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CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

FOR

PERIOD ENDING SEPTEMBER 30, 1949

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QUARTERLY PROGRESS REPORT
for Period Ending September 30, 1949

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ABSTRACT

CHEMISTRY OF SOURCE, FISSIONABLE AND STRUCTURAL ELEMENTS

Solution Chemistry. Emphasis is placed in this program on the elucidation of the physical chemistry of aqueous solutions of source and fissionable elements, of elements having analogous properties and of elements of potential usefulness as structural materials in reactors.

The acid constant of U^{+4} was determined as a function of ionic strength for chloride and perchlorate solutions. Since it was found that the (molarity) constants could be fitted to the *Debye-Huckel* limiting law, the data were extrapolated to zero ionic strength and the activity constant obtained. Through extension of the data the activity coefficient ratios $\gamma UOH^{+3}/\gamma U^{+4}$, $\gamma UOHX_3/\gamma UX_4$ were estimated as well as the activity coefficients of UX_4 as a function of ionic strength.

A number of experiments on the hydrolysis of $ZrCl_4$ are described. It was found that in the acid range 0.1 to 0.001 *M* H_3O^+ Zr(IV) is extensively hydrolyzed with hydroxyl numbers $n > 2.33$. A trimeric (or poly-trimeric) intermediate in the polymerization of Zr(IV) seems indicated. The hydroxyl numbers appeared to approach steady state values in 1-2 hours.

In order to determine the identity of the species formed upon hydrolysis of thorium in aqueous solutions and the values for the hydrolysis constants, the distribution of thorium between the aqueous solutions and benzene solutions of TTA is being studied. The value for the first hydrolysis constant obtained in this manner is larger by a factor of almost 100 than that determined by direct titration. The existence of a stable double complex containing both hydroxide and TTA is considered as an explanation.

Phase Rules Studies—Fuel Media for Homogeneous Reactors. The determination of the solubility of UO_3 in uranyl sulfate solutions has been discontinued because it has been found that excess acid will be necessary to prevent the precipitation of UO_4 formed as a result of radiation decomposition.

Apparatus has been assembled and is being calibrated to determine with reasonable precision the vapor pressures of aqueous solutions, initially of uranyl sulfate solutions, at temperatures above 200°.

Preliminary indications are that the corrosion of uranium by uranyl sulfate solutions can be prevented by application of a counter-voltage. Therefore, the possibility still exists that this technique may be useful in preventing corrosion of the fuel tank in a homogeneous reactor.

Studies were extended to the determination of the phase relationships in the uranyl nitrate-water system. Because thermal decomposition of the nitrate ion occurs, determination of the composition of the vapor phase in the high temperature range will be necessary.

The feasibility is being investigated of producing uranium oxide slurries, sufficiently stable for a fuel system, by thermal decomposition of uranyl oxalate and uranyl formate.

NUCLEAR CHEMISTRY

Elements in the Fission Product Region. In general, the nuclear chemistry program is concentrated upon (1) the low-yield fission products (those occurring at the wings and saddle of the distribution curve), (2) those having extremes in half-lives whose study is made possible by the proximity of the reactor and/or the unique facilities of the hot-laboratory for work with high-levels of activity, and (3) those about which more detailed information is required for the success of other problems.

In the search for Zr^{93} and Mo^{93} lower limits of half-life have been set at 4×10^6 y and 2 y respectively. Although no indication of the presence of Zr^{93} in fission has been obtained, a long-lived molybdenum isotope, presumably Mo^{93}, has been found.

Considerable progress has been made in the clarification of the states of the numerous tin radionuclides. Assignments have been made to most of the known periods with the exception of the 80 m, 3 h and 17 h.

Evidence has been found for branching in the decay scheme of I^{135}, in which 6% decays with a ~0.5 Mev β and 94% with the previously known 1.4 Mev β-ray. In addition to the known 0.53 Mev gamma ray, a 0.85 Mev gamma occurs in about 5% and a 1.4 Mev gamma in about 1% of the disintegrations.

Long-lived Se^{79} has been isolated as a product of fission, identified and characterized. The half-life is calculated to be 6.5×10^4 y on the basis of the observed disintegration rate and the smooth-curve fission yield.

The feasibility of isolating large amounts of rare gas fission products has been proved in the hot-laboratory by adsorption on charcoal of about one curie of 10 y krypton from a Hanford slug. Rare gas nuclides are desired for nuclear measurements by spectrographic methods and for the radioisotope distribution program.

Absorption coefficients of the hard gamma ray, 2.765 Mev, of Na^{24} were measured for iron, copper and graphite.

Lighter Elements. By application of an electroplating technique to prepare thin films of nickel and thereby reproducible self-absorption of soft radiations, more accurate values for the decay constants of Ni^{59} and Ni^{63} have been obtained. For Ni^{63} a half-life has been found of 5.3 y with a probable error of 2%. For Ni^{59} a value of $1.5 \pm 0.25 \times 10^5$ y was obtained for the partial half-life based on the K electron capture process only.

RADIO-ORGANIC CHEMISTRY

Procedures were developed for the preparation of (1) ethyl malonate-2-C^{14} in 21% overall yield from ethyl acetate-2-C^{14}, (2) ethyl acetoacetate-3-C^{14} on a macro scale from acetyl-1-C^{14} chloride and the sodium derivative of acetoacetic ester, (3) methylamine in 98% yield from sodium cyanide, and (4) diazomethane in 54% yield from sodium cyanide. Syntheses are being developed for (1) glycerol-1-C^{14} from β-bromoethyl benzyl ether, (2) ethanol by reduction of acetic acid with lithium aluminum hydride, and (3) 5-methylcholanthrene-1-C^{14}. In order to accumulate a stock of 50 mc of C^{14}-labeled Vitamin K, two approaches are being taken: (1) preparation of sufficient 3-(p-tolyl)-propyl bromide for use in the synthesis, and (2) investigation of an alternate synthesis starting with oxidation of indene to homophthalic acid.

The extent of formation of gases in Hanford irradiated beryllium nitride prepared at Clifton Products Company and canned at ORNL is being determined along with the identity of the gases. Because as long an exposure in the reactor as possible is desired to prepare high specific activity barium carbonate-C^{14}, knowledge of the pressure build-up, if any, is essential.

Volatility Studies. The long range objectives of this recently initiated program are now quite definite. It is planned to establish the properties of the systems and compounds, which have usually been considered for volatility applications, to determine the feasibility of their direct use as reactor fuel or blanket materials. Preliminary data indicate that the solubility of thorium fluoride in anhydrous hydrofluoric acid is too low to render this system attractive as a blanket.

Solvent-Extraction Principles and Applications. Because of the recently recognized potentialities of solvent-extraction employing tributyl phosphate in the organic phase, fundamental studies were begun with this system. As a first step in the determination of the chemical species of thorium responsible for its extraction, the distribution of thorium between nitrate solutions and hexane solutions, 0.551 f in tributyl phosphate was determined as a function of thorium nitrate concentration. The ratio of tributyl phosphate molecules to thorium atoms in the organic phase approaches three at high thorium concentrations.

Although it is now believed that other solvent-extraction systems, notably the thiocyanate-hexone procedure developed at Y-12, possess many advantages over a TTA-solvent method for separating zirconium and hafnium, fundamental studies have continued because of their general applicability. The fourth power TTA dependence of the extraction of Hf from dilute nitric acid solutions has been confirmed, in contradiction to results at other installations. As in the case of Hf, the extraction of Zr from HCl solutions is complicated by the extractability of more than one species, one or more of which contains chloride and by the existence of an aqueous chloride complex.

Electrodeposition. The plating of zirconium onto a uranium cathode from a solution of the oxychloride in fused ethyl pyridinium bromide has been shown to be possible, although it is not yet known whether the deposit is the metal or an oxide. Electrodeposition of aluminum from a similar solution was successful onto copper but not onto uranium. Because of the possible application of such techniques to the canning of uranium slugs, this investigation will continue.

Ion-Exchange. An exact thermodynamic treatment of ion-exchange equilibria has been made, assuming a Gibbs-Donnan mechanism to determine the distribution of electrolytes between the exchange and aqueous solution.

A more rapid fractionation of the halides by anion-exchange is being sought by decreasing the selectivity of the anion-exchanger. The possibility of separation of Mo, Tc and Re by anion-exchange appears promising. The separation of Nb, Ta and Pa by anion-exchange in HCl-HF media was found to be strikingly effective.

Fission Product Separations. The feasibility of the proposed silica gel process for removing Zr and Nb from the Redox Process waste solution (IAW) has been demonstrated in a series of experiments with waste from the Redox Pilot-Plant.

CHEMICAL PHYSICS

The first three problems in this field represent use of the unique facilities of the Laboratory in furthering the study of the structure of matter and the mechanism of chemical reactions. The fourth represents the application of a classical technique of the field to problems in radioactivity. The varied nature of the problems conceals to some extent the considerable unity in philosophy and methods which leads to their being considered together.

Microwave Spectroscopy. Structural details both of nuclei and of molecules are determinable by measuring the rotational spectra of suitable molecules, now opened to direct study by the advent of microwave spectroscopy. The principal aim of the program here is the determination of nuclear spins, quadrupole coupling and magnetic movements of radioactive nuclei. Systematic study of the radioisotopes of iodine began with the recently concluded work on I^{129}. Remote control equipment has now been about completed to extend this work to I^{131} and the other iodines requiring the use of more highly radioactive samples. Study of the antimony nuclei has been initiated by the synthesis of a sample of SbD_3. A search for its rotational transitions is under way at Duke University as part of the cooperative program.

Neutron Diffraction. Crystal structure has long been a field of interest for chemists, although the most powerful tool for investigating it, X-ray diffraction, is a development of physics. Physics has now supplied another tool, neutron diffraction, and structural studies of chemical interest are now under way in the chemistry division.

The feature of neutron diffraction of most interest to chemistry is probbably the possibility of locating hydrogen atoms in crystals. Potassium bifluoride, KHF_2, is being studied as a relatively simple, structurally interesting test of this possibility. Results to date indicate that the hydrogen atom in each bifluoride ion is probably located symmetrically between the fluorines.

Molecular Beams. In the field of reaction mechanisms, there has long existed the possibility of performing a number of fundamental experiments by the molecular beam technique provided detection methods for molecules of interest could be developed. It is believed that neutron activation will be sufficiently sensitive for a number of elements of interest, and work is under way to test this on the reactions of potassium with bromine and organic bromides, using neutron activation to measure the bromine. Preliminary investigations have been concluded, and the apparatus for actual experiments has been completed.

Calorimetry of Radioactivity. Here a standard physical chemical technique is being applied to problems in radioactivity, the reverse of the situation obtaining in the three researches just described. The present program is directed toward the measurement of very small rates of energy input with the hope of being able ultimately to measure the energies of n-gamma reactions using a neutron beam from the reactor.

Toward this end, a liquid helium calorimeter suitable for measurements on beta emitters has been designed and built following the general lines of the liquid nitrogen calorimeter previously developed. The sensitivity and stability of this present instrument are such that heat inputs of 2×10^{-3} cal/hr can be measured to 1% within about an hour. This can probably be improved, if necessary, by improving the thermal shielding to lower the background evolution of helium.

RADIATION CHEMISTRY

Pile experiments on the decomposition of UO_2SO_4 solutions have demonstrated the feasibility of continuous pressure measurement under these conditions. A run in a silica-lined stainless steel bomb gave pressures very close to those calculated from previous experiments done in sealed silica ampoules and using gas analysis to measure the decomposition. These results confirm the previous

conclusion that at 65-100° C the steady-state pressure over aqueous UO_2SO_4 (about 5.5 g U^{235}/l) is very high (above 8600 lb/in.^{2}).

Most of the non-pile work has been concerned with setting up apparatus for experiments with the Van de Graaff generator, and in planning for a Co^{60} gamma radiation source to supplement the Van de Graaff. Some orienting experiments have been performed on radiation effects in ionic crystals, with the principal aim of accounting quantitatively for the energy stored in various modes.

PHYSICAL MEASUREMENT AND INSTRUMENTATION

Optical and Electron Microscopy. A variety of cooperative work was performed during this quarter. Some work on the microstructures of beryllium seemed of sufficient interest to report separately.

Instruments for Detection of Radiation. The use of a proportional counter as a beta and X-ray spectrometer was first suggested at this laboratory, and was subsequently demonstrated elsewhere. One has recently been in use here, and has been found to have sufficient resolution to resolve the K X rays from Mn, Co and Cu (around 7 Kev). In a test of the application to beta rays, a proportional counter yielded a beta spectrum for Tm^{171} for which the Kurie plot was very close to that obtained from a magnetic lens beta ray spectrometer and for which the end points (at 100 Kev) agreed within 2%. A special differential or integral discriminator was built to obtain the energy distribution curves from the counter pulses.

The growing use of scintillation counters has demanded a supply of anthracene crystals. An apparatus has been built to grow them from the melt, and several large, clear crystals have been produced.

