate	10 sharp lines	100
	77° K	Bromide	10 sharp lines	90
5000 A	193° K	Nitrate	structureless blur	
	77° K	Nitrate	4 or 5 sharp lines	40
	77° K	Bromide	7 sharp lines	100

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Europium bromide hexahydrate possessed absorption lines of extreme sharpness at 77° K as was to be anticipated. The group at 4600 A consisted of four lines, two of which were separated by about one-half angstrom. This group has been identified as a transition from J = 0 to J = 3 with a maximum of seven lines (in fields of highest dissymmetry). The appearance of only four lines indicates that there is only one species of europium ion, Eu^{+++}, present in solution rather than a mixture of configurations.

The spectrum of thulium bromide hexahydrate in the same solvent consisted of considerably more diffuse lines, 10 A to 15 A wide except for two (of some sharpness) in the ultra-violet.

The electrical conductance of the solutions was measured at 193° K and 77° K. They were very sensitive to temperature, viscosity and seemed to vary for a while after a given temperature was thought to have been reached. The values were very low and sporadic.

We are much indebted to Dr. Fred J. Leitz, Jr. for his collaboration in the design of apparatus and in the early exploratory work.

Experiments with Molecular Beams -(P. J. P. Chastagner, Jr., E. H. Taylor)

The experimental work of the quarter has been preliminary, but some decisions have been made as to the specific experiments to be attempted first. It is planned to study the reaction pf potassium with bromine using neutron activation to measure the bromine and the surface ionization gage for the potassium.

This reaction is typical of those studied by Polanyi and his associates, and appears favorable for a trial of the presently proposed technique. The molecular beam method will enable direct measurement of the cross-sections of the molecules for scattering and for reaction, thus testing the indirect measurements which seem to show the reaction cross-section to be the larger.

All of the apparatus for the scattering - reaction experiment has been designed and is in the process of construction, with some parts being presently tested. A glass - metal apparatus for testing of beam sources (ovens) has been built, and will be used also for development of the technique of the neutron activation measurement of bromine deposited on a collector from the beam.

Experiments have shown that the bromine can probably not be measured by direct counting of an irradiated collector foil, since polystyrene, considered to be the best possibility, shows too high a counting rate after irradiation. Chemical separation of the activated bromine will apparently be necessary.

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Calorimetric Study of Nuclear Processes - G. H. Jenks and F. H. Sweeton

Now that liquid helium is available at the Laboratory, we have considered in detail the feasibility of using this substance in carrying out calorimetric measurements of the type in which we are interested, i.e., the measurement of the total energies of β and γ disintegrations.

It is quite probable that a calorimeter which will absorb 98% of the most penetrating γ radiations can be constructed and operated so that a heat input of 10^{-7} cal/sec can easily be measured to within 1%. This rate of heat input is equivalent to that from 0.1 millicuries of 1.0 Mev radiation and represents a 10^4 gain in sensitivity over that of the present γ calorimeter. In order to obtain this sensitivity, however, it will be necessary to use a heavy metal such as gold or platinum as the γ absorbing material so that the overall dimensions as well as the heat capacity of the calorimeter can be kept reasonably small.

A calorimeter of this sensitivity can be used to measure the decay energy of a large number of radioactive isotopes. Such measurements are, of course, useful in studying the decay mechanisms of the isotopes. There is also the possibility that a calorimeter of this sensitivity can be used to measure the total γ energy emitted upon neutron capture by a given nucleus. Neutron currents as high as $10^7/cm^2/sec$ can be obtained in beams from the pile. If 5×10^6 neutrons are absorbed by the nuclei under investigation, and the emitted γ's absorbed in the calorimeter, the heat input would be of the order of 10^{-6} cal/sec and measurable.

Before starting construction of a calorimeter containing a large mass for absorbing γ rays to the extent mentioned above, we have planned first to undertake the simpler problem of developing a calorimeter containing only enough mass to absorb β and low-energy γ rays. From experience with this calorimeter, we should be able to predict the characteristics of a calorimeter containing a larger mass.

The construction of the β-absorbing calorimeter is well under way. The various parts for the calorimeter proper, which is to be of metal, have been obtained, and the calorimeter is now being assembled. Construction of the various gas handling systems associated with the calorimeter has also been partially completed.

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The Crystal Structure of Potassium Perruthenate: (M. D. Silverman and H. A. Levy)

Although potassium perruthenate was first prepared in 1876, its crystal structure has never been determined. The original preparation[1] was first reported to be isomorphous with potassium permanganate; however, in later reports, Debray and co-workers[2,3] described the perruthenate as black, tetragonal octahedra, stable in air, and not isomorphous with potassium permanganate.

Essentially pure $KRuO_4$ was first prepared by the method of Debray and Joly. The starting ruthenium salt was a mixture of $RuCl_3$ and $RuCl_4$ which was fumed several times with H_2SO_4 to eliminate chlorides. Ruthenium tetroxide was then distilled from the sulfuric acid solution into a 1 M KOH solution after addition of potassium permanganate as oxidizing agent. The solution of the distillate was orange-colored due to ruthenate ion (which was first formed) and gradually changed to the dark green color of the perruthenate. Small black crystals were deposited on the walls of the receiver; this crystalline material was washed with the mother liquor several times, then with ice-cold freshly distilled water, and was finally dried *in vacuo* over anhydrous calcium sulfate.

Copper radiation Debye-Scherrer patterns of $KRuO_4$, which were successfully indexed on the basis of a tetragonal lattice,[4] showed the structure to be isomorphous with scheelite ($CaWO_4$). Other crystals which have this structure are the periodates of sodium, potassium, ammonium and rubidium; the perrhenates of silver, sodium, ammonium and rubidium; the molybdates of lead, strontium, calcium and barium, and tetragonal bismuth arsenate. The lattice constants were obtained with greatest precision from reflections in the back-reflecting region on a pattern in which NaCl was mixed with the $KRuO_4$ in order to provide calibrating lines. The lattice spacings considered most precise are as follows:

$hk\ell$	a_o, Å	c_o, Å
440	5.6089	
620	5.6089	
640	5.6083	
0·0·16		12.991

(Values adopted: $a_o = 5.609 \pm .002$ Å, $c_o = 12.991 \pm .002$ Å, based on a_o for NaCl = 5.638 Å)

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(1) Sainte-Claire, Deville and Debray, Compt. rend. 83, 926 (1876).
(2) Debray and Joly, Compt. rend. 106, 1494 (1888).
(3) Dufet, Bull. soc. franc. mineral 11, 216 (1888).

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The pattern shows the following systematic absences: $hk\ell$ when $h + k + \ell$ is odd, corresponding to a body-centered lattice; hk0 when h or k is odd; 00ℓ when ℓ is not a multiple of 4. These absences and no others are required by the space group C_{4h}^{6} - $4_1/a$, which is the space group to which scheelite and its isomorphs belong. The symmetry of this space group requires that 4 milecules of $KRuO_4$ be present in the unit cell, with Ru and K occupying the 4-fold special positions (a) and (b)[4]. The 16 oxygen atoms could be in two sets of 8-fold positions (c), (d), or (e), or in general positions (f). The former are not consistent with the observed intensity data, nor do they lead to a chemically plausible structure. The calculated density is 3.20 g. cm^{-3}.

Single crystals of the salt, required for the assignment of parameters to the oxygen atoms, were obtained by distilling RuO_4 into an alkaline solution of potassium ruthenate, placing the mixture in a refrigerator for several days, and washing the crop of small black crystals as described above. Several crystals, whose shapes were approximately that of an elongated tetragonal octahedron, about 0.03 x 0.02 cm. were mounted on glass fibers, and rotation and Weissenberg (moving camera) photographs, using Cu unfiltered radiation, were taken. The shape of the reflections on the photographs indicated that absorption of radiation by the crystal was considerable and that structure factors from the intensities were not to be trusted. Calculations verified this belief; accordingly, new equatorial Weissenberg photographs about the a and c axes were taken, using Mo unfiltered radiation.

Intensities of hk0 and $h0\ell$ reflections were estimated visually, using a multiple film technique, and observed structure factors $|F|$ were computed. Absorption corrections were ignored after graphical estimates indicated that relative $|F|$ values would not be disturbed more than $\pm$ 5% for hk0 or $\pm$ 8% for $h0\ell$.