ANALYTICAL CHEMISTRY

In addition to the normal analytical services of all types for the Laboratory, the program in analytical chemistry is concerned with research on, and development of, procedures to meet anticipated or present needs, particularly

of the radioisotope production and chemical development programs. Among such procedures which were, or are being, developed are the following: (1) methods for assaying Be^{7}, Se^{75}, $Hg^{203,205}$, Zr^{95} and Pu; (2) analysis for phosphate in organic solutions of tributyl phosphate; (3) determination of thermal neutron activation cross section of Zr^{96}; (4) polarographic procedures for I_2, Co, Hg, Sb, Pb, Se and U, and (5) determination of water in ion-exchange resins.

PROJECT LITERATURE ISSUED BY THE CHEMISTRY DIVISION

MARCH, 1949 - SEPTEMBER, 1949

MonC-166 *Spark Spectra of Elements 43 and 61,* D. Timma.

MonC-397 *Absolute Beta Counting Using End-Window Geiger-Muller Counters and Experimental Data on Beta-Particle Scattering Effects,* L. R. Zumwalt.

ORNL-153 *A Solvent Extraction Method for Plutonium Analysis,* F. L. Moore, J. E. Hudgens, Jr.

ORNL-247 *The Application of Kinetic Theory to the Critical Curve for Aqueous Solutions of 1-1 Electrolytes,* C. H. Secoy.

ORNL-300 *Chemistry of Protactinium. II. A Method of Analysis of Ore Residues for Protactinium,* K. A. Kraus, A. Garen.

ORNL-303 *The Extraction of Hafnium from Nitric Acid Solutions with Thenoyl Trifluoroacetone,* J. P. McBride.

ORNL-329 *Chemistry of Protactinium. IV. Adsorption of Protactinium from Hydrochloric Acid Solutions by Anion Exchange Resins,* K. A. Kraus, G. E. Moore.

ORNL-330 *Chemistry of Protactinium. V. Separation of Thorium, Protactinium and Uranium with Anion Exchange Columns in HCl Solutions,* K. A. Kraus, G. E. Moore.

ORNL-354 *A Procedure for the Complete Electrodeposition of Small Amounts of Ruthenium,* J. C. Griess, Jr.

ORNL-383 *Automatic Precision Glass-Electrode-pH Measurement with a Vibrating Reed Electrometer,* K. A. Kraus, R. W. Holmberg, C. J. Borkowski.

ORNL-395 *Production of Methanol-C^{14} by the Lithium Aluminum Hydride Process,* R. F. Nystrom, W. J. Skraba, R. G. Mansfield.

ORNL-404 *Decomposition of Water at High Temperatures and Pressures under Reactor Irradiation,* L. W. Fromm.

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CHEMISTRY OF SOURCE, FISSIONABLE AND STRUCTURAL ELEMENTS

SOLUTION CHEMISTRY

THE ACID CONSTANT OF U(IV)—EVALUATION OF THE ACTIVITY CONSTANT

Frederick Nelson and Kurt A. Kraus

During the last quarter the earlier work on the determination of the acid constant of U(IV)[1] has been extended. The main emphasis was placed on the determination of the molarity constant K_m in chloride and perchlorate media, as a function of ionic strength (up to $\mu = 2$) for the reaction

$$U^{+4} + 2H_2O \longrightarrow UOH^{+3} + H_3O^{+} \qquad (1)$$

The experimental procedure was as previously described[1] and essentially consisted of a spectrophotometric study of U(IV) in solutions of various acidities and various ionic strengths. Whenever necessary the data were extrapolated to zero time (time of mixing).

The results of the experiments are summarized in Tables 1 and 2. It was found that K_m decreases with increasing ionic strength (up to $\mu = 2$) in both chloride and perchlorate solutions.

To confirm that U^{+4} is the species of U(IV) in acidic solutions, i.e., that the starting species in equation (1) has been correctly chosen, the acidity of a number of UCl_4 solutions has been determined and from the measurements the hydroxyl number n of U(IV) (number of hydroxide ions per uranium ion) has been calculated. If the starting species is U^{+4}, the hydroxyl number is expected to be between zero and one. The amount of acid liberated on dissolution of UCl_4 in a solution of known initial acidity was determined with a vibrating reed electrometer assembly[2] and a glass electrode-calomel electrode system. The ionic strength of the solutions was made high enough ($\mu = 0.5$) compared with the concentration of uranium (ca. 10^{-3} M) to permit the assumption that the liquid junction potentials and the activity coefficients of the oxonium

(1) K. A. Kraus and F. Nelson, MonN-370 (September, 1947), CNL-37 (April 1948), AECD-1888 (April 1948).

(2) K. A. Kraus, R. W. Holmberg and C. J. Borkowski, Report ORNL 383 (September 1949).

ions do not change and that the approximation,

$$\Delta E = 0.05915 \log (m_1/m_2) \qquad (2)$$

can be made, where m_1 and m_2 are the initial and final molarities of acid. If M_4 is the concentration of U(IV) the hydroxyl number n is given by

$$n = m_2 - m_1/M_4 . \qquad (3)$$

Since the UCl_4 samples contained a small amount of U(VI) in unknown initial form [concentration determined polarographically[3]], an uncertainty of ca. 10-20% is introduced in the value of n. Within this error it was found that n is less than unity and of the order of magnitude expected from the numerical values of the acid constants given in Tables 1 and 2 at final acidities of the order of 10^{-2} M. This agreement is close enough to appear to constitute positive proof of the existence of U^{+4} in acidic solutions.

An attempt was made to evaluate the activity constant K_m for reaction (1) from the molarity constants K_m at the various values of μ given in Tables 1 and 2. The relationship between K_a and K_m is

$$K_a = K_m \quad \gamma_{H_3O^+}\gamma_{UOH^{+3}}/\gamma_{U^{+4}} . \qquad (4)$$

It was assumed that the activity coefficients of the ions in equation (4) follow a *Debye-Huckel* limiting law of the form

$$\log \gamma_i = -0.509 \, Z_i^2 \, (\mu^{1/2}/1+0.3286 \, \mathring{a}_i \, \mu^{1/2}) . \qquad (5)$$

where Z_i is the charge of the ion and $\mathring{a}_i$ the "closest distance of approach" with respect to the negative ions of the medium.[4][5][6]

(3) K. A. Kraus and F. Nelson, J. Am. Chem. Soc. 71.2517 (1949).

(4) R. A. Robinson and H. S. Harned, Chem. Rev 28.419 (1941).

(5) Equation (5) differs from the Debye limiting law in that γ_i has been substituted for f_i, the activity coefficient on a mol fraction basis, and Z_i^2 for Z_iZ_i, the product of the charges of the positive and negative ions which interact. In view of the limited precision of the data no distinction will be made between f_i, γ_i, and y_i, the activity coefficients on a mol fraction, molality and molarity basis since the errors introduced is less than 10% even at an ionic strength of 2. For the relationship between f_i, γ_i and y_i, see ref. (4).

(6) For values of the constants in equation (6) see G. G. Manov et al., J. Am. Chem. Soc. 65.1765 (1943).

TABLE 1

Acid Constant of U^{+4} in Perchlorate Solutions

μ	M U(IV) $\times 10^3$	FINAL (H_3O^+)	E_{648}	UOH^{+3} (Percent)	K
2.004	0.886	.0082	20.4	73.6	.0228
		.0175	29.2	57.3	.0234
		.0325	37.5	41.9	.0234
		.0568	44.5	28.9	.0231
		.105	49.5	19.5	.0254
				av.	.0236
1.014	0.886	.0320	35.3	46.0	.0273
		.0560	42.0	33.5	.0282
				av.	.0278
0.503	0.183	.0107	19.1	76.0	.0338
		.0201	28.4	58.8	.0287
		.0390	37.2	42.5	.0288
		.0769	44.4	29.1	.0316
		.153	52.5	14.0	(.0250)
		.304	56.1	7.2	(.0244)
				av.	.0307
0.520	0.725	.0047	14.3	85.1	.0268
		.0143	23.2	68.4	.0310
		.0234	29.2	57.3	.0314
		.0422	37.0	42.8	.0316
		.080	44.8	28.3	.0316
		.155	50.7	17.3	.0324
		.305	55.3	8.8	.0294
				av.	.0312
0.519	0.886	.0094	17.05	79.9	(.0373)
		.0204	27.0	61.4	.0324
		.0323	32.8	50.6	.0333
		.0680	43.1	31.5	.0312
		.128	49.5	19.5	.0310
		.250	54.0	11.2	.0316
				av.	.0319

TABLE 1 (Continued)

μ	M U(IV) $\times 10^3$	FINAL (H_3O^+)	E_{648}	UOH^{+3} (Percent)	K
0.55	3.55	.025	27.0	61.4	.0398
		.043	34.2	48.4	.0399
		.061	40.0	37.3	.0362
		.106	46.0	26.1	.0375
		.133	49.8	19.0	.0312
		.170	51.8	15.3	.0307
		.240	53.5	12.1	.0335
					av. .0355
.272	.886	.0146	19.3	75.7	.0455
		.0208	23.6	67.7	.0436
		.0395	31.6	52.9	.0443
		.0708	39.7	37.9	.0432
		.131	47.5	23.3	.0398
					av. .0433
.116	1.228	.105	42.1	33.4	.0508
		.0555	34.3	47.8	.0526
					av. .0517
.115	1.222	.0190	19.4	75.5	.0585
.112	0.662	.0047	9.75	93.6	(.0686)
		.0110	14.5	84.6	.0605
		.0204	19.6	75.1	.0615
		.0360	26.7	62.0	.0588
		.0674	35.1	46.0	.0585
		.090	38.1	40.8	.0620
					av. .0603
.108	.616	.0160	18.7	76.8	.0530
.0634	.890	.0469	26.1	61.0	.072
.0452	.890	.0288	20.4	73.6	.0785
.0349	.890	.019	14.5	84.6	.101
.0328	.616	.0285	19.7	75.0	.0855
.0173	.616	.0134	11.7	89.9	.118

TABLE 2

Acid Constant of U^{+4} in Chloride Solutions

μ	M U(IV) $\times 10^3$	FINAL (H_3O^+)	E_{648}	UOH^{+3} (Percent)	K
2.004	1.00	.0032	14.4	84.9	.0170
		.0063	22.0	70.7	.0152
		.0069	22.8	69.1	.0155
		.0159	34.0	49.5	.0156
		.0257	39.2	38.8	.0163
		.0546	46.9	24.4	.0176
		.1040	52.2	14.6	.0178
		.253	56.0	7.5	.0205
					av. .0164
1.014	9.48	.0065	18.8	76.7	.0214
		.0013	26.0	62.2	.0186
		.0162	30.5	54.9	.0197
		.0310	39.8	37.7	.0188
		.0555	46.5	25.1	.0186
		.129	52.9	13.3	.0198
		.250	55.4	8.6	.0235
					av. .0191
0.67	9.23	.0535	42.4	32.9	.0262
		.130	50.4	17.9	.0283
		.230	55.3	8.8	.0222
		.348	56.1	7.1	.0266
					av. .0258
0.519	0.932	.0064	15.8	82.2	.0295
		.0163	26.9	61.6	.0262
		.0260	33.4	49.5	.0255
		.0550	42.7	32.3	.0262
		.503	56.6	6.4	.0344
					av. .0260
0.529	1.34	.0139	22.1	70.4	(.0320)
		.0181	28.7	58.2	.0252
		.0283	35.1	46.4	.0245
		.0483	43.7	30.4	.0211
		.109	50.2	18.3	.0244
					av. .0238

TABLE 2 (Continued)

μ	M U(IV) $\times 10^3$	Final (H_3O^+)	E_{648}	UOH^{+3} (Percent)	K
0.506	0.679	.0057	16.5	80.9	.0242
		.0166	25.7	63.8	.0292
		.0216	30.6	54.7	.0261
		.0365	38.0	41.0	.0254
		.0765	46.1	25.9	.0267
		.201	53.3	12.5	.0287
				av.	.0267
0.272	0.932	.0113	20.1	74.2	.0323
		.0162	24.0	66.9	.0327
		.0312	31.9	52.3	.0342
		.0561	40.2	37.1	.0331
				av.	.0331
0.123	0.932	.0165	20.1	74.2	.0475
		.0261	25.2	64.7	.0478
		.0550	36.4	44.0	.0432
		.104	45.4	27.2	.0388
				av.	.0443
0.115	1.22	.0160	21.8	71.0	.0392
		.0160	20.2	74.0	.0455
	1.228	.0257	25.5	64.7	.0470
		.0266	25.7	63.8	.0468
		.0460	35.4	45.8	.0389
		.105	44.8	28.3	.0414
		.1055	42.5	32.6	.0510
				av.	.0443
0.108	1.228	.0431	32.3	51.6	.0460
0.0654	1.315	.055	31.8	52.5	.0608
0.0449	1.315	.0352	24.8	65.8	.0677
0.0395	1.22	.0305	21.2	72.1	.0786
0.0345	1.315	.0253	19.8	74.8	.0752
0.0327	0.616	.0282	21.9	70.8	.0685
0.0250	1.315	.0163	14.1	85.4	.0960
0.0235	0.616	.0155	13.6	86.3	.0980

Assuming that an average value $\mathring{a}_i$ can be used for the three different ions of equation (4), substitution of equation (5) into equation (4) yields

$$\log K_a = \log K_m - 0.509\ \Delta Z^2\ (\mu^{1/2}/1 + 0.3286\ \mathring{a}\ \mu^{1/2}), \qquad (6)$$

where $\Delta Z^2 = -6$.

Using $\mathring{a} = 7.5$ Å the experimental data can be fitted to equation (6) within the rather wide limits of experimental error (ca. ± 10%) up to $\mu = 2$. The agreement is illustrated in Fig. 1 where $\log K_m$ has been plotted as a function of $\mu^{1/2}(1 + 2.46\ \mu^{1/2})$. The solid line in Fig. 1 has been drawn with the theoretical slope -6. The choice of $\mathring{a} = 7.5$ Å appears reasonable since even for 2-1 electrolytes (i.e., for electrolytes of considerably lower valence type than occur here) values of $\mathring{a} = 6$ Å have been used.[4] Similarly $\mathring{a} = 7.5$ permits a reasonable fit of the data for 3-1 electrolytes to the *Debye-Huckel* limiting law.

Extrapolating the data to $\mu = 0$, $K_a = 0.21 \pm 0.02$ was found for the perchlorate solutions. The values of K_m in chloride solutions are generally lower than those in perchlorate which may be due to some systematic error at low ionic strength, but at higher μ it is most probably due to (weak) chloride complexing of U(IV). In view of the theoretical inadequacies of equation (6) the agreement between the observed values of K_m and this rather simple relationship is surprising, particularly since the agreement persists up to an ionic strength of 2.

Using $K_a = 0.21$ and equation (6) (with $\mathring{a} = 7.5$) the activity coefficient ratios of equation (5) were calculated as a function of μ (Table 3). In the same table estimates of the activity coefficient ratios $\gamma_{UOH^{+3}}/\gamma_{U^{+4}}$ and $\gamma_{UOH_3}/\gamma_{UX_4}$ (where X denotes ClO_4^- or other non-complexing anions) are given. For the evaluation of these ratios it was assumed that $\gamma_{H_3O^+} = \gamma_{\pm HCl} = \gamma_{\pm HClO_4}$. The values $\gamma_{\pm HCl}$ given by Harned and Hamer[7] for 0.01 *M* HCl solutions in KCl were used. If a suitable assumption is made for the activity coefficients of γ_{UOHX_3} the data in Table 3 should permit an estimation of γ_{UX_4}. Since $UOHX_3$ can be considered a 3-1 electrolyte and since the activity coefficients of most 3-1 electrolytes differ only by a few percent for values of $\mu < 1$[4] and appear to obey the *Debye-Huckel* limiting law for $\mathring{a} = 7.5$ Å, $\gamma_{\pm UOHX_3}$ was correspondingly calculated. The results have been included in Table 3 as well as the calculated values of $\gamma_{\pm UX_4}$.

(7) H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. 55.2194 (1933).

FIG. 1

ACID CONSTANT OF U^{+4} AS A FUNCTION OF IONIC STRENGTH

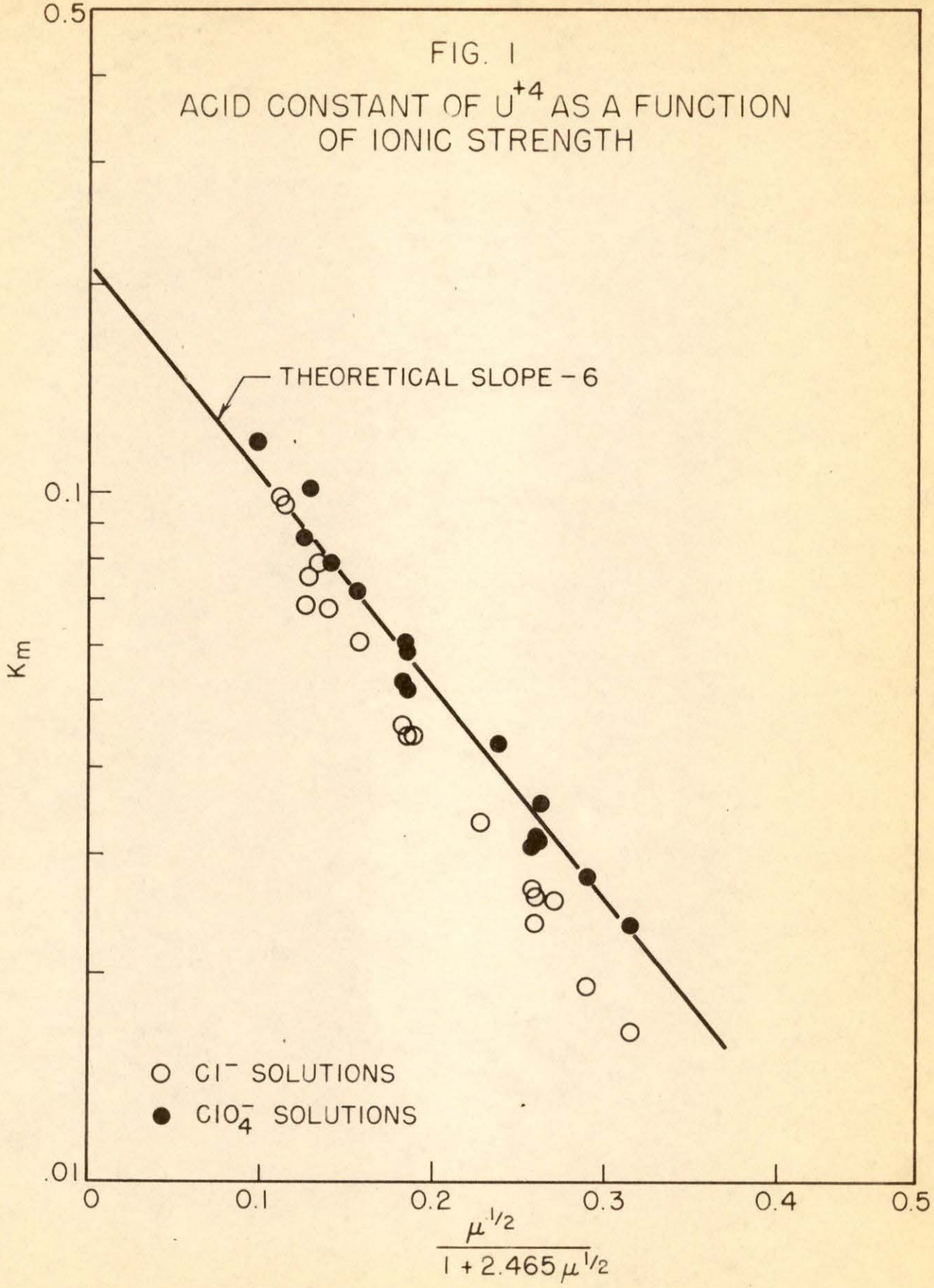

TABLE 3

Activity Coefficients in the U^{+4}—UOH^{+3} System

μ	$\frac{\gamma_{H_3O^+}\,\gamma_{UOH^{+3}}}{\gamma_{U^{+4}}}$ (a)	$\gamma_{\pm HCl}$ (b)	$\gamma_{UOH^{+3}}/\gamma_{U^{+4}}$ (c)	$\gamma^4_{UOH_3}/\gamma^5_{UX_4}$ (d)	$\gamma_{\pm UOHX_3}$ (e)	$\gamma_{\pm UX_4}$ (f)
.01	1.79	.904	1.98	.683	.75	.68
.02	2.09	.873	2.39	.613	.69	.61
.04	2.56	.836	3.14	.559	.63	.53
.06	2.93	.815	3.59	.515	.58	.48
.10	3.49	.790	4.42	.460	.54	.43
.20	4.46	.752	5.93	.396	.47	.38
.50	6.13	.706	8.67	.327	.41	.29
1.00	7.61	.719	10.58	.253	.36	.26

(a) Calculated using equation (5).

(b) From Harned and Hamer ref. 7. It will be assumed that $\gamma_{\pm HCl} = \gamma_{\pm HClO_4}$.

(c) Calculated from column (2) assuming $\gamma_{H_3O^+} = \gamma_{\pm HCl}$.

(d) Calculated from column (2) by dividing by the $\gamma^2_{\pm HCl}$. "X" indicates a non-complexing negative ion, particularly ClO_4^-.

(e) Calculated from $\log \gamma_{\pm} = -0.509\, Z_i Z_j\, (\mu^{1/2} / 1 + 0.3286\, \mathring{a}\, \mu^{1/2})$, using $\mathring{a} = 7.5$.

(f) Calculated from columns (5) and (6).

SOME OBSERVATIONS ON THE HYDROLYTIC BEHAVIOR OF ZIRCONIUM

S. Y. Tyree, Jr. and Kurt A. Kraus*

A number of measurements were made on the amount of acid liberated on dissolution of $ZrCl_4$ in HCl-KCl solutions of ionic strength $\mu = 1$ to determine the hydroxyl number n of Zr(IV) as a function of acidity. The technique of measurement was as previously described[8] and essentially consisted of *p*H measurements (with a glass electrode assembly) of HCl solutions before and after dissolution of a known amount of $ZrCl_4$. Calculation of n was carried out according to equation (3) of the previous paper of this quarterly report.

Zirconium tetrachloride was prepared by vacuum sublimation of a "crude" material which was obtained from the Foote Mineral Company. It is of interest that during the sublimation an exothermic reaction occurred which caused the deposition of a metallic-looking mirror on the tube. The nature of this reaction is not known although it appears probable that it was due to a reduction of $ZrCl_4$ with ZrC_2, which may have been present as an impurity.

Analyses of three $ZrCl_4$ samples yielded 39.2, 39.7 and 41.0 % Zr and 60.4, 60.2 and 60.3 % Cl which compare favorably with the corresponding theoretical percentages 39.37 and 60.63.[9][10]

The results of the experiments are summarized in Fig. 2 where the hydroxyl numbers at zero time (for those cases where extrapolations to the time of mixing were feasible) at 6 minutes and at 60 minutes are given as a function of log m_2. It was found that the hydroxyl numbers did not change appreciably after 60 minutes suggesting that the hydrolysis products attain an equilibrium (or steady state). It may be noticed from Fig. 2 that the hydroxyl numbers at final acidities $m_2 > 0.01$ are approximately 2-1/3 at zero time for both 10^{-3} and 7.3×10^{-3} *M* Zr(IV) solutions. The hydroxyl numbers increase with time particularly at final acidities $m_2 < 6 \times 10^{-2}$ for all Zr(IV) concentrations studied. The hydroxyl numbers apparently reach equilibrium (or steady state) values which lie along a straight line of rather shallow slope. There seems to be little concentration dependence of these steady state values for zirconium concentrations $M > 1 \times 10^{-3}$, although at higher concentrations the hydroxyl numbers tend to be higher. During the investigation no evidence was found for the existence of the zirconyl ion ($n = 2.00$).

(8) K. A. Kraus, R. W. Holmberg, F. Nelson, Report ORNL-65, June 1948.

(9) We are indebted to Miss E. V. Kazlauskis and Mr. W. J. Wolkowitz of the Analytical Section of the Chemistry Division, ORNL for the analyses.

(10) In the calculation of the theoretical percentages it was assumed that the zirconium contained 2% Hafnium.

* Participant in ORINS-ORNL Research Program, Dept. of Chemistry, University of North Carolina.