The x and y parameters were determined systematically from the hk0 reflections. Greatest weight was given to reflections occurring at the same value of the Bragg angle (e.g., hk0 and kh0, $h \neq k$). Final values were selected by a least squares procedure.

The z parameter was determined from the $h0\ell$ reflections. Optimum agreement with the data required the use of separate temperature factors for Ru, K and O. The final values of the atomic positions are Ru at (000), K at (00 1/2), O at (xyz) and crystallographically equivalent positions, with

$$x = 0.75_6, \quad y = 0.11_7, \quad z = 0.92_8,$$

accurate to about 0.002.

The ruthenium coordination is a tetrahedron slightly flattened along the c-axis, with a Ru to O distance of 1.80 Å.

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(4) "International Tables for the Determination of Crystal Structures", Gebruder Borntraeger, Berlin (1935).

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VII. Radiation Chemistry

Radiation Chemistry: (J. W. Boyle, J. A. Ghormley, D. M. Richardson, reported by E. H. Taylor)

General: There has been little experimental activity in this field during the present quarter, most of the effort being directed toward the future. Planning and following the construction of the building for the Van de Graaff generator has occupied one man. Toward the end of the quarter, consideration began to be given to the reconstitution of the program in radiation chemistry, and to the recruitment of replacements for the staff.

Uranium Oxides as Catalyst for Recombination of H_2 and O_2 (J. W. Boyle)

An experimental test has been made of the suggestion (by A. O. Allen) that a U_3O_8 - UO_3 mixture might catalyze the recombination of H_2 and O_2 formed under radiation in an aqueous solution. Such a catalyst would be attractive, since such oxides might be the fuel in a heavy water slurry pile. Experiments showed, however, that the recombination was not thus catalyzed, even at temperatures up to 326° C.

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VIII. Physical Measurements and Instrumentation

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Electron and Optical Microscopy, Electron Diffraction
(L. T. Newman, T. E. Willmarth)

(1) Beryllium

A sample of machined beryllium rod which corroded at room temperature, as submitted by James Reed of the Technical Division, was examined to determine the type of surface defects, nature of the corrosion product formed in surface "blisters", and microstructure. The sample, very fibrous and of poorly defined grain structure, when examined microscopically at high power showed the presence in great abundance of crystalline material of hexagonal structure in the faces and at the interfaces of the beryllium grains. This material was subsequently identified by Dr. M. Bredig of the X-ray section as beryllium oxide. Quantitative analysis by W. Wolkowitz of the Analytical Section gave a figure of 5.6% BeO present.

Two other samples of beryllium, not from the same billet, were examined for comparison purposes. X-ray examination showed one of these to contain approximately as high a percentage of BeO as the original sample, the other, a small amount of BeO. These samples were also cross-sectioned and the microstructure examined at high power. The sample containing the high percentage of BeO presented much the same appearance under the microscope as the original sample, whereas, in the second, although a little BeO was observed, it was more widely dispersed. However, local concentrations were found, especially in the region where fibrous fractures had taken place. Material identified as beryllium carbide was also found in this sample in much greater abundance than those previously examined. A complete report covering this work will be issued in the near future.

(2) Particle Problem

Some time has been spent on various phases of the particle problem, mainly in connection with questions connected with particle size.

(a) In co-operation with J. Gost and J. S. Cheka micrographs of cascade impactor samples collected by R. H. Wilson, University of Rochester, were made and radioautographs of these samples made by Health Physics were compared with those of the cyclone and filter samples collected by the Chemistry Division (R. Livingston, et al). The following comments appear to be warranted:

1. The cascade impactor did not collect the large particles (those above approximately 20 microns) which appeared to carry a large fraction of the activity in the cyclone samples.

2. For particles between 1 or 2 and 10 microns the deposition from the different jets showed a good correlation

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between the size expected from the different jets and the size calculated from the intensity of the radioautographs, assuming 1 disintegration per minute per cubic micron.

The impactor samples indicated a somewhat larger number of particles in the 5 to 10 micron range than the cyclone samples, which may have been due to the pile conditions occurring at the time or to the fact that the larger particles in the cyclone samples obscured the images of the smaller particles in the radioautographs.

3. The amount of uranium shown by analysis on the deposits from the finer jets and filter in the case of the impactor samples, and on the filter in series with the cyclone, was much larger than could be accounted for by the density and number of particulate images shown in the radioautographs, assuming the specific activity used above. It had been assumed that the uniform, diffuse activity shown by the radioautographs was all due to the presence of decay products of fission gases, whose presence was proved by the three filter experiment. However, the high uranium analysis made it necessary to consider the presence of large numbers of uranium oxide particles, so small that they cannot be distinguished as single particles in the radioautographs. Another factor of importance in the interpretation is that the number of particles of the order of 1 to 5 microns escaping the cyclone and being caught on the filter was extremely small. These facts suggest that the dispersion may consist of 2 distributions, one being rather coarse and due to mechanical action, and the other consisting of very fine particles (less than 1 micron) possibly produced by the fission process.

(b) In co-operation with J. Gost radioautographs were made of FG-50 filters which had been in service in the filter building for some time. As expected most of the active particles were on or near the front surface of the first filter, but a few fair sized particles were found on the back surface of this filter and on the surfaces of the second filter. Since particles of such a size (several microns, calculated from density of radioautographs assuming 1 disintegration per minute per cubic micron) would not be expected to penetrate such a filter on the basis of CWS tests of penetration, Gost carefully separated the pads into sections parallel to the surface, and radioautographs were made of these inside surfaces. These sections showed no large particles, so it seems probable that the particles formed on the outer surfaces were deposited there during filter removal, or less probably by leaks around the filters. A very few particles of estimated size of approximately 1 micron or less were found inside the filter pad and this appears to be consistent with CWS measurements on the effect of size on penetration through somewhat similar filters.

A noticeable deposit of active dust occurred close to the wires holding the glass wool in place; this is an interesting demonstration of the action of electrostatic precipitating forces.

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(c) At the request of C. J. Borkowski experimental Air-way filter bags were examined microscopically and found to be made of coarse wood pulp fibres. There was no evidence of any very fine fibres, which greatly increase the effectiveness of filters, especially for small particles. The pore size of these filters was measured by D. Trauger, K-25, and found to be from 10 to 25 microns. This compares with 6.5 microns for CWS #6 paper, also measured by Trauger. On the basis of these measurements and the lack of fine fibres in the Air-way filters it is obvious that they would not compare with CWS filters, especially with small particles, and this was found to be the case when their efficiency is tested with these small particles. From previous experience with similar filters, however, it seems extremely probable that they would be reasonably efficient for particles of 1 to 2 microns diameter and that the efficiency would increase to approximately 100% for particles only a little larger than this size. It would be expected, therefore, that they would catch with reasonable efficiency any active particle whose presence could be demonstrated by a radioautograph of 1 day exposure, assuming the specific activity mentioned above.

(d) In co-operation with S. Beall, photographs of the oxidation effected in a punctured slug suspended in an air-stream at 250° C. for several weeks were made. It was very interesting that the oxidation resulted in uniform, concentric layers of oxide around the whole slug although the original puncture consisted of only one very small hole at one end. These layers easily broke up into thin, rather brittle flakes; in general the particle size of these flakes was large enough to be seen with the naked eye and in some cases they were ¼" across. This supports the prediction of a rather coarse particle size distribution for slow oxidation of the uranium slugs.

(e) Small segments of concrete taken from the filter house were examined microscopically to note the nature of particles imbedded in the material as previous examination by J. Gost and radioautographs had shown them to be radioactive. Numerous black particles or agglomerates similar to those observed in cyclone samples were found. Most of these appeared to be of the order of 100 microns and over.

(3) K-25 Work

Work for K-25, in connection with their research for the new plant, K-29, took up a large percentage of the time. This work consisted in the main of the examination of numerous powder samples with the optical and electron microscope to determine the shape and particle size. A large number of barrier samples were also examined microscopically. All of this work involves techniques in sample preparation which are time consuming. Work is being continued as samples are presented.

(4) Ion Exchange Resins

Photomicrographs of Dowex 50 resins, oven dried and air dried, were made to determine comparative size after drying.

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(5) Chlororuthenium

Photographs were made to show the appearance of solutions at various stages in the preparation of chlororuthenium.

(6) Fission Tracks

Photomicrographs at 750X were taken of fission tracks for M. Shapiro of the Physics Division in connection with the meeting of the American Physical Society.

(7) Corrosion of Beryllium

A great number of photographs were taken of samples submitted by the Technical Division to show results of various corrosion tests.

Considerable time was also spent with a representative of the Technical Division suggesting types of photographic equipment for their set-up for photographing corrosion specimens and instructing him in the lighting, camera operations, placement of material to be photographed, and the processing of negatives and prints.

(8) Zirconium

Samples of zirconium were obtained and work started to develop suitable technique for mounting and polishing this metal to retain inclusions for metallographic observation, inasmuch as future project work is contemplated with this metal.

(9) Metal Evaporation

A number of jobs were done during this period evaporating aluminum, gold, silica, etc., to deposit a film on various materials for members of the Chemistry and Physics Divisions. Considerable time was also taken improving techniques in making replicas of metallic surfaces and shadow-casting for the electron microscope.

(10) Photographic Work

Lantern slides were made for various members of the laboratory for presentation at technical meetings, which occurred during this period. The usual volume of prints was also made.

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X-Ray Diffraction
(M. A. Bredig)

a) Crystal Structures of Beryllium Oxide, Nitride and Carbide.

In order to avoid considerable difficulties encountered with the maintenance of a controlled atmosphere in the electric carbon resistor furnace at Norris, a somewhat improvised high-temperature heating device was used in the latest experiments. It consisted simply of a small tungsten wire coil, surrounded by a cylindrical nickel radiation shield, and suspended in the center of a spherical 2 liter glass flask. Using up to 1000 watts, pellets of beryllium oxide mixtures with nitride or carbide were heated inside the wire coil in an argon, helium or nitrogen gas atmosphere to temperatures exceeding 2000°C.

While all experiments to date on the subject of the new crystal phases of beryllium oxide and nitride are being written up in greater detail in a separate report, the main results of these latest tests may be summarized here as follows:

1) Beryllium nitride is now definitely established as the compound responsible for producing, in amounts corresponding to a minimum mole fraction $N:(N+O) = 0.15$, or to a composition Be_3N_2:14 BeO, approximately, the new, optically biaxial, crystal phase in beryllium oxide above 2000°C. At a mole fraction of 0.21 or a composition Be_3N_2: 8BeO, the limit of solid solubility of nitride in the new phase had not been reached.

Elucidation of the phase relations at the higher nitride concentrations would require further study. The variability in composition, accompanied by considerable changes in the lattice spacings, suggest the assumption of a solid solution, not of beryllium nitride in the hexagonal phase of the oxide, but of the oxide and the nitride in a possible binary compound, an oxynitride, of as yet unspecified composition, $Be_{(1.5x+y)}N_xO_y$.

2) Beryllium carbide, in the absence of nitrogen, does not produce this phase, but does so in the presence of nitrogen through conversion into nitride.

3) More highly concentrated preparations of a new crystal phase observed in a high-fired beryllium nitride (see previous report) do not bear out the original assumption of a simple hexagonal structure similar to that of lanthanum sesquioxide. Reservations made at that time in regard to the structure proposed turned out to be justified. Weak lines are present in the x-ray pattern which rule out the hexagonal structure and suggest a lower symmetry. It remains to be seen whether at the high temperature at which the phase was produced true hexagonal symmetry similar to the one suggested actually may exist.

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b) Radiation Effects in Copper-Beryllium Alloys
(with R. H. Kernohan)

X-ray back reflection photographs were taken of a series of specimens which had previously been examined in the spectrometer. Difficulties in attempts to measure accurately lattice spacings were encountered due to the high degree of orientation and distortion in these precipitation-hardened alloys. With these limitations it may be said that no measurable change in lattice dimensions under the influence of the rather small dosage of radiation, of three weeks in the X-10 pile, was observed.

c) High-Temperature Heating Chamber for X-Ray Spectrometer
(with F. ". Sherrill)

After an extended interruption due to manpower shortage, work was resumed. A new bottom part was made and beryllium metal was procured for use in windows. A heating element consisting of tantalum wire wound on an aluminum crucible has been designed and is nearing completion.

d) Miscellaneous

Work included the identification, in an airborne particle collected by Health Physics, of U_3O_8 in combination with SiO_2 (probably a sand grain from the sand-blasting of the pile channels), the detection of unsuspected beryllium oxide in several beryllium metal samples, the examination of various substances to be used in neutron diffraction studies (C.G. Shull) and of irradiated, ordered and disordered, copper-gold alloys (S.Siegel).

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Beta Proportional Counters

C. J. Borkowski, R. A. Dandl, R. Stone

A method for determining absolute disintegration rates of x-ray emitters has been developed. A proportional counter having 50% geometry is used. The chamber in which the source is mounted is first filled to a pressure of 80 cm. Hg with Argon-Butane mixture and the counting rate is observed. The pressure is then reduced to 40 cm. and the counting rate again obtained. From the ratio of the counting rates the absolute number of x-rays (all of the same energy) can be calculated as follows:

$$\frac{1 - e^{-2x}}{1 - e^{-x}} = \text{Ratio of counting rates}$$

This expression can be simplified to:

$$I_o = \frac{R_x}{1 - \frac{R_{2x}}{2R_x}}$$

where I_o = disintegration rate

R_x = counting rate at lower pressure

R_{2x} = counting rate at higher pressure ($2xR_x$)

All that is necessary is to obtain the counting rate at pressures which vary by a factor of two.

The following data illustrates the method, 7.0 KEV x-rays from Ni^{59} were used.

Counting rate/min. at 80 cm. pressure = R_{2x} = 296,300

Counting rate/min. at 40 cm. pressure = R_x = 185,000

I_o from this data equals 986,000 dis/min.

Another set of pressures were used:

Counting rate/min. at 40 cm. pressure = R_{2x} = 185,000

Counting rate/min. at 20 cm. pressure = R_x = 103,700

I_o from this data equals 990,000 dis/min in close agreement with the previous pressures used.

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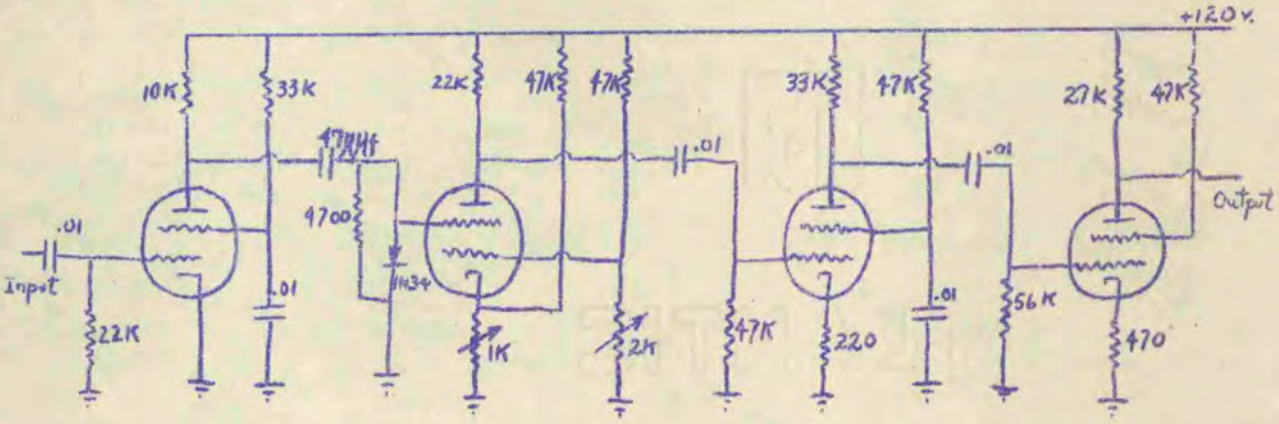
A beta amplifier was sought capable of handling a wide dynamic range of input pulses without introducing multiple pulses or losing small pulses which closely follow large ones. This indicates an amplifier in which we control overshoot and grid current.

The first step would seem to be to get a stage which will compress the range of pulses fed into it, limiting the large pulses and amplifying the small ones. Simple tube saturation will not do, since the grid current drawn in such a situation will introduce undue dead time following a large pulse.