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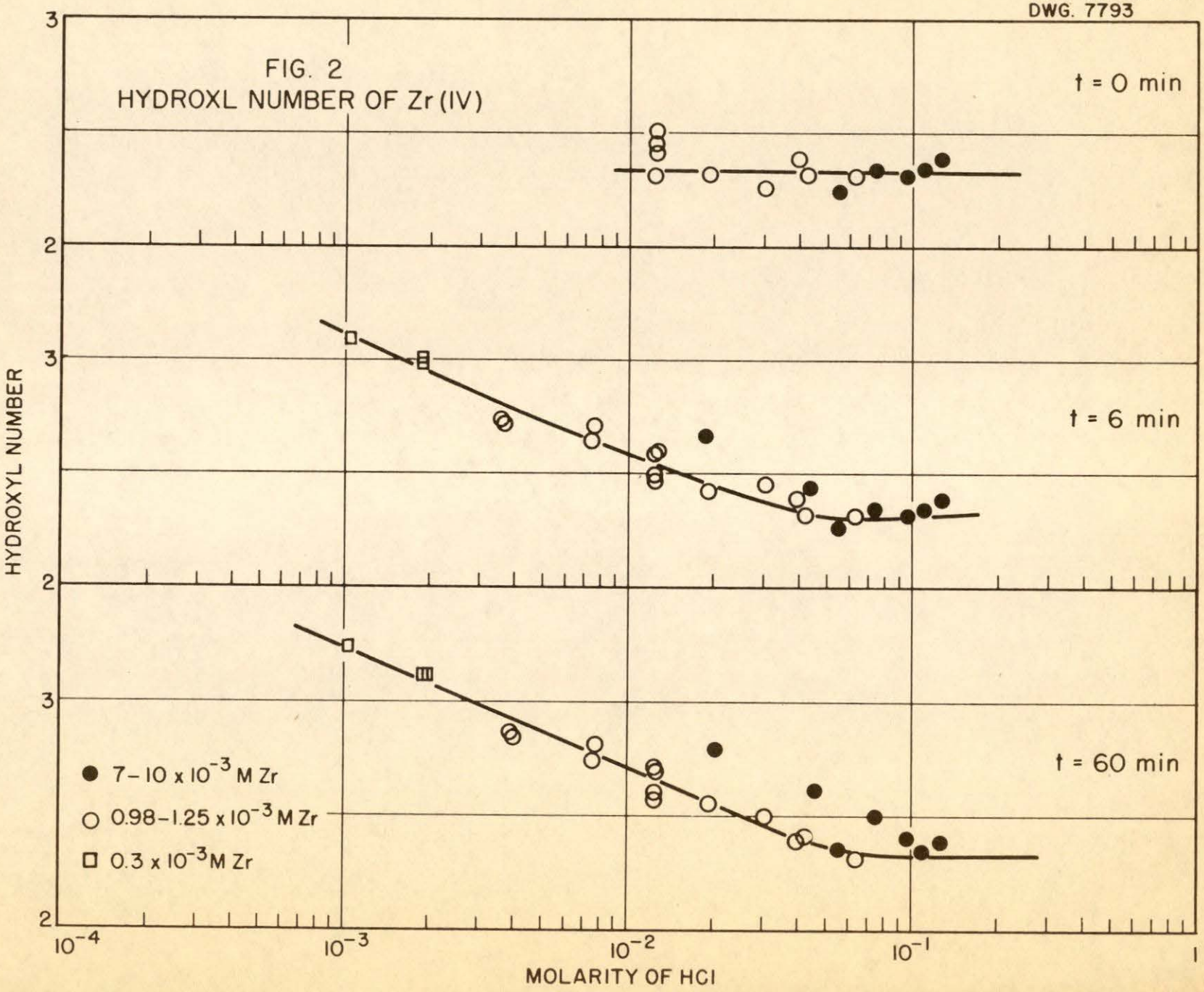
FIG. 2
HYDROXL NUMBER OF Zr (IV)



The data for zirconium are reminiscent of the data which have been obtained for Ce(IV).[8] A particular point of resemblance is the value $n = 2.33$ at zero time at the high acid range which suggests that polynuclear aggregates, whose number of metal ions in the aggregates is divisible by three, are important intermediates in the hydrolytic polymerization processes. The data for zirconium, however, differ from those of cerium in the extent to which the polymeric reactions proceed. Thus with Ce(IV) the hydroxyl numbers rise rapidly to considerably larger values than those of Zr(IV) and they do not appear to approach steady state values.[11]

STUDY OF AQUEOUS THORIUM HYDROLYSIS BY BENZENE-TTA EXTRACTION

W. C. Waggener and R. W. Stoughton

Thorium Hydrolysis Studies. The distribution of thorium between benzene and aqueous phases of the following initial composition was studied: HCl (0.5 to 7.25×10^{-5} *M*), KCl to maintain an ionic strength of 0.5 in the aqueous solutions; TTA (0.1 to 1.6×10^{-4} *M*), Th^{232} (10^{-6} *M*), Th^{234} (tracer) in benzene. Thorium distribution ratios have been determined for 48 solutions covering the concentration ranges indicated above for TTA and H^+. These results confirm preliminary observations previously reported,[12] and also agree with recent work of E. Zebroski and W. H. Alter[13] using a similar TTA extraction method.

Thorium was introduced initially into the benzene phase. Aliquots were taken from the benzene phase and in most instances from the aqueous phase after each of 3 or 4 successive periods of equilibration at room temperature. The total time of equilibration was from 3 to 7 hours.

Material balances were averaged for 18 solutions in the *p*H range 0.30 to 2.14 giving (a) 98.5 ± 2.1% calculated from analyses of both phases and the original activity introduced, and (b) 100.1 ± 1.1% calculated from analysis of back extracted activity in the benzene phase and the original activity introduced. In the *p*H range from 2.14 to 4.14 material balances fell off rapidly with time of equilibration from nearly 100% to 55-80% for solutions of highest *p*H and greatest TTA dilution.

(11) R. W. Holmberg and K. A. Kraus, Report ORNL 229 (February 1949).

(12) W. C. Waggener and R. W. Stoughton, ORNL 286, 121 (1949).

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

Though the material balances of these solutions decreased with time, fairly good agreement (better than 7%) was obtained for distribution ratios for successive equilibrations by centrifuging and sampling both phases within 10-15 minutes after ceasing equilibration.

It was at first assumed that only the species represented in the following equations existed in our solutions:

$$Th^{+4} + Cl^- = ThCl^{+3} \qquad k_{cl} \tag{1}$$

$$Th^{+4} + H_2O = ThOH^{+3} + \overset{+}{H}\ k_h \tag{2}$$

$$Th^{+4} + HT_b = ThT^{+3} + H^+\ k_T \tag{3}$$

$$Th^{+4} + 4HT_b = ThT_{4b} + 4H^+\ K_T \tag{4}$$

Here k_{cl}, k_h, k_T, K_T are the equilibrium constants with the substances in (1), (2), (3) and (4) respectively, expressed as moles per liter; HT represents TTA, and the subscript *b* indicated benzene phase. The distribution ratio (aqueous/benzene) becomes

$$R_b^a = [(Th^{+4}) + (ThCl^{+3}) + (ThT^{+3}) + (ThOH^{+3})]/(ThT_{4b}) \tag{5}$$

$$= [(\overset{+}{H})^4/K_T(HT_b)^4][1 + k_{cl}(Cl^-) + k_T(HT_b)/(\overset{+}{H}) + k_h/(\overset{+}{H})] \tag{6}$$

This equation may be put into the form,

$$R_b^a\ (HT_b)^4K_T/(\overset{+}{H})^4 - [1 + k_{cl}(Cl^-)] = k_T(HT_b)/(\overset{+}{H}) + k_h/(\overset{+}{H}) \tag{7}$$

Then by plotting the log of the expression on the left side of equation (7) against the *p*H, one should obtain a curve which starts at about zero slope and then shifts to unit slope at higher *p*H; it is assumed here that the ratio $(HT_b)/(H^+)$ does not vary greatly and that the first term on the right side of the equation is not large compared to the second. The intercept obtained on extrapolating back along the unit slope portion of the curve to *p*H 0 should be log k_h.

The value of 3.3×10^{-2} for k_h thus obtained (Fig. 3) is larger by almost a factor of 100 than that obtained by John Kasper[14] viz., 2.5×10^{-4}, by method of direct titration.

(14) John Kasper, Ph.D. Dissertation, Johns Hopkins University (1941).

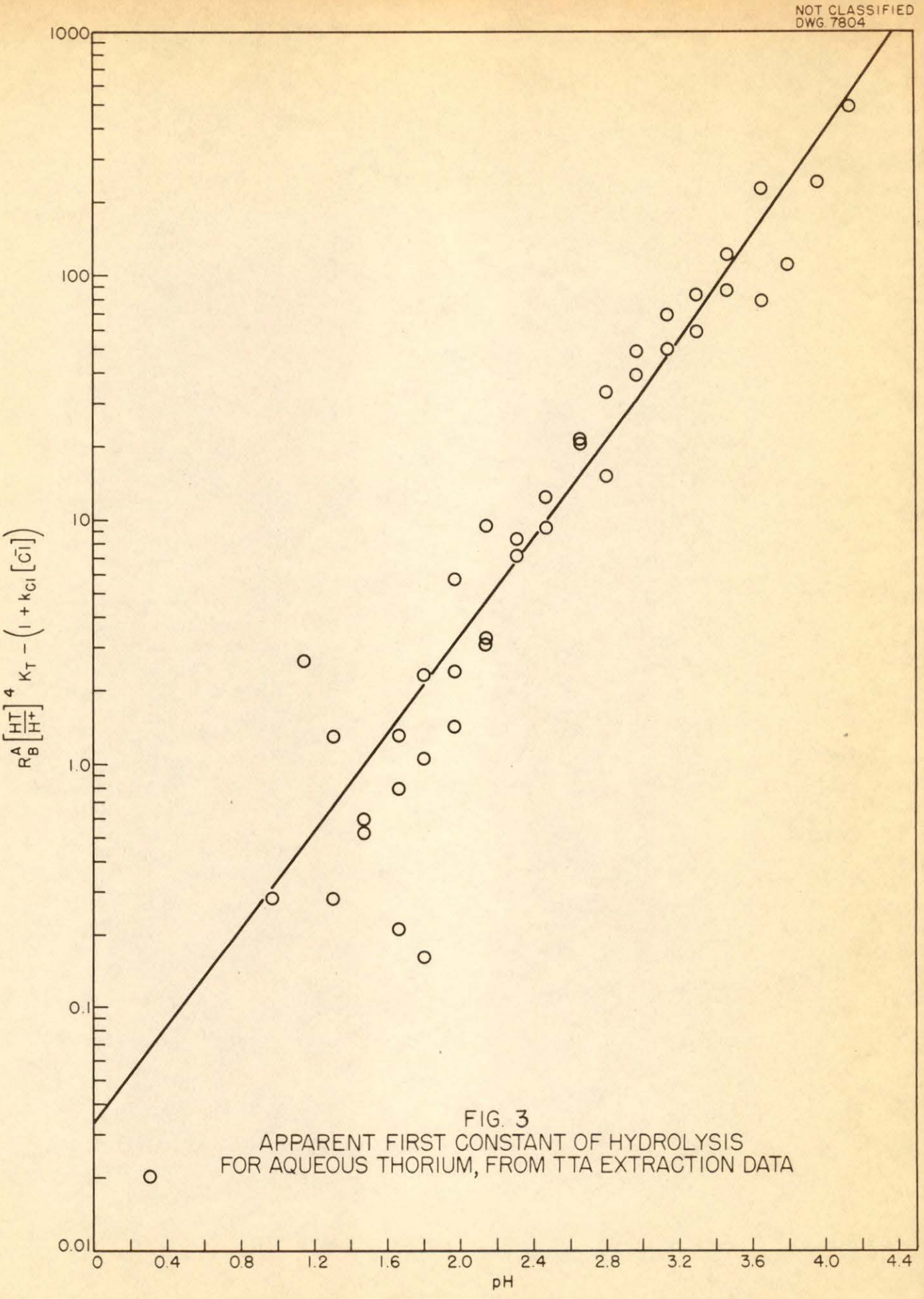


FIG. 3
APPARENT FIRST CONSTANT OF HYDROLYSIS
FOR AQUEOUS THORIUM, FROM TTA EXTRACTION DATA

A possible explanation for the high value of the apparent first hydrolysis constant for thorium obtained by this extraction method may be the existence of a stable double complex involving both OH^- and T^-, e.g., $ThOHT^{+2}$. Such a species is not without parallel, as complexes of thorium containing both hydroxide and iodate, as $ThOHIO_3^{+2}$ and $ThOH(IO_3)_2^+$, have been shown to exist and their equilibria were determined by Fry, Barney and Stoughton.[15]

The formation of the species $ThOHT^{+2}$ may be expressed by the equation

$$Th^{+4} + HT_b + H_2O = ThOHT^{+2} + k_{hT} \qquad (8)$$

Assuming this reaction to be occurring in our solutions involves the addition of the term $k_{hT}\ (HT_b)/(H^+)^2$ to the right side of equations (6) and (7); at constant $(HT_b)/(H^+)$ this term simplifies to $k/(H^+)$, where $k = k_{hT}(HT_b)/(H^+)$. With the assumption of the existence of this new species, the value of 3.3×10^{-2} obtained in the extrapolation of the curve in Fig. 1 is interpreted as the value of k. Since $(HT_b)/(H^+)$ did vary somewhat in these experiments, an accurate value of k_{hT} cannot be obtained from this extrapolation; only the order of magnitude is obtained.

If $(HT_b)/(H^+)$ is not kept constant as the *p*H varies and if the species $ThOHT^{+2}$ is assumed to exist, a more useful form of equation (7) is

$$[(H^+)/(HT_b)]\,[(R)_b^a\{(HT)/(H^+)\}^4 K_T \cdot \{1 + k_{Cl}(Cl^-)\}] = k_T + k_{hT}/(H^+) + k_h/(HT_b) \qquad (9)$$

In the work carried out here the $(HT_b)/(H^+)$ ratios did not vary greatly from unity. Therefore, if k_{hT} is considerably greater than k_h, the last term in equation (9) may be neglected for the present purpose. Hence a plot of the log of the expression on the left side of equation (9) against *p*H should give a curve which starts with zero slope and then goes into a slope of unity [similar to that obtained on plotting the expression in equation (7)]. Fig. 4 shows such a plot. The length of the zero slope portion depends on the relative magnitudes of k_T and k_{hT}. The value of k_T obtained by Zebroski and Alter[16] was about 0.17 for an ionic strength of 0.5, indicating that only a rather short portion of the curve should remain at zero slope as is also the case in Fig. 3. An extrapolation of the straight line portion of the curve of unit slope to *p*H 0 should give the value of k_{hT} as the ordinate intercept. The value of k_{hT} obtained in Fig. 4 was 4.4×10^{-2}. The straight line portions of the curves in Figs. 1 and 2 were drawn using a least squares method.