Various schemes were tried, including reduction of filament voltage in an attempt to saturate before grid current was drawn, and a multiple tube stage wherein low pulses went through a high gain tube and high pulses through a low gain. The latter worked satisfactorily when properly adjusted, but was complicated, and required overall adjustment whenever a tube was changed.

The next circuit tried was a stage whose gain varied inversely with input voltage, so as to saturate without drawing grid current, and cut overshoot to a minimum. This was achieved by feeding the signal into the screen and giving the control grid an adjustable potential with respect to ground. The minimum potential of the cathode above ground is also adjustable. Increase in plate current increases the negative bias on the control grid, and since this grid is much more effective than the screen so far as tube control goes, the signal range is compressed.

This circuit was simple, and worked well when properly adjusted. An amplifier was designed around it using this circuit as the second stage. The complete layout is as below.



All Tubes 6AK5's

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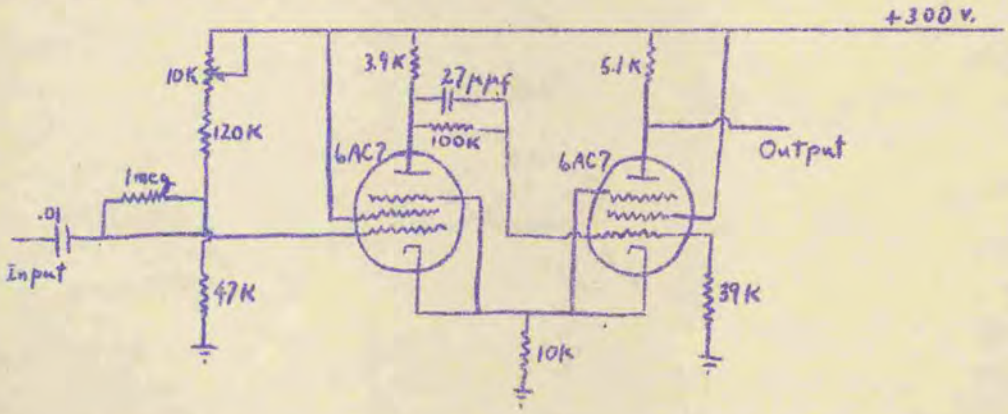
With a pulse input and a scope on the output, the two pots should be adjusted until overshoot is just eliminated. This setting will vary for different tubes, and since gain may be secured at the expense of overshoot reduction, the setting may also be a matter of application.

It was found that the circuit did not eliminate multiple pulsing under all circumstances, and that for proper operation it should work into a trigger pair designed to take its output. The Schmidt type circuit given in Chapter 4 of the LA electronics reports was found to work well when modified to take negative pulses, as shown below.



The main disadvantage of this trigger is that it requires a 300 v. supply, and also that the 6AC7's are somewhat bulky. A 6J6 trigger pair, working on 120 v., could probably be designed along the same lines, and would no doubt be more satisfactory.

However, since R. A. Dandl has in the meantime developed a 3-tube 2-stage feedback amplifier which acts in much the same way as this circuit, and over a much wider dynamic range, it was decided to leave this circuit in its present state. The latter circuit will be described in the next quarterly report.

Special Instruments
E. Fairstein

An ionization chamber for alpha energy measurements was designed and built. It is expected that this chamber will improve the resolution of the alpha range analyzer by a factor of at least five.

An electronic multiple-pulse generator is being built at the present time to investigate some of the factors affecting the resolution of the analyzer. The generator will also be very useful in determining dead-times and recovery-times of scalers and other counting equipment.

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Some time was also spent on developing a method for recording electrical data on a logarithmic scale. A maximum practical range of four cycles will be available with a stability associated with mechanical systems rather than electronic systems.

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Analytical Chemistry

Ionic Analyses - Research and Development

The Polarographic Determination of Lead in Micro Volumes (W. H. Davenport)

The lead used as a carrier in the radioactive barium production process is removed by an electrolysis step. The solution after the electrolysis contains barium, lead, iron, chromium and nickel in trace amounts. Analysis of this solution for lead by the dithizone extraction method is hazardous from the radiation standpoint and the usual lead concentration, 0-10 γ/ml., represents the lower limit of sensitivity for the method.

A polarographic method for lead has been developed which may prove to be a satisfactory substitute for the dithizone method.

Lead is determined polarographically in a 1 N sodium hydroxide medium using a cell designed to handle from 100 λ to 2 ml. of solution. Iron, if present, will precipitate, and must be complexed with sodium tartrate.

The polarographic wave obtained for lead in a strongly alkaline medium (Figure 1) corresponds to the reduction of the biplumbite ion. The half-wave potential is a function of the hydroxyl ion concentration. In 1 N sodium hydroxide E 1/2 = 0.755 versus the saturated calomel electrode (1). In order to work with small volumes, a micro polarographic cell is used. This cell, (Figure 2) similar to the one developed at Argonne (2), has a mercury pool anode and a side arm for mercury overflow which maintains a constant level for the pool. The half-wave potential for the lead wave versus the mercury pool anode was found to be about -0.6 V.

Any oxygen present will of course result in an interfering wave but its removal by degassing with nitrogen is impractical when working with micro volumes. Therefore, sodium sulfite is used to reduce the oxygen. The concentration of sodium sulfite is not critical provided an excess of that required to remove oxygen is present.

It was found that the interference, due to precipitation of iron in basic solution, could be removed satisfactorily by complexing the iron with sodium tartrate. The tartrate shifts the iron wave to a more negative value than the lead wave and the two are sufficiently far apart to permit accurate measurement of the diffusion current of the wave due to lead. This diffusion current of lead is depressed slightly by sodium tartrate. The decrease in wave height seems to be a linear function of the concentration of tartrate ion. Therefore, the supporting electrolyte should contain only enough tartrate to complex completely the expected iron present and calibration curves should be prepared using the same tartrate concentration.

(1) I. M. Kolthoff and J. J. Lingane, "Polarography" (1941), p. 165.
(2) J. I. Watters, "Micropolarograph Cells", p. 15, AECD-1988, May 18, 1948.

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NOT CLASSIFIED
DWG. 6809

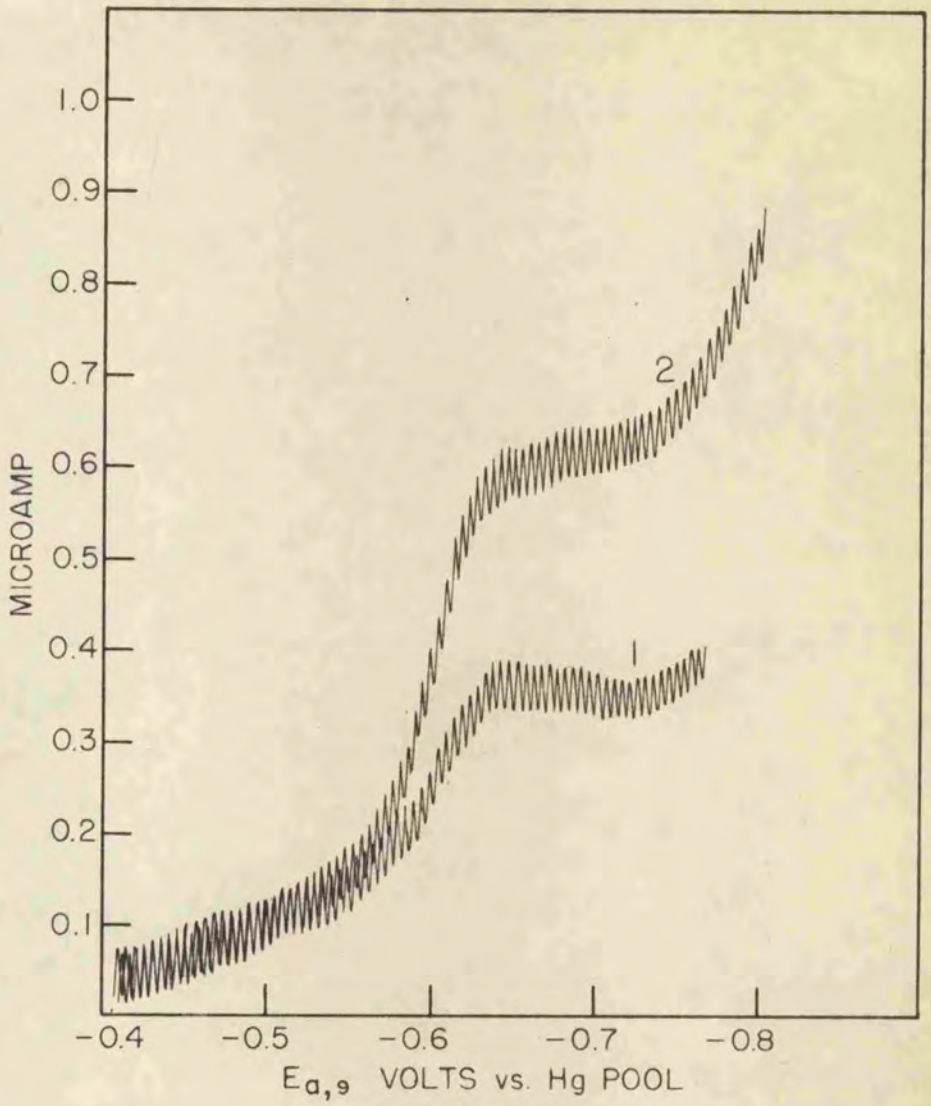

Figure 1.

POLAROGRAMS FOR REDUCTION OF BIPLUMBITE ION IN SODIUM HYDROXIDE

1. 4 γ Pb/ml PLUS 6 γ Fe/ml, 50 γ Ba/ml 4 γ Ni/ml 4 γ Cr/ml
2. 10 γ Pb/ml PLUS 15 γ Fe/ml, 125 γ Ba/ml 4 γ Ni/ml 4 γ Cr/ml

NOT CLASSIFIED
DWG. 6808

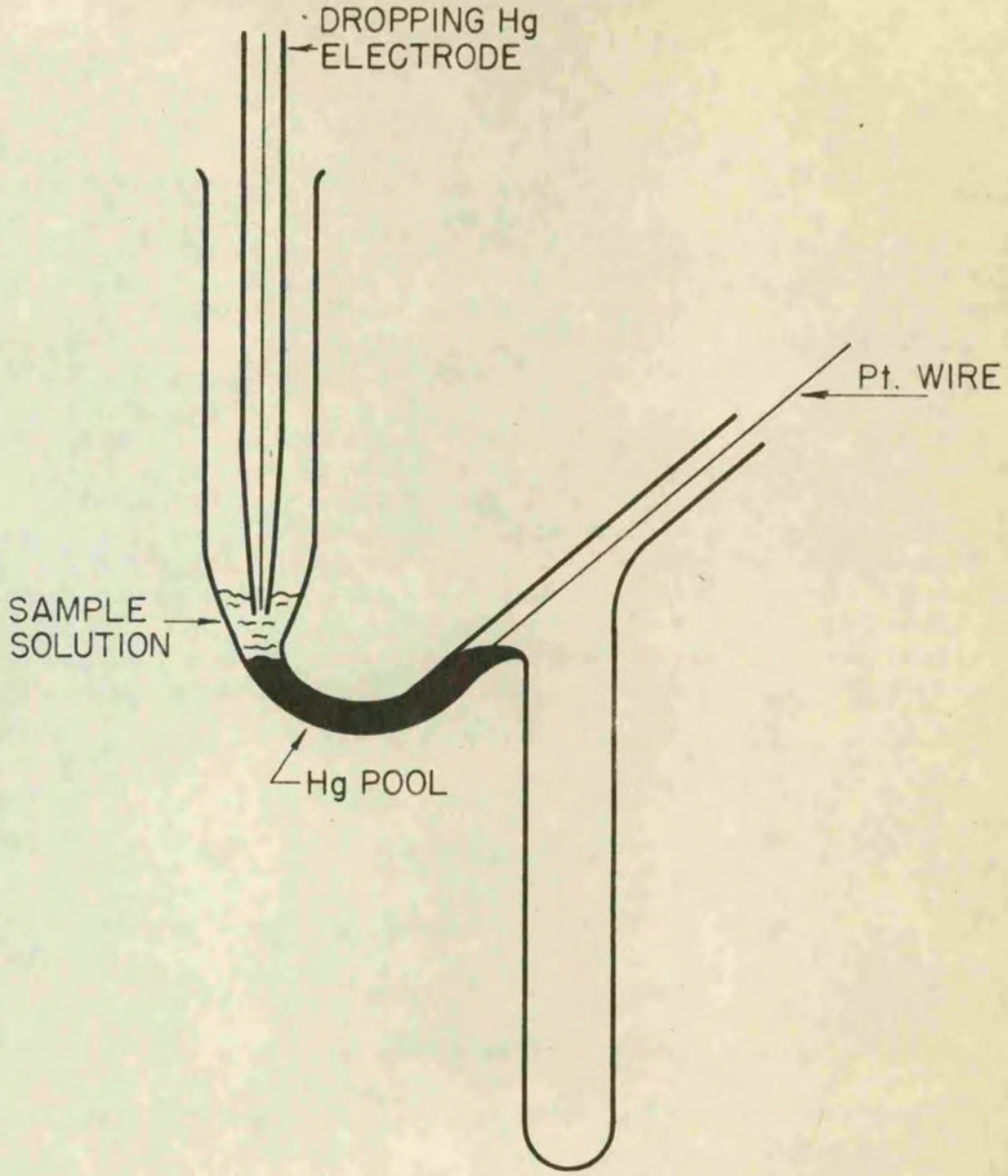

Figure 2.

MICROPOLAROGRAPH CELL
FULL SCALE

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Chromium and nickel give no interfering waves when present in concentrations equal to that of lead. Larger amounts were not investigated. Barium when present in the ratio 25 parts of barium to 1 part lead does not interfere.

A standard calibration curve was prepared for lead in the concentration range (4 γ - 60 γ) Pb/ml.

Polarography of Cobalt (P. F. Thomason)

Several samples of electroplated cobalt metal that is used to monitor thermal neutrons were submitted by Mr. O. Sisman of the Technical Division for the determination of nickel. As the nickel impurity was expected to be less than 0.1%, the polarographic standard addition method of Lingane and Kerlinger (1) was used for the analysis.

Baker's analyzed reagent grade cobaltous chloride was used as a synthetic sample to test the method. Polarograms were obtained of a 0.2% solution of the cobaltous chloride in a 0.1 molar pyridinium chloride, 0.1 molar pyridine supporting electrolyte. The nickel reduction wave, at a 1/2 wave potential of approximately -0.75 vs. the saturated calomel electrode, was measured. Then sufficient nickelous chloride was added to the solution to increase the nickel concentration by .0001 molar and the polarogram recorded. The increase of the nickel wave was measured on the polarogram and the concentration of nickel was calculated by the following equation:

$$C_1 = \frac{i\ v\ C\ std}{\Delta i\,(V+v) + v}$$

where

C_1 = original concentration of the nickel

i = the original diffusion current

Δi = the increase of the diffusion current

V = the original volume of the unknown solution with cell

v = the volume of standard solution added

C_{std} = the concentration of the standard solution.

The original concentration of nickel was calculated to be 14×10^{-6} molar. This corresponds to 0.039% nickel in the reagent grade cobaltous chloride.

The cobalt metal samples were dissolved in concentrated hydrochloric acid and diluted to 100 ml. Polarograms were obtained for 5 ml. aliquots diluted to 10 ml. containing 0.1 molar pyridine and 0.1 molar

(1) Lingane, J. J., and Kerlinger, H., Ind. Eng. Chem. Anal. Ed., 13, 77, (1941).

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pyridinium chloride. Then 1.0 ml. of a 0.001 molar nickel chloride solution was added and the polarogram recorded. A polarogram of a blank containing the reagents indicated a small correction for the nickel impurity. The results of the analyses are shown in Table I.

Table I

Nickel in Cobalt Metal

Sample No.	Wt. of the Sample in 100 ml.	Original Diffusion in Microamperes	Increase of Diffusion Current in microamperes	Concentration of Nickel	% Ni
1	0.3704 g.	.164	.615	3.0×10^{-5} molar	.046
2	0.8182 g.	.287	.595	6.8×10^{-5} molar	.048
3	0.4739 g.	.195	.404	4.0×10^{-5} molar	.049

Precision Dow Recordomatic Titrator (F. J. Miller, P. F. Thomason)

A Dow Precision Recordomatic Titrator has been received by the analytical group to facilitate routine volumetric analyses. The chief advantages offered by the titrator are the speed of a titration, accuracy, by elimination of human errors, and a permanent record is obtained of the titration. It also lends itself to being adapted to the automatic titration of highly radioactive solutions without exposure of the operator to the radiation.