(15) A. J. Fry, J. E. Barney II, R. W. Stoughton, AECD 2429 (1948).

(16) E. Zebroski and H. W. Alter, private communication.

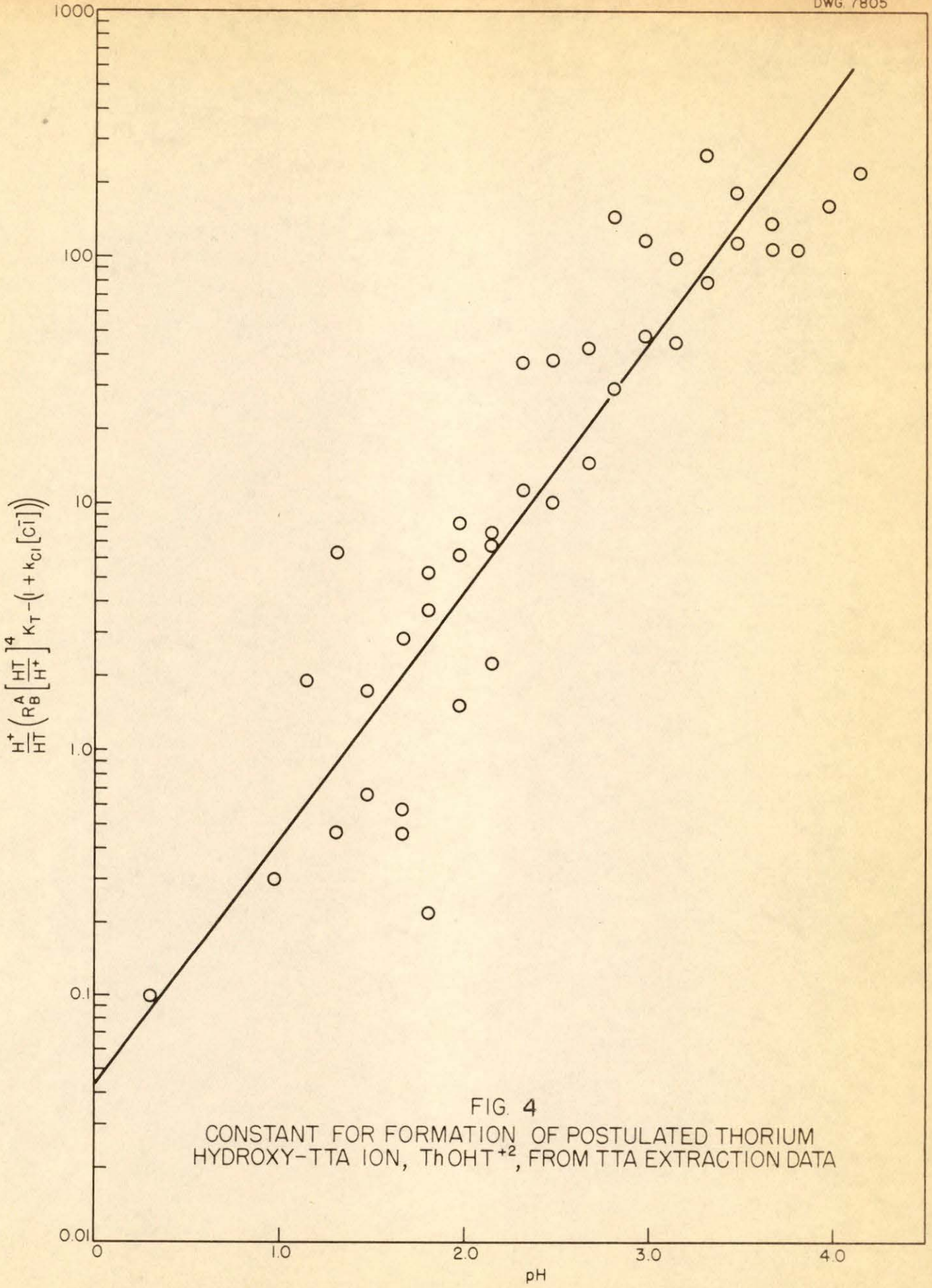


FIG. 4
CONSTANT FOR FORMATION OF POSTULATED THORIUM HYDROXY-TTA ION, $ThOHT^{+2}$, FROM TTA EXTRACTION DATA

Admittedly the data reported here can be interpreted in terms of a hydrolysis constant k_h which is much larger than expected; we, however, prefer the interpretation presented here. It is in principle possible to obtain the value of k_h using equation (9) and suitable experimental conditions. It appears though, on preliminary investigation, that values of (HT) and (H^+) which give unfeasible values of R_b^a would have to be employed.

Activity Losses in Sampling at Low TTA Concentrations. In the previous quarterly report[12] losses of thorium activity from benzene solutions containing low concentrations (10^{-2} to 10^{-4} *M*) of TTA were reported. The loss was due to adsorption or precipitation onto the glass vessel walls of the thorium species, and the "lost" material was removable with strong nitric acid. Recently, losses of thorium activity have been observed to occur in sampling such benzene solutions with pyrex glass pipets, and it has been found necessary to rinse the pipets with strong nitric acid if activity losses are to be avoided.

Results given below for one series of experiments indicate that large errors in sampling and aliquoting may occur due to adsorption of thorium activity on the walls of pipettes. In some instances errors have been found to be appreciable in 0.1 *M* TTA.

In one series of experiments the percent of activity retained after delivery of the aliquot and flushing the pipette three times with benzene was determined from the activity removed by rinsing subsequently with warm nitric acid. The results in Table 1 involve one 100 microliter, and two 50 microliter aliquots from the benzene phase of each of 18 solutions in the two phase system: Th^{232} (10^{-6} *M*), Th^{234} (tracer), TTA (0.1-0.01 *M*) in benzene; HCl (0.5 to 7.25 $\times$ 10^{-3} *M*) plus KCl to maintain an ionic strength of 0.5 in the aqueous phase.

TABLE 1

Losses in Sampling Benzene Solutions of Low TTA Concentration

			PERCENT LOSSES	
No. dtns.	*M* TTA	Avg.	Min.	Max.
18	0.10	1	0.01	5
18	0.03	1.5	0.06	5
18	0.01	5	1	20

PHASE RULE STUDIES

C. H. Secoy, W. L. Marshall, Jr. and J. S. Gill

ABSTRACT

Work on the solubility of UO_3 in uranyl sulfate solutions has been discontinued since experiments indicate that excess acid will be necessary to prevent the precipitation of UO_4 from sulfate solutions in an intense radiation field.

Apparatus has been assembled which will determine with reasonable precision the vapor pressure of aqueous systems at temperatures above 200° C. The apparatus is now being calibrated and will be used first to study uranyl sulfate solutions.

Table-top experiments indicate that corrosion of uranium by uranyl sulfate solutions can be effectively prevented by the application of a counter-voltage. There is a remote possibility that such a technique might be useful in preventing tank corrosion in a homogeneous reactor.

A phase study of the system uranyl nitrate-water has been started. In the high temperature range, determination of the composition of the vapor phase will be necessary since thermal decomposition of the nitrate ion is indicated. Only preliminary results have been obtained.

A brief study of the thermal decomposition of uranyl oxalate and uranyl formate has been started. Analytical, crystallographic, and electron microscope data for the solid products are being obtained but are, as yet, incomplete.

THE SYSTEM UO_3-UO_2SO_4-H_2O

J. S. Gill and C. H. Secoy

A study of the solubility of UO_3 in uranyl sulfate solutions was started some time ago with the hopes that a less acidic solution would decrease the corrosive action on metals, this corrosive action being one of the objectionable characteristics of the use of uranyl sulfate solutions in a homogeneous reactor.

Additional data to that previously reported[17] indicate that the solubility of UO_3 increases with temperature to approximately 180° C and decreases at higher temperatures.

[17] ORNL 286, Chemistry Division Quarterly Report for April, May, and June, 1949.

Work on this system was discontinued during this quarter since it was found[18] that excess H_2SO_4 was necessary to prevent precipitation of UO_4 from the solution under the action of radiation in the ORNL reactor. This result was not entirely unexpected but had not previously been demonstrated in a definite manner by experiment.

THE SYSTEM UO_2SO_4-H_2O

J. S. Gill and C. H. Secoy

Development of apparatus to measure the equilibrium vapor pressure of uranyl sulfate solutions in the temperature range 200° C to 400° C has been continued. Calibration runs are being made and, unless unforeseen difficulties appear, useful data should be obtained in the near future.

The apparatus consists of a stainless steel pressure bomb with a silica liner to which is attached a Baldwin transducer. The Baldwin is fundamentally a strain gauge with refinements to give maximum precision. A Lindberg air-circulating furnace is being used to heat the bomb. A ten-junction iron-constantan thermocouple placed in the furnace operates a Leeds and Northrup controller to give a temperature constant to ± 1° C. The period of oscillation of the furnace temperature is 40 seconds. Under these conditions the temperature inside the bomb remains constant to ± 0.1° C after the steady state has been reached. The final temperature calibration will be made against a Bureau of Standards calibrated platinum resistance thermometer and the pressure readings are being checked against the saturated vapor pressure of steam.

As soon as calibration of the apparatus is completed, P-T-C data for any of several aqueous salt solutions in the temperature range above 200° C should be readily obtainable.

USE OF COUNTERVOLTAGE TO PREVENT URANIUM CORROSION IN AQUEOUS URANYL SULFATE SOLUTIONS

W. L. Marshall, Jr. and C. H. Secoy

Uranium is considered a possible metal for construction of a reactor tank for a homogeneous pile using aqueous uranyl sulfate solutions as the pile

[18] J. W. Boyle, private communication.

fluid. However, uranium is corroded by acidic uranyl sulfate solutions due mainly to an electromotive potential between the solution and the metal. It was the object of this investigation to stop all apparent corrosion of the metal by placing a back potential on the system sufficient to stop reaction of uranium.

Experimental. Two electrodes, one uranium, the other platinum, were set up in a beaker under gas burets. The beaker and burets were filled with a given solution. By means of a potentiometer, the cell voltage was counterbalanced to zero. Solutions used were a 5.85% UO_2SO_4 and a 5.8% UO_2SO_4, 0.7 *N* in H_2SO_4. These concentrations are favorable in the development of a homogeneous pile.

Results. No apparent corrosion of uranium metal occurred at room temperture; however, due to the brevity of the work, this experiment is not to be regarded as conclusive evidence for the behavior of the system.

THE URANYL NITRATE-WATER SYSTEM

W. L. Marshall, Jr.

The system, uranyl nitrate-water, is being investigated to determine its potentialities as a reactor fuel in a homogeneous pile. Preliminary data have been obtained on the system from 25° C to 300-400° C. Two concentrations, 0.171 molal (40 g uranium/liter) and saturated (at 22° C), have been used.

The experimental procedures were carried out as described by Secoy[19]. The same apparatus as described in reference[19] was used in the investigation. Ten centimeter length quartz capillary tubes closed at one end were filled with solution to one-third volume. The excess atmospheric gases were removed and the tube ends sealed by torch. The tubes were rocked and slowly heated in a steel bomb. The temperature was measured by a thermocouple, and observations were made through a slit in the bomb.

Results. No apparent change was observed in the 0.171 molal clear, yellow solution until at about 290° C a yellow, cloudy solid appeared at the "dry" end of the capillary and increased to some extent with temperature rise. At the highest temperature, 335° C, the solution was still a clear yellow, the vapor colorless, and the cloudy solid still present in the originally "dry" end.

[19] C. H. Secoy, ORNL 98.

The first observed change in the clear, yellow saturated (22° C) solution occurred at about 264° C. A yellow, cloudy solid similar to that in the previous experiment appeared at the "dry" end of the tube and increased somewhat with temperature. At 290° C the vapor assumed a yellowish coloration which slowly deepened to a wine red at the highest temperature (380° C). At 335° C a yellow precipitate was observed which increased with temperature. Upon lowering the temperature from 380° C the vapor phase slowly became lighter from a wine red to yellow, then to colorless below 210° C. The solution remained a clear yellow throughout the experiment.

Preliminary Conclusions. Evidently, in the case of decomposition, yellow UO_3 (hydrated) has been formed together with some oxides of nitrogen. Also, the vapor phase color is most likely due to the equilibrium, N_2O_4 (colorless) $\longleftrightarrow$ $2NO_2$ (red-brown). At lower temperatures NO_2 then combines with water to form HNO_3 and colorless NO.

Work on this system is still in progress, and a more complete report will be given later.

SLURRY EXPERIMENTS

J. S. Gill, C. H. Secoy

Due to limited manpower no extensive work on slurry systems is contemplated by this group. However, a few simple experiments have been started which may be worth mentioning.