The titrator consists of four essential parts:

(1) A Dual Automatic Reagent - Feeding Unit
(2) An Electronic Control System
(3) A Brown Electronik Type K Recording Potentiometer
(4) A Vacuum Tube Bridge - Type Voltmeter

The dual automatic reagent-feeding unit comprises two separate units, each consisting of a 50 ml. Pyrex glass feed pump, which holds and delivers the reagent to the titration beakers. One unit may be filled and adjusted while the other pump is performing a titration. The feed pump is synchronized with the strip chart, and both are driven simultaneously by a relay-operated motor.

In the electronic control system, the small current is picked up from the Brown balancing system and amplified before it is fed to a sensitive relay which operates the reagent-feeding system. The simultaneous action of the Brown recorder with the input impulses automatically operates the reagent-feeding unit.

A modified Brown Electronik type K recording potentiometer is used to record the titration. The modification consists of the addition

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of five bridge systems for the five voltage ranges in the instrument. The input to the potentiometer consists of a line-operated vacuum tube voltmeter of the balanced tube type. Titrant is allowed to be added only when the potentiometer is automatically balanced - thereby allowing the recorder to plot equilibrium values.

A vacuum tube bridge-type voltmeter is used for compensation of electrical characteristics for different types of electrode systems.

The Recordomatic Titrator was received in a damaged condition from the Precision Scientific Company. The chart drive was out of alignment and a mercury solenoid switch was broken, evidently in shipment. The damage was repaired by the instrument group and preliminary acid, base titrations were performed. The performance of the instrument was rather disappointing as it was prone to over titrate the sample. This was due to an insensitive feed control which was apt to feed a large slug of the titrant and the titration curve would show an equivalence point without further addition of the titrant. Dr. M. T. Kelley revised the electronic relay feed control so that only a 1 - 2 millivolt impulse is required to stop the feed. This sensitive control permits a small increment addition of the titrant during the entire titration.

One of the 50 ml. syringes has been replaced with a 10 ml. syringe in order to titrate with smaller volumes of titrant without loss of accuracy. The pyrex feed syringes have been fitted with smaller capillary tubing to the buret, and the buret tip has been drawn to a finer tip. This was found necessary to prevent streaming of the titrant from the buret after the feed was automatically stopped by the electronic control. It was found necessary to change the gears of the chart drive in order to increase the speed of the chart in relation to the feed rate.

The instrument seems to be satisfactory after these changes and is being tested for precision and accuracy. The results obtained to date are shown in Table II.

Table II

Acid - Base Titrations with Recordomatic Titrator

2 ml. of .052 N H_2SO_4 Titrated with 1.04 ml. of 0.1 N NaOH

Chart Travel in Cm.		Max. Dev.	Average Dev.
1.	7.79*	0.7%	0.39%
2.	7.85	1.9	0.89
3.	7.75	1.3	0.67
4.	7.75	1.9	0.86
5.	7.72	1.9	0.79
6.	7.69	1.8	0.75
7.	7.80	1.9	0.92
8.	7.69	0.8	0.35
9.	7.71	1.4	0.51

*Note: Each value shown for the chart travel represents the average of ten titrations.

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These data show the instrument is capable of titrating in this range with a maximum deviation of less than 2% and an average deviation of less than 1%.

Colorimetric Determination of Palladium (E. K. Hanig, P. F. Thomason)

A palladium iodide precipitation is used in the xenon process (4). Several samples of PdI_2 have been analyzed for Mr. A. R. Brosi and Mr. G. W. Parker. As the total amount of palladium was expected to be approximately one milligram, a colorimetric method was to be desired.

It has been reported by Yoe and Overholser (1) that thiourea gives a yellow color with Pd^{++} both in an acid and an ammoniacal solution. Therefore, the possibility of utilizing this color for a spectrophotometric method was investigated.

A solution of palladium chloride was made by dissolving approximately 900 mg. in 5% hydrochloric acid and diluting to 100 ml. This solution was standardized gravimetrically by the conventional dimethylglyoxime method (2). A dilution of the standard solution was made to give a solution containing 5.39 micrograms of Pd per ml. Aliquots of this solution were pipetted into 25 ml. volumetric flasks and 5 drops of concentrated HCl were added followed by 1 ml. of 10% thiourea. The solutions were diluted to volume with distilled water and the transmittancy determined with a Beckman spectrophotometer at a wavelength of 380 mμ vs. a reference containing all of the reagents but palladium.

It was found that the color complex formed immediately and was stable for at least an hour. It obeyed Beer's law from 25 to 500 micrograms of palladium in the 25 ml. final volume. The acidity of the solution was not critical as twice the amount of HCl did not affect the transmittancy. An excess of thiourea did no harm. Interference from other cations was not checked since the samples were expected to be pure palladium iodide. Known synthetic samples of palladous iodide were recovered with an accuracy of ±3%.

Equipment for the Redox Analytical Group (H. L. Hemphill)

The automatic fusion device used for the fluorimetric analysis of uranium has been improved by limiting the motion of the spider which holds the platinum fusion dishes to a simple rotation. This is accomplished by using an electric motor in place of the hydraulic lift on the previous models. It had been found that the hydraulic lift was subject to wear which caused erratic rotation of the spider. The smooth operation of the revised device produces a more uniform fused plate which should improve the precision of the method.

A new sampler has been made utilizing a Greiner micro burette (3) mounted on a small mechanical elevator. The positive control of the mercury column by the calibrated plunger permits the delivery of accurately measured samples. It should be especially useful for the delivery of small

(1) Yoe, J. H., and Overholser, L. G. Ind. and Eng. Chem. Anal. Ed. 14, 435-7 (1942).
(2) Hillebrand, W. F., and Lundell, G.E.F., Applied Inorganic Chemistry, John Wiley and Sons, Inc., N.Y., Page 281, (1929).
(3) Gilmont, Roger, Anal. Chem. 20, 1109, (1948)
(4) Mon-432, p. 75.

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volumes of liquid for the falling drop specific gravity determinations (1).

The ionic analyses of the contents of the O.R.N.L. uranium waste storage tanks have been completed and the results are available in a memo of W. K. Eister to F. L. Steahly (2).

Polarograph for Routine Control Laboratory (M. T. Kelley)

It was mentioned in quarterly report ORNL-229 that a recording polarograph was being constructed by the instrument group. This instrument has been completed and is being used by the control group for the analysis of redox process solutions.

The instrument is somewhat similar to the Sargent Model XX polarograph that has been studied by Sweeton (3). The bridge slide wire consists of a Beckman Model A helipot that is engaged by a clutch mechanism (4) to a synchronous motor drive. The position of the slide-wire is shown by a vernier dial which is mounted on the helipot shaft. A Brown electronic potentiometer is used to record the current-voltage curve. As the chart drive is also driven by a synchronous motor the motions of the bridge and chart are essentially locked together during a run.

This instrument differs from the Sargent instrument in the following respects:

1. A Brown recorder with high impedance input is used so that the dead space of recorder does not increase with increasing sensitivity as with the Sargent instrument.

2. The use of the high impedance input enables one to use a high resistance damping circuit (using oil-filled rather than electrolytic condensers) which eliminates errors due to leakage through the condensers.

3. The high resistance damping circuit (300,000 ohms) eliminates the change of damping characteristics with change of sensitivity on all but the most sensitive scales.

4. A special compensator has been added to eliminate the rapid rise of current of high sensitivities which is due chiefly to "condenser" current. Since the condenser current changes linearly with applied voltage, it is compensated out by applying a potential in the current measuring circuit proportional to the applied voltage, but opposing that due to the cell current. Further work will be done to try to compensate the "condenser" current more effectively by changing the rate of application of compensating voltage at the electrocapillary zero potential, since the "condenser" current curves change slope at this point.

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(1) Quarterly Report, CNL-37, April 16, 1948, p. 140.
(2) Central Files No. 49-2-142, Feb. 8, 1949.
(3) Results of a Study of Sargent Model XX Polarograph Memo from F. H. Sweeton to L. B. Rogers, Aug. 21, 1947.
(4) Drawing No. D-4967.

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With this type of compensator it is hoped to improve the precision of measurement of small concentrations of ions (10^{-6} to 10^{-5} molar).

Several known synthetic uranium samples were submitted to the control laboratory to check the accuracy and precision of the polarograph. The results are shown in Table III.

Table III

Sample No.	Uranium Present	Uranium Found	% Error
1	53 γ/ml.	54 γ/ml.	+2.0
2	106 "	109 "	+3.0
3	212 "	214 "	+2.0
4	265 "	272 "	+2.6
5	265 "	259 "	-2.3
6	212 "	205 "	-3.3
π	106 "	110 "	+3.8

These data show this polarograph is capable of accuracy in the order of ±3% which is the degree of accuracy expected by the polarographic method.

The polarograph is proving particularly useful in analyzing uranium samples containing phosphate and for checking results obtained by other analytical methods for uranium.

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Radiochemical Analyses - Research and Development

Summary

The decay scheme of Ba^{140} has been investigated, with evidence for a new gamma ray. Work is in progress on determination of gamma efficiencies of the conventional G-M counter. Development and testing of activation-analysis methods are going forward. Seven radioisotope target materials are being studied to determine product yields and nature and yield of impurities. Development of TTA-extraction methods for radiozirconium is partially completed.

Decay Scheme of Ba^{140} (W. S. Lyon)

In attempting to use Ba^{140} in determination of gamma efficiencies (See 2 below), a soft radiation was noted in absorption curves. This appeared to be a beta of energy 0.3 - 0.4 Mev. Although Engelkemeier, Novey and Shover (1) noted the soft radiation in absorption curves, other investigators (2,3,4,5) found only a 1.05 - 1.2 Mev β. In the single previous spectrometer investigation (6) only a 1.05 Mev β and 0.5 Mev conversion electrons were found. From coincidence counting and absorption studies, Engelkemeier (7) concluded that the decay scheme involved a 1 Mev β (75%), and a 0.4 Mev β followed by a 0.5 Mev gamma (25%).

A sample of Ba^{140} was obtained from 706-D Operations personnel. After addition of carrier it was purified by sulfate precipitation, ferric hydroxide scavenging, chromate precipitation, and repeated HCl-ether precipitation. Decay studies have been begun. In addition, the material was then diluted, and a suitable aliquot (containing about 100 microcuries) was evaporated and examined on the spectrometer. Measurements had to be completed in two hours because of La^{140} growth. Two different batches were used, and several series of measurements were made from each. Two betas were found, of 0.99 and 0.46 Mev. Conversion electrons from gammas of 0.15 and 0.53 Mev were found. Gamma energies will be determined by use of the spectrometer, and coincidence counting will be employed to clarify the decay scheme.

Gamma Efficiencies (W. S. Lyon)

Since a knowledge of gamma efficiencies for the conventional gamma-counting technique would be valuable for assaying certain radioisotopes, such efficiencies are being determined by use of nuclides whose decay schemes are known. Aliquots of a given material are counted for gamma in the conventional way (sample on second shelf, lead-aluminum sandwich on first). The disintegration rate is then determined on the gamma chamber (8) and by absolute beta counting (9). Data for Zr^{95}, Cb^{95}, Na^{24}, and Co^{60}, have been obtained. It is believed that data for Sc^{46} will complete the work.

Instruments (W. S. Lyon, S. A. Reynolds)

An automatic decay counter is being designed by the Instrument Department. It will count up to twelve samples at intervals of one to six hours, recording the sample position and the number of counts for a preset time. Two simple automatic counters are now in use. These will count at intervals of one to four hours, recording the "register counts" (scale of

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64 to 1024) as pen-strokes on a five-pen Esterline-Angus recorder. A new coincidence counter will soon be in use. The tubes will be argon-butane filled, and will be operated in the proportional region of voltage, allowing high counting rates.

Standards for Routine G-M Counting (W. A. Brooksbank)

Beta and gamma standards for normalization of routine counting have been made, standardized, and delivered to all analytical groups requiring them. The beta standards contain U_3O_8, and the gamma standards are made of radium. Standardization was achieved by counting each standard on 14 - 16 counters, then averaging consistent results. See previous quarterly report (10) for further details.

Activation Analysis (W. A. Brooksbank)

Four zirconium samples are to be analyzed for hafnium by the activation method previously employed (10). Two must be purified before bombardment. Samples enriched in Zr^{96} have been received for determination of activation cross sections. The yields of Zr^{95} and Zr^{97} activities will be determined by beta counting and gamma chamber measurements. In various radioisotope target materials (see next topic) the amounts of impurities will be calculated from the observed activities resulting from (n, γ) reactions on these impurities.

Radioisotope Target Materials (W. A. Brooksbank, G. W. Leddicotte, S. A. Reynolds)

Several samples of radioisotope target materials have been submitted by J. A. Cox for bombardment and determination of product yields, as well as nature and yields of impurities. Below is tabulated information available at present.

(a) Na_2CO_3

Activities: Na^{24}, (~99.9% of total), S^{35}, Ca^{45}, Sr^{89}, Cs^{134}, Ti^{51}, Sn, Sb (latter three tentative).

(b) $AgNO_3$

No activity other than Ag^{110} detected (no search for activity of half-life less than hours).

(c) Fe_2O_3

Activities: Fe^{55} and Fe^{59} (~99%), P^{32}, probably S^{35}, one unidentified radioelement with reasonably long life and much gamma.

(d) $CaCO_3$

Activities: #3B - Ca^{45}, Sr^{89}, (0.03% maximum)
#4, #5 - Ca^{45}, Sr^{89} (0.5% maximum)
Possibly another.

[redacted]

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(e) As_2O_3

Only As^{76} activity detected. Others possible.

(f) TiO_2

Activities: Ti^{51}, P^{32}, one short-lived.

(g) $Cd(NO_3)_2$

Various activities, as yet unassigned.

Radiozirconium Procedure

A. TTA-Separation with Colorimetric Determination of Carrier Yield - (R. H. Powell)

Much effort was expended in the past (10, 11) to secure an understanding of the mechanism of the colorimetric procedure for analysis of zirconium. It is now felt that continuation of such investigation is unreasonable, because of the time required. Effort is now being concentrated on obtaining a reproducible colorimetric method which can be used to measure carrier yield after a TTA extraction with stripping of the organic phase with dilute fluoride solution. The most significant findings in the past quarter have been that a "spiked" blank (containing 10 γ Zr) gives better results on low-Zr samples than a blank containing no Zr, that NaF can be substituted for HF, with better results, and a smooth transmittance-concentration curve is obtained after addition of fluoride followed by boric acid, and that this curve follows Beer's law better than that for solutions containing no fluoride.

B. Simple TTA Separation Without Carrier (F. L. Moore)

Since Zr is quantitatively extractible by TTA and may be subsequently stripped quantitatively from the organic phase, it seems logical to avoid use of carrier altogether. The effect of various substances in the aqueous phase on the extraction has been investigated. The optimum TTA concentration in xylene solutions has been established.

Nitric acid concentrations of 0.5 - 8 M and 1 - 12 M HCl allow essentially quantitative extraction (98 - 100%).

In eight minutes, equilibrium is attained in extraction from 2 M HNO_3. Ten minutes has been selected as the standard mixing time.

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Effect of TTA Concentration

Conditions: 2 M HNO_3, 10 Min., Equal Vol. Aqueous and Xylene Solutions

TTA Conc.	% Zr Extracted	TTA Conc.	% Zr
0.01 M	1.9	0.2	78.7
0.03	15.1	0.3	95.0
0.05	33.1	0.4	96.9
0.1	65.7	0.5	98.1

0.5 M TTA has been used in all work.

No extraction was noted from 1% oxalic acid solutions containing no added mineral acid. If acid is added, the extraction increases, but is only 50% from 10 M HCl, and 87% from 13 M HNO_3. Addition of aluminum (which complexes oxalate) raises the extraction insufficiently. It was decided to use $KMnO_4$ to destroy the oxalic acid, with destruction of excess $KMnO_4$ by hydroxylamine. This procedure works quite well, giving 95-100% recovery of Zr.

Phosphate interferes strongly in the extraction of Zr. No method of removing this interference has yet been found.