Among other factors, the method of preparation of oxide powders would be expected to have an effect on the stability of a slurry. Due to some previous experience of one of us on the preparation of finely divided metal powders by thermal decompositions of oxalates and formates under controlled conditions, the analogous decomposition of uranyl formate and uranyl oxalate seemed worth a short investigation. Although analytical data and optical and electron microscope examination of the products have not been completed, the powders do not look favorable for the preparation of stable slurries. None of the products has the color and appearance of the expected UO_2 or possibly UO_3 and more than one crystal form has been observed in each case.

Experimental. Ten g of salt was suspended in 200 cc of dibutyl phthalate in a 500 cc, 3-necked flask equipped with an efficient stirrer and a reflux condenser. With vigorous stirring the flask was heated at the temperature and

for the period of time indicated in the following table. The solid product was removed by centrifugation, washed with absolute ethyl alcohol until the wash liquid remained free of color and finally dried at 110° C. Conditions for each run and the results to date are summarized in the table.

TABLE 1

Thermal Decomposition of UO_2C_2O and $UO_2(HCO_2)_2$

				PRODUCT				
NO.	SALT	TEMP.	TIME HRS.	% U TOTAL (GRAV.)	% U TOTAL (VOL.)	% U as U^{IV} (1)	% C	OBSERVATIONS
1	Oxalate	200	3	64.3	67	14.1	*	Light yellow powder. At least 3 crystal forms.
2	Oxalate	220	3	61.0	66	14.2	*	Dirty yellow powder. More than one crystal form.
3	Oxalate	240	3	57.5	61.5	16.7	*	Gray powder.
4	Formate	185	2	*	*	*	*	At first orange, then light yellow.
5	Formate	205	2	*	*	*	*	Darker yellow powder.
6	Formate	255	2	*	*	*	*	Gray-black powder.

* Data not yet available.

(1) Calculated on the assumption that no other material capable of reducing cerate ion was present.

NUCLEAR CHEMISTRY

ELEMENTS IN THE FISSION PRODUCT REGION

SEARCH FOR Zr^{93} AND Mo^{93}

G. E. Boyd and Q. V. Larson

As was indicated in the previous quarterly report (ORNL 286, p. 68) a long-lived molybdenum isotope, presumably Mo^{93}, has been identified in a sample of pile irradiated molybdenum metal. A lower limit of 70 days was placed on its decay by K-capture. Now, from measurements of the decay of the gross radiations, and of the Mo K_α X ray with two samples, a half-life greater than 2 years may be reported.

Decay measurements on a series of fission product Zr samples have continued without any indication of the presence of Zr^{93} in the predominant 65 d Zr^{95} activity (ORNL 229, p. 31 and ORNL 336, p. 38) despite the decay of the latter at least through 23 half-lives. A half-life greater than 4×10^6 years for Zr^{93} would be consistent with these observations.

THE RADIONUCLIDES OF TIN

C. M. Nelson and G. E. Boyd

During the past quarter a very considerable clarification of the status of many of the tin radionuclides has been effected through the work of three independent groups of observers. At present the assignment of most of the known periods can be made with the exception of the pile neutron induced 80 m, 3 h and 17 h activities. In the isotope by isotope summary given below, we shall first give our contribution up to this time and then compare this with the results of others.

(1a) Sn^{125}. A 9.5 ± 0.1 m negative β-emitting period was formed in maximum yield in the slow neutron irradiation of enriched Sn^{124}. A further study of the radiations beyond that reported in ORNL 336, p. 39, has been made

using coincidence counting techniques employing a beta proportional counter together with a scintillation counter for the gamma rays. A simple beta spectrum of 2.05 Mev maximum energy appears to exist in the decay of the 9.5 m Sn^{125} which is followed by gamma rays of 0.36 and 1.86 Mev, respectively. This beta energy does not agree with the recent report of Lee and Pool [Phys. Rev., 76, 606 (1949)] who give a value of 1.3 Mev, but does confirm apparently the provisional value of Sullivan and Wyatt [Mon 243, p. 3 (1947)] of 2.2 Mev.

(1b) 10 d Sn^{125}. A 2 mg sample of enriched Sn^{124} was irradiated with slow neutrons in the Oak Ridge pile for 7 days and allowed to cool for 15 days after which the antimony activity was separated by coprecipitation with PdS formed in 2 *M* HCl. The purified tin fraction then decayed with a 10-11 d half-life emitting beta rays of ~2.1 Mev maximum energy together with a small amount of gamma radiation. Thus far attempts to establish a parent-daughter relation between the 10 d Sn and the 2.7 y Sb^{125} have not been successful. Better chemical separations methods are now under investigation. Recently values of 2.1 and 2.38 Mev for the maximum beta particle energy associated with 10 d $Sn^{123,125}$ have been published by Lee and Pool (loc. cit) and by Newton and McDonell (UCRL 395), respectively.

(2a) 40 m Sn^{123}. A 40 m negative beta emitting period is formed in maximum abundance upon slow neutron irradiation of Sn^{122}. A range of 475 mg Al/cm^2, corresponding to a maximum beta energy of 1.12 Mev, was obtained in a Feather comparison with RaE. The presence of Sb K_α X rays was also revealed by the aluminum absorption curve. A provisional half-thickness value of 4.3 g Pb/cm^2 corresponding to a gamma ray energy of 0.4 Mev, may be reported also. A beta ray energy of 1.32 Mev and the presence of a gamma have been reported by Lee and Pool. Newton and McDonell (loc. cit.) give ~1.7 Mev for E_β and ~0.17 Mev for E_γ, and further have demonstrated the Sb X ray by critical absorption measurements.

(2b) 130 d Sn^{123}. A 120 day tin activity has been found to be produced also in maximum yield by slow neutron irradiation of Sn^{122}. A provisional value of ~1.3 Mev for the maximum beta energy may be estimated from a visual end-point of ~590 mg Al/cm^2 in the aluminum absorption curve. A very small amount of γ is suggested by the aluminum curve. There is now a general agreement as to the assignment and radiation characteristics of this isotope. Both Lee and Pool and Newton and McDonell assign the activity to mass 123. The former workers give 1.3 Mev as its beta energy whereas the latter give 1.5 Mev.

(3) 27.5 h Sn^{121}. A 27 h negative beta emitting activity is produced in maximum yield in the slow neutron irradiation of Sn^{120}. This radionuclide appears to decay solely by the emission of a 0.4 Mev beta particle in agreement with Lindner and Perlman [Phys. Rev., 73, 1124 (1948)] and with Lee and Pool (loc. cit.).

At no time has there been any indication of the formation by slow neutrons of a 41 m energetic beta emitting (E_{max} ~2.5 Mev) isomer at this mass. Newton and McDonnel (loc. cit), however, find such an activity with 14 Mev deuterons on Sn^{120} whereas Lee and Pool apparently failed to see it with 10 Mev deuterons on Sn^{120}.

(4) $Sn^{119\,m}$. An 80 m period has been observed to be formed in good yield, with slow neutrons on enhanced Sn^{118}, but as yet it has not been established that this activity is in tin or that it resides in mass 119.

(5) $Sn^{117\,m}$. At present no definite period can be assigned at this mass as a result of the slow neutron activation of enriched Sn^{116}.

(6) $Sn^{115\,m}$. It appears from the decay curve taken with a sample of enhanced Sn^{115} bombarded for one week in the Oak Ridge pile that a 16 d activity must belong to $Sn^{115\,m}$ or Sn^{116}. The decay has been followed over 60 days, and the curve shows roughly three half-lives of pure 16 d activity. Aluminum absorption curves indicate two groups of conversion electrons with ranges of about 20 and 120 mg Al/cm^2 together with an X ray in the In-Sn-Sb region.

(7a) $Sn^{113\,m}$. A 30 minute tin activity was produced in maximum yield in the pile irradiation of enriched Sn^{112}. This period had been noted earlier in the bombardment of $Sn^{116}O_2$ and $Sn^{117}O_2$. As yet its radiations have not been characterized beyond our earlier report (ORNL 286 p. 70).

(7b) 112 d Sn^{113}. This activity, which may be the same as the previously reported 105 d Sn^{113} [Seaborg and Perlman, Rev. Mod. Phys., 20, 585 (1948)] was formed in maximum yield also in the slow neutron irradiation of enriched Sn^{112}. There is an abundant yield of e^- of 120 mg Al/cm^2 (0.40 Mev) range together with an X ray in the In-Sn region. Soft gamma radiation showing a half-thickness of about 3.6 g Al/cm^2 (~90 Kev) is also given out in the decay. There is also an indication of the presence of very soft conversion electrons. Taken altogether, the above observations are consistent with the earlier observations of S. W. Barnes [Phys. Rev., 56, 414 (1939)]. The 0.40 Mev conversion electrons are associated with the 105 m $In^{113\,m}$ formed by the K-capture decay of the Sn^{113}. The soft gamma (~90 Kev), the low energy e^- and the In K_α X ray are associated with the decay of the 112 d Sn^{113}.

Slow neutron irradiation of enhanced Sn^{114} has produced an activity quite similar to (possibly identical with) the 112 d Sn^{113}. The half-life, however, is unmistakably lower at 97 d. Also the composition of the radiations differ, particularly in the presence of sizeable amounts of a 190 mg Al/cm^2 component in the latter activity. Further studies are being conducted in order to clear up this point.

DECAY SCHEME OF I^{133}

*A. R. Brosi and P. M. Gross, Jr.**

Introduction. In assaying fission product iodine samples for 6.7 h I^{135}, ionization currents have been measured with 4 inches of lead between the source and the ion chamber. In all cases the ion current decay curves could be analyzed into two components, one with a 6.7 h half-live and another with a 21 h half-life. The intensity of the 21 h component was of the order of 10^4 times that expected from 21 h I^{133} assuming it to decay with a 0.53 Mev gamma ray as previously reported. The work described below was done in order to understand this discrepancy.

Summary. Evidence has been found for branching in the decay scheme of I^{133}. About 6% decays with an ~0.5 Mev β ray and 94% with the previously known 1.4 Mev β. There are gamma rays with energies of ~0.85 Mev and ~1.4 Mev in addition to the previously known 0.53 Mev gamma ray. The 0.85 Mev gamma ray occurs in about 5% and the 1.4 Mev gamma in about 1% of the disintegrations.

Experimental. All measurements were made on fission product iodine prepared in such a way that 98% of the disintegrations were those of I^{133} and 2% were those of 8 d I^{131}. This was accomplished by bombarding UO_2SO_4 for one hour in the ORNL reactor. About two hours after the bombardment a standard fission product Te separation (CN 2815) was made. The Te was dissolved and iodine was separated and discarded. Three hours after the bombardment the Te was re-precipitated. This was the zero time for growth of I^{133} from Te^{133}. The Te was redissolved and an iodine separation made after a one-hour growth period. This iodine was allowed to stand until I^{132} and I^{134} had decayed (24 hrs) before measurements were made. In I^{133} tracer made in this way 6.7 h I^{135} contributed less than 0.1% of the disintegrations.

* Participant in ORINS-ORNL Research Program—Department of Chemistry, University of Virginia.

Coincidence Measurements. Coincidence measurements were made on I^{133} samples using a proportional beta counter, a scintillation gamma counter and a coincidence circuit of the type described by Dandl in ORNL 286. Both aluminum and lead absorption curves were taken. These showed that in addition to the previously known 1.4 Mev beta group, there was a lower energy beta (~0.5 Mev) in coincidence with more energetic gamma radiation than the known 0.53 Mev gamma ray. There was no evidence for delayed gamma emission which would be present if I^{133} decayed to a metastable state with a half-life of the order of or greater than the 1 μ-sec resolving time of the instrument. Finally, the measurements showed the presence of gamma-gamma coincidences. The number of gamma-gamma coincidences in I^{133} per disintegration relative to the number in Co^{60} indicated that cascading of gamma rays occurred in about 5% of the I^{133} disintegrations. This conclusion assumes the same angular correlation between the gamma rays in the two isotopes. Coincidence measurements were made on three separate preparations of I^{133} with essentially the same results in each case.

Energy of Gamma Rays. A lead absorption curve of the I^{133} gamma radiation showed only a slight deviation from a straight line. The half-thickness, however, was somewhat greater than expected for the known 0.53 Mev gamma ray.

At this time an anthracene crystal was made, as described elsewhere in this report, which was suitable for use in a scintillation spectrometer. A spectrometer built for us by C. J. Borkowski was used to measure the I^{133} gamma rays. The data show the presence of three different gamma rays which decay with the I^{133} half-life. A preliminary calibration of the spectrometer indicates that these gamma rays have energies of 0.53 Mev, 0.85 Mev and 1.4 Mev with relative probable errors of about 10%. The intensity ratios in the order of increasing energy are 100:5:1. These ratios are consistent with the gamma-gamma coincidence data reported above.

Experiments with Xe^{133}. Both Te^{131} and Ba^{135} which have the same number of neutrons as Xe^{133} have metastable states. Xe^{131} and Xe^{135} also have metastable states. This suggested the possibility that a metastable state of Xe^{133} might exist. Xe^{133} was removed from the I^{133} parent using the technique described in ORNL 65. Both very short and very long growth periods were used. No evidence was found for an activity other than the well known 5.3 d Xe^{133}. This, of course, does not exclude the existence of a metastable state of Xe^{133} nor the possibility that I^{133} decays to such a metastable state in a very small fraction of the disintegrations.

RADIATIONS AND HALF-LIFE OF LONG-LIVED FISSION SELENIUM

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

Introduction. L. E. Glendenin[1] and L. Winsberg[2] have described the unsuccessful search for a long-lived fission selenium activity at mass 79. Winsberg established a very low half-life limit of about 30 years and treated his data in terms of different assumed fission yields. On the basis of the smooth-curve yield (~0.035%) Glendenin concluded that a minimum half-life value was $> 7 \times 10^6$ y. Since no other fission isotope has been assigned to this mass, there is no evidence which definitely establishes the chain.

Summary. In the present investigation, having significant advantages over earlier work in quantity of source materials and improvements in fission-product chemistry, the isolation and characterization of a long-lived fission-product selenium activity at mass 79 has been accomplished. Preliminary mass-spectrographic evidence for the assignment has been obtained from R. F. Hibbs at the Electromagnetic Plant Mass-Spectrographic Laboratory. The single electron radiation observed appears to have a maximum energy of about 160 Kev. The half-life, calculated from the observed disintegration rate and the smooth-curve fission yield is 6.5×10^4 years. During the investigation, some difficulty was encountered in obtaining interchange of fission-selenium with chemical carrier.

Experimental. Run No. 1. The highest level, long-cooled Hanford uranium was used in this separation which was adapted from the established fission-product sulfide process[3].

The selenium was first isolated with milligram quantities of selenium carrier from a uranyl chloride-ferric sulfate solution from which the long-lived I^{129} had just been distilled. Details of the chemical procedure are given under Run No. 2 which was more satisfactory. In the very first attempt, it was found that little or no selenium could be recovered from the fission product sulfides after dissolution in a mixture of H_2O_2 and NH_4OH. Assuming that this was due to a difficultly soluble sulfide, CS_2 extraction of the metal and/or sulfide was attempted and also abandoned as unsatisfactory. Finally the metal

(1) L. E. Glendenin; MDDC-1694-C, February, 1948; PPR Vol. 9B 7.3.5.

(2) L. Winsberg; PPR Vol. 9B 7.3.4.

(3) Parker. G. W., J. W. Ruch, and J. Reed, AECD-2043 (Jan. 1948).

solution was freed of sulfide ion by boiling, the acid strength was increased to 6 *N*, and selenium was reduced with SO_2. After washing, the selenium fraction was dissolved in aqua-regia and removed from the shielded cell for purification. The final activity was extremely low but was sufficient to provide conclusive evidence of the radiations and identity of the activity.

Run No. 2. Since the first run had resulted in such an extremely weak sample as well as a very poor chemical yield, a second run was made, using a new uranium slug identical with the first.

In this run, immediately after the metal was dissolved in conc. HCl, 20 milligrams of inactive selenium as selenous acid was added to the UCl_4 slurry. The UCl_4 was then oxidized by the careful addition of 30% H_2O_2. After the oxidation was complete, the mixture was boiled to recover iodine and to effect a volume reduction. After cooling, cold conc. HCl was added to increase the acidity to above 6 *N*. SO_2 was then passed through the solution for several hours during which time a red color was formed and changed to a darker one. The entire solution was then filtered and the selenium washed and dissolved in aqua-regia as before.

Nitric acid was removed by evaporation with HCl, and the selenium was then distilled in silica with two 50 ml portions of 48% HBr into 50 ml of conc. HCl. The selenium was re-precipitated with SO_2 from the 8-10 *N* HCl-HBr mixture, filtered and weighed in a sintered glass filter crucible. After one distillation the activity in the entire sample was only a few microcuries and was found to be essentially free of all activities except that of selenium and lesser amounts of those of antimony and tellurium.

The yield was 14 milligrams of the 20 milligrams added and the 2-3 milligrams expected from fission, or about 60%. The total activity at 2% geometry was about 230 counts per second. The aluminum absorption curve showed essentially a 2.5 milligram half-thickness with a small portion having a 20 milligram half-thickness and a low gamma count.

Final Purification of Selenium. It was expected and was found that the contaminating activity in the selenium was the 2.7 y Sb^{125} and mixtures of the 90 d Te^{129} and the metastable Te^{125}. Accordingly, holdback carriers of antimony and tellurium were added before the second HBr distillation. As an indication of the progress of the purification, Sb and Te were also added to the HBr distillate before the recovery of the Se by SO_2 precipitation. The selenium was again precipitated and weighed. The activity was found to have been reduced from 230 to about 170 counts per second for 13 milligrams. The difference in counts was found to be equally divided between the antimony fraction in the HBr distillate and the Te fraction in the HBr still residue.

By weighing Sb_2S_3 and Te metal precipitated in 1-3 *N* HCl-HBr, it was also found that about 1/3 of the total antimony consistently distilled with the selenium, while the active antimony was almost completely distilled with this portion. The antimony remaining in the still residue was essentially inactive.

The selenium was again distilled with HBr in the presence of Sb and Te holdback carriers and both carriers were also added to the HBr distillate. The Te fractions were inactive but again the Sb fraction in the distillate was active, counting about 20% as much as the first one. Absorption curves indicated that the Sb carried activity was normal for Sb^{125} and could not be confused with the bulk Se activity.

Finally the Se activity was redistilled with holdback carriers of Sb^{+3}, Sn^{+4} and As^{+3}. Again each of these was added to the distillate before the Se was precipitated. Each was isolated and counted by means of fractional precipitation of the sulfides starting in 10 *N* HCl, although the arsenic was found only in the distillate.

None of the above fractions was found to be active except for a trace of Sb in the distillate. The Se did not precipitate cleanly in the presence of all of the holdback carriers and was reduced to about 10 milligrams. It was redissolved and reprecipitated from 8 *N* HCl in the absence of holdback carriers. The activity was about 130 counts per second. The rough absorption curve indicated less than one part per thousand of any radiation harder than the previously observed 2.5 milligram half-thickness (Fig. 5).

Electrodeposition of Selenium. A method described by Jílek and Lukáš[4] has been adapted for the codeposition of copper and selenium on platinum disks for weighing and counting. The plates are dull-black and adhere well particularly if plated slowly on a thin film of copper over the platinum. The voltage was started at 1.9 and the current at 1 ma. The plating solution was a mixture about 6% in sodium tartrate and 0.5 *N* in HNO_3. The sample was washed free of the plating solution before disconnecting the current.

In Table I, the near quantitative plating of selenium and the relative activity of the sample are compared with the previously weighed amount of the metals added to the plating solution. In the above reference, at least equivalent amounts of Cu are suggested for codeposition. However, the yields are believed to have been improved by doubling the amount of copper added.

Energy Approximation of Se^{79} by Comparison with S^{35} and C^{14}. In order to estimate the energy of the beta in Se^{79}, it was found relatively simple to compare its half-thickness value with those of two other well-established nuclides, namely S^{35} (168 Kev) and C^{14} (154 Kev). In Fig. 6, the three absorption

(4) Ant. Jílek and Jam Lukáš, Chem. Listy 21, 576-583 (1927) Chem. Abst. 1734, 22.

NOT CLASSIFIED
DWG. 7833

FIG. 5
ALUMINUM ABSORPTION CURVE
OF 6×10^4 y FISSION SELENIUM

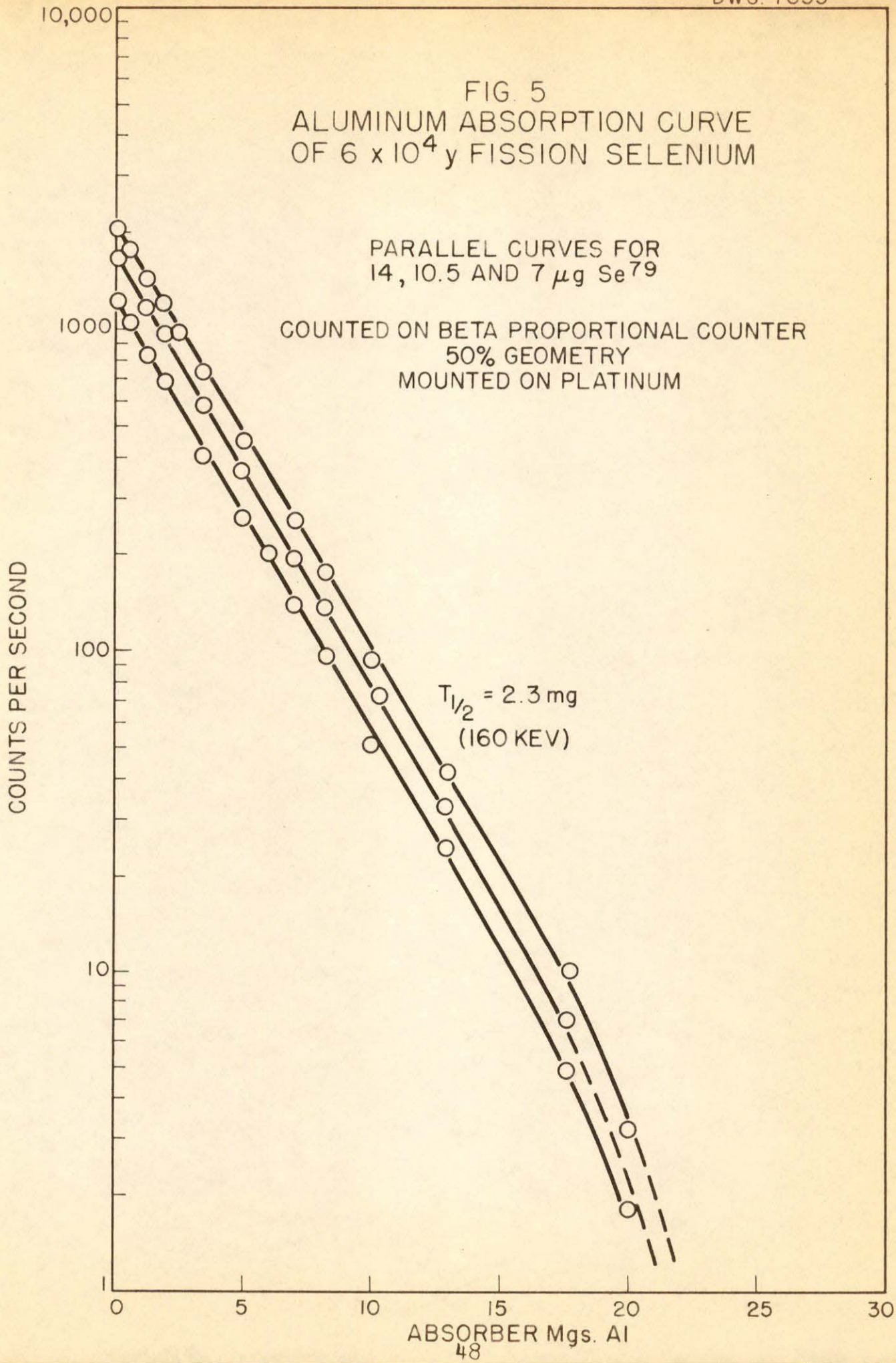


FIG. 6
ENERGY OF LONG-LIVED FISSION SELENIUM FROM RELATIVE ABSORBER HALF-THICKNESS VALUE COMPARED WITH C^{14} AND S^{35}

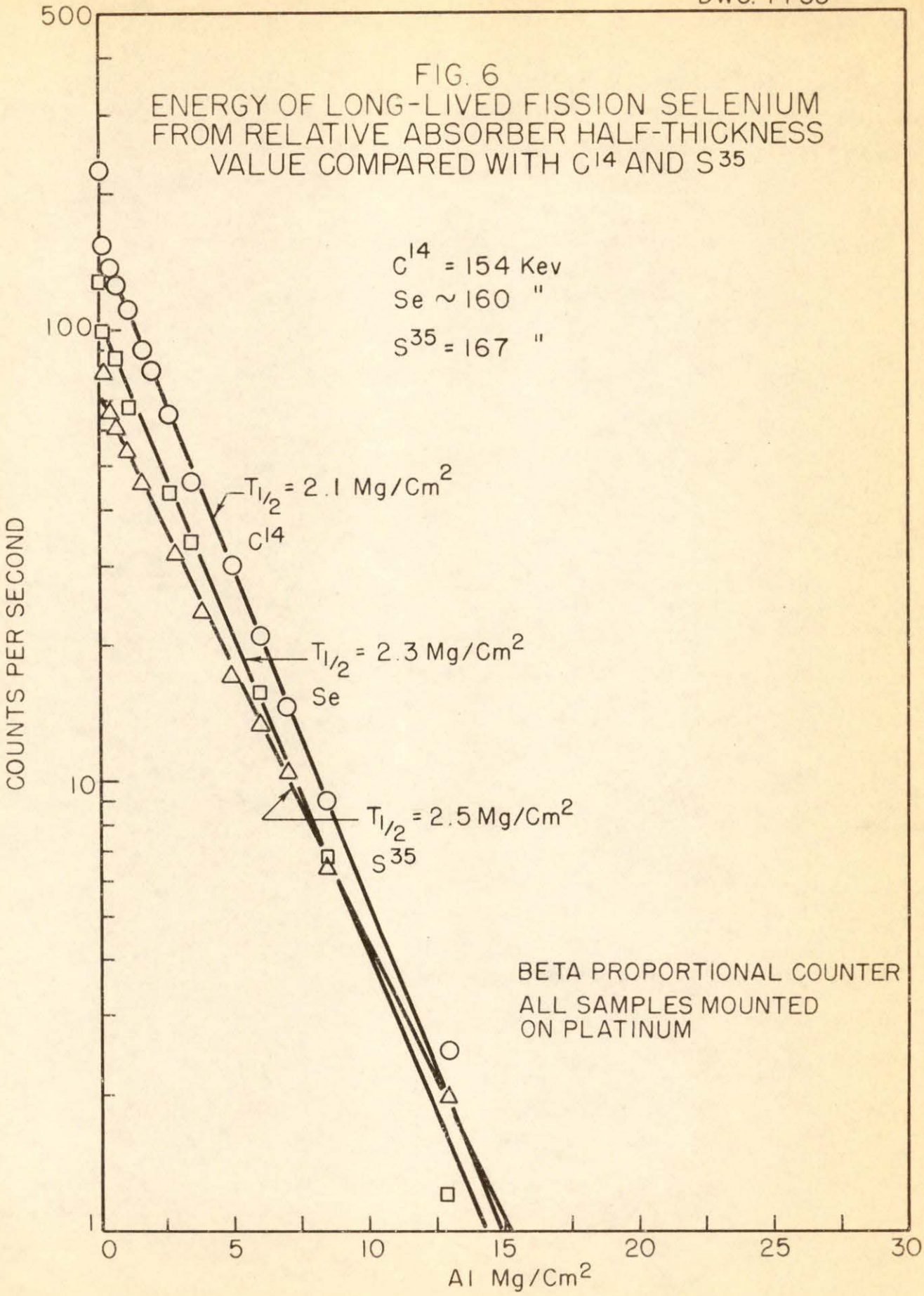


TABLE I

Electrodeposition of Selenium with Copper

SAMPLE No.	PLATING TIME (Hrs)	Se ADDED (mgs)	Cu ADDED (mgs)	Cu-Se YIELD (mgs)	PERCENT YIELD	RATIO OF ACTIVITY FOUND (Corr. for Self absorption)
I	16	0.5	1.0	1.53	102	1.0
II	10	0.75	1.5	2.17	96	1.47
III	10	1.0	2.0	2.84	95	1.94

TABLE II

Disintegration Rate and Half-Life of Long-Lived Selenium

	COUNTING RATE					
SAMPLE No.	OBSERVED 50% geom.	CORR. FOR SELF ABSORPTION Area = 1.75 cm^2	CORR. FOR BACK SCATTER (50%)	MASS Se^{79} (Calc. 1.4% See Table I)	d/s/μg	
					Se^{79}	T½
I	919 c/s	1380 c/s	1220 c/s	7.0 μg	263	6.4×10^4 y
II	1352	2030	1700	10.5	258	6.5×10^4
III	1778	2670	2100	14.0	254	6.6×10^4

TABLE III

Energy Approximation for Se^{79} by Relative Half Thickness Values

ISOTOPE	ENERGY (Kev)	OBSERVED ABSORBER HALF-THICKNESS in Mgs. Al	ESTIMATED VALUE FOR Se (Kev)
C^{14}	154	2.1	
Se^{79}	--	2.3	160 ± 5
S^{35}	168	2.5	

curves are given as observed under the same counting conditions. It is apparent that the initial half-thickness value for Se is approximately at the mid-point between the other two. While this method of energy determination is probably valid only when the spectra are similar, it is of considerable value for approximation.

Specific Activity and Half-Life of Se^{79}. It was noted that Run No. 2, in which the Se^{+3} carrier was added before the UCl_4 oxidation was performed, gave a selenium product with a specific activity approximately 100 times as high as in Run No. 1. Since the samples should have been identical, it has been presumed that the fact that the selenium activity could have been in the selenic state while the carrier was added in the selenous form would account for the very incomplete equilibration between the two. It is also possible that this effect accounts for the considerable difference between the observed half-life and the much greater lower limit proposed by Glendenin. The additional unusual behavior of the antimony here is also indicative of the reason for the early controversy over the existence of the 2.7 y antimony(5).

In Table II, the data used in the calculation of the half-life are summarized. The very high counting rates and the incidental agreement in value between samples are indicated.

Because abundance data on the mixed isotopes are just being obtained, it was necessary to base initial calculations on the theoretical values. In preliminary work in preparing for the spectrographic analysis, plates were made by Hibbs and Fultz of purified chemical selenium in which the positions at 79 and 81 are entirely clear and mass 74 ($< 1\%$) is quite clearly indicated. A 4 milligram selenium sample in a 1/16 in. tantalum tube was given to this group at the Electromagnetic Plant for preliminary study.

They have reported additional lines at 79, 81, 83 and 84 in order of decreasing intensity with the 79 line somewhat heavier than the Se^{74}. The presence of all these lines is not quite understandable. However, the 79 and 81 could possibly indicate a trace by bromine. Even so, the intensity of the 79 indicates it would have had to be enhanced by another particle (assumed to be Se^{79}). Transfer radioautographs and a higher degree of purification of the selenium should help assign the extraneous lines.

In evaluating the half-life data, it is believed that the value 6.5×10^4 y should be considered as a maximum. Further work to improve the specific activity to a point where the radiation may be studied on the beta-ray spectrometer will be continued. A procedure in which tellurium may be employed as an isomorphous carrier would be decidedly useful.

(5) G. Leader and W. H. Sullivan, (H)-CN-3465, Jan. 1946.

FEASIBILITY TEST OF THE LARGE SCALE COLLECTION OF FISSION RARE-GASES

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

Introduction. Long standing interest in the large scale direct collection of fission-product gases has encouraged a test of the absorption of 10 y Kr^{85} from a dissolving of a high-level Hanford slug. Current interest in rare-gas nuclides arises from the radioisotope production program and from the need for isolated, pure samples for nuclear measurements.

Small quantities (mm^3) of gas have been extracted previously from small samples of irradiated Clinton metal by Arrol, Chackett and Epstein[6] for isotopic abundance measurements and development of adsorption separation techniques for argon, krypton and xenon.

Collection of curie amounts of Xe^{135} from the Los Alamos homogeneous reactor were made by Sugarman[7] and others for the growth of the 10^6 y Cs^{135}.

Summary. An exploratory experiment involving the complete cleaning of the off-gas stream from a hydrochloric-acid dissolver operation and the adsorption of the rare-gases on activated charcoal has been completed. Nearly quantitative recovery of the gas resulted as was indicated by the yield of the 10 y krypton activity.

The gas stream, diluted with helium, was passed through a series of alkaline scrubber columns under a slight negative pressure provided by a jet in the exhaust stack. Residual moisture was removed in a liquid nitrogen-cooled trap following which the krypton and xenon were collected in a 250 gram charcoal adsorber.

Experimental. Dissolving and First Adsorption of Krypton-Xenon. An irradiated Hanford slug was decoated in a series of alkali, acid-fluoride and acid washes and placed in a glass dissolver by means of a platinum wire basket.

The dissolver was closed with a mercury weighted, spherical-jointed cover to which was attached a manometer tube. The dissolver and the connected scrubber train were flooded with a slow helium stream for the removal of air (Fig. 7).

(6) W. J. Arrol, K. F. Chackett and S. Epstein, CRC 297 (1947).

(7) N. Sugarman, LAMS-769 (August , 1948).

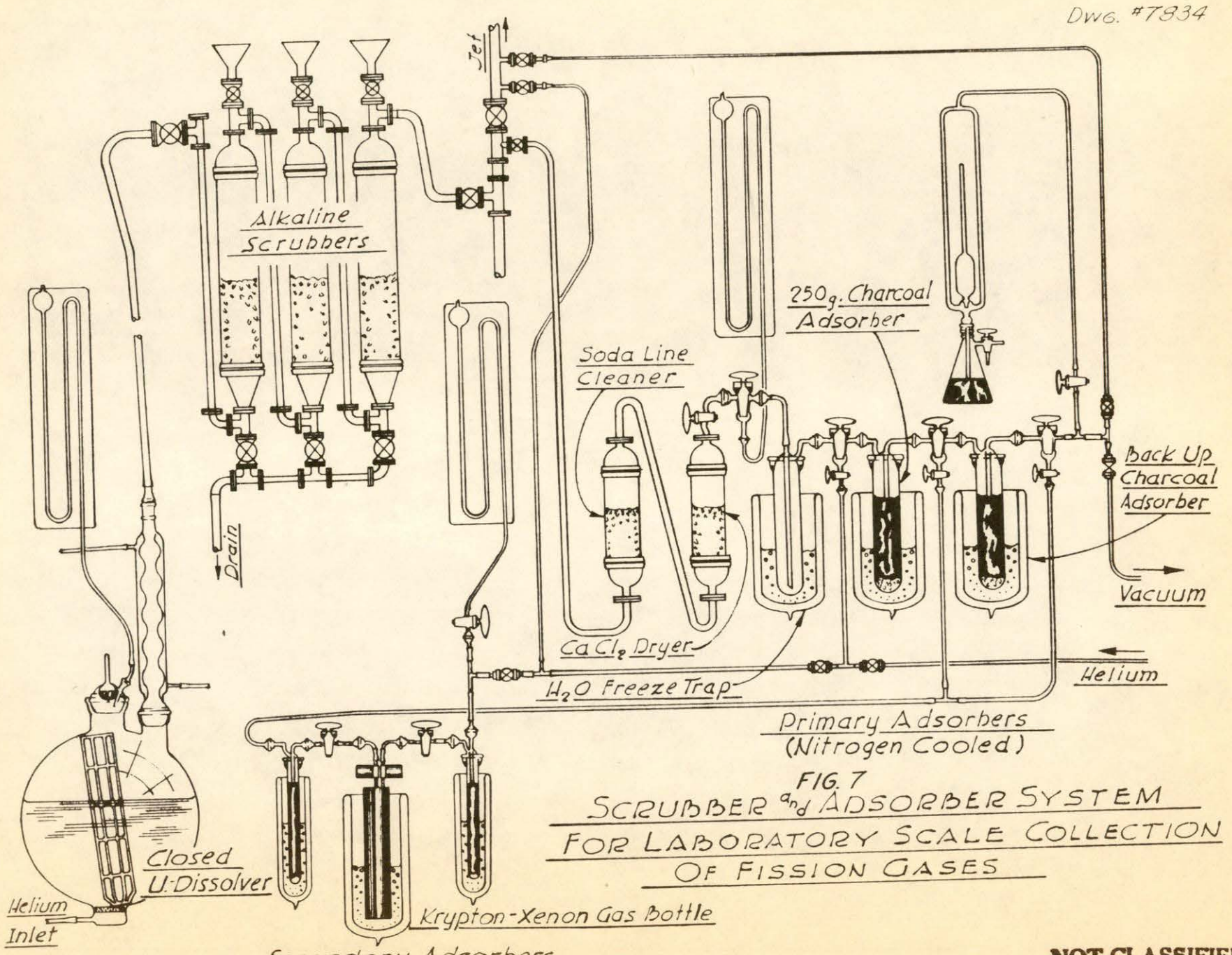


FIG. 7
SCRUBBER AND ADSORBER SYSTEM FOR LABORATORY SCALE COLLECTION OF FISSION GASES

The air-flushing operation was by-passed to the stack jet around the charcoal system marked "Primary Adsorbers" while these were pumped down and refilled several times with helium before adding the coolant.

The dissolution of the uranium was initiated by adding a 1:1 dilution of conc. HCl at room temperature. Approximately 1/5 of the required amount of acid was added at the start and 1/5 at each successive interval of 1/2 hr. In this way the dissolving step was regulated to give a smooth flow of gas consisting mainly of hydrogen and the added helium which was serving for agitation of the dissolver. The jet was regulated to indicate about 3 inches of water below atmospheric pressure in the dissolver vessel.

During the dissolving of the metal, the gases were passed through both of the primary adsorbers and into the stack. By means of a portable survey meter the rate of collection of activity in the first charcoal trap was constantly observed. The second adsorber was surveyed for an indication of break-thru from the first. The activity measured through the trap (up to 25 mr/hr) was presumed to be due to bremsstrahlen since the Kr^{85} activity is known to be a pure beta emitter. The second charcoal trap was found to be completely free of activity although the system was not especially free of air leaks.

Transfer of Gas to Pressure Bottle. In the course of the experiment, the first transfer was made by necessity because of a fracture of the glass in the first adsorber. While making the change, the coolant was removed from the active charcoal bed and, in addition, was warmed with an air stream. The progress of the activity down the charcoal bed was easily observed as was the duration of the stripping period. The transfer was complete in about 1/2 hour.

It was next proposed to transfer to a 25 gram