Plutonium Analysis (F. L. Moore)

It has been found that in analysis of hexone solutions for plutonium quantitative results are obtained by destruction of the organic matter with HNO_3 - $HClO_4$. 0.5 M HF can be used to "strip" Pu from hexone. Plutonium can be quantitatively extracted from HF solution if a large excess of boric acid is added. Attempts were made to break down the Pu(IV) polymer by use of HF, followed by addition of H_3BO_3 and TTA extraction. Up to 4 M HF, negative results were found (in a reasonable time).

"Service Analyses" (D. J. Coombe)

"Service analyses" and "trouble shooting" are frequently done by members of this group. Such work included non-routine or troublesome plutonium analyses, assay of Fe^{55}, and Fe^{59}, and other radioisotopes.

References

(1) Engelkemeier, Novey, and Shover, CC-793 (1943).
(2) Freedman and Engelkemeier, CC-1331 (1944).
(3) Metcalf, et al. MUC-NS-230 (1944).
(4) Born and Seelmann - Eggebert, Naturw, 31, 201 (1943).
(5) Levy and Stang, CC-1204.
(6) Wilkinson and Rall, PPR 9B 7.45.5, CP-2590.
(7) Engelkemeier, PPR 9B 7.45.2, CC-1959.
(8) Overman and Jones, MonC-399 (1948).
(9) Zumwalt, MDDC-1346 (1948).
(10) ORNL-229 (Quarterly Report).
(11) ORNL-176, p. 76.

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Spectrochemical Analyses - Research and Development

(Cyrus Feldman, M. Murray, J. Gillespie, A. Estepp)

I. Study of stigmatic spectra obtained with a polarized intermittent arc showed that when a porous cup electrode (ORNL-131) is used as a source,

(a) The general intensity level of trace element lines is heavier when the PCE is the anode than when it is the cathode.

(b) The intensity of a given line near the (dry) opposing electrode increases as the exposure progresses, probably because of the building up of a residue. At the end of three minute exposure, the density of the line is usually at least as great near the opposing electrode as near the PCE.

II. With a view toward expediting the spectrochemical determination of Hf/Zr ratios (ORNL-183) a study was made to see whether there was anything to be gained by using the ratio of the sum of the intensities of two Hf lines to the sum of the intensities of two Zr lines as an experimental quantity, rather than the ratio of one Hf intensity to one Zr intensity.

It was found that the same accuracy and precision could be obtained by measuring (Hf 2641. + Hf 2820.)/(Zr 2761.9 + Zr 2589.1) in duplicate exposures as could be obtained by measuring any single line ratio in quadruplicate exposures. This permits halving the number of exposures, provided that the Hf/Zr ratio lies between 0.05 and 0.9.

III. A study has been begun on the effect of extraneous elements on trace line intensities and intensity ratios in PCE exposures. The severity of the effect depends on the identity and amount of extraneous element used and the identity of the trace line. Traces of Be, Mo, V, La, Cr, Ga, Mn, and B have been studied in the presence of Na, K, Mg, Al, Zn, P, and Be. Atomic ratios of extraneous element to trace element up to 20,000:1 have showed trace intensities in most cases to be depressed more and more as the atomic ratio rises. As much as 50-60% of the original trace line intensity may be lost. Large amounts of alkali metals, however, enhance the intensities of some of the lines studied by as much as 100%.

The effect observed so far are of a lower order of magnitude than those observed in the D.C. arc work. The study is being continued with a view toward making it possible to estimate trace concentrations in solutions without the use of standards.

IV. It was found that decontamination of the spectrographic spark chamber could be expedited greatly by coating parts to be exposed to contamination with Amercoat "cocoon" beforehand. This coating is peeled off after the exposure. The stripping alone has given decontamination factors of 20 - 200; this seems to be the most convenient and effective method tried so far for protection against chemically intractable elements such as Pu, W, Cb, cet

It is planned to expedite further handling of radioactive samples by stamping liners of the proper form from sheets of "cocoon" and cementing these to the exposed spark chamber surfaces immediately before an exposure.

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Analytical Service

The service work of the analytical groups has increased by about 10% in the past quarter largely due to increased numbers of radiochemical analyses. The phenomenally increased demand for radiochemical analyses has been due to increased work from the Technical Division and Chemistry Division and also to a considerable load from people working on the particle problem. It has'been found possible to handle this increased load by reorganizing the groups involved without acquiring any additional personnel.

The "hot" pilot plant has submitted fewer samples to the control group this quarter because of the higher activity level of present operations. Since the hotter samples require more time for safe handling, the same personnel complement is being retained in this group.

An accelerated interest in general ionic analyses was noted during this quarter and two people are being added to do this work. The aluminum-uranium alloy work previously handled by this group has become completely routine and has been transferred to the laboratory control group, and as a consequence the increased demand is not yet reflected in an increased number of analyses in this group.

In all other respects the demands on the groups remained essentially constant, and the present personnel (including recent acquisitions and offers outstanding to replace recent terminations) is adequate to handle present service requirements.

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Summary of Service Analytical Work for Quarter
November 15, 1948 to February 15, 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 Control	Production Control	Totals
Personnel										
Tech.	5	5	4	10	2	1	2	6	5	40
Non. Tech.	2	2	0	12	2	3	8	19	17	65
Biology	Development Only Less than 1% Service Analyses		1							1
Physics			35		4					39
Chemistry		3	120	1020	32	3			9	1187
Technical		154	12	7494	98	1024	7054	9624	188	26548
Metallurgy			112		27					38
Operating Div.		22	65	1905	3	76	20		5752	7843
Health-Physics			1	2452	1					2454
K-25				162						162
Misc.				12						12
	0	179	245	13033	177	1103	7074	9624	5949	38234

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PROJECT LITERATURE ISSUED BY THE CHEMISTRY DIVISION

SEPTEMBER, 1948 - FEBRUARY, 1949

ORNL-63 "Chemistry of Thorium in Aqueous Solutions. I. The Thorium-Iodate System: Solubility and Complexes", A. J. Fry, J. E. Barney, III, R. W. Stoughton.

ORNL-128 "Decomposition of Tritium Oxide under Its Own Radiation", J. A. Ghormley, A. O. Allen.

ORNL-131 "The Direct Spectrochemical Analysis of Solutions Using Spark Excitation and the Porous Cup Electrode", Cyrus Feldman.

ORNL-155 "Decomposition under File Radiation of Concentrated Sulfuric Acid and Solutions of Hexavalent Uranium in Concentrated Sulfuric Acid", J. W. Boyle, A. O. Allen.

ORNL-183 "The Spectrochemical Determination of Hafnium-Zirconium Ratios", Cyrus Feldman.

ORNL-188 "Chemistry of Aqueous Uranium (V) Solutions. I. Preparation and Properties. Analogy Between U(V), Np (V) and Pu (V)", K. A. Kraus, G. L. Johnson, F. Nelson.

ORNL-189 "Chemistry of Aqueous Uranium (V) Solutions. II. Reaction of UCl_5 with Water. Thermodynamic Stability of UO_2^+ Potential of U(IV)/(V), U(IV)/(VI) and U(V)/(VI) Couples", K. A. Kraus, F. Nelson.

ORNL-210 "Note on the Arc Spectrum of Element 61", Cyrus Feldman.

ORNL-239 "Some Observations on the Chemistry of Protactinium", K. A. Kraus, Q. Van Winkle.

ORNL-300 "Chemistry of Protactinium. III. A Method of Analysis of Ore Residues for Protactinium", K. A. Kraus, A. Caren.

CL-KAK-99 "Isolation and Purification of Protactinium from Uranium Ore Residues", K. A. Kraus, Q. Van Winkle.

CL-KAK-104 "Hydrolytic Behavior of Pu (IV). III. Solubility of Pu (IV) Hydroxide in Perchlorate and Sulfate Solutions as a Function of pH", K. A. Kraus.

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Swartout, J. A., "Introductory Remarks", (Symposium on Radiochemistry Laboratory Design), Ind. & Eng. Chem. 41, 227, (1949).

Tompkins, P. C., Levy, H. A., "Impact of Radioactivity on Chemical Laboratory Techniques and Design", Ind. & Eng. Chem. 41, 228, (1949).

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Levy, H. A., "Remodeling a Laboratory for Radiochemical Instruction or Research", Ind. & Eng. Chem. 41, 248 (1949).

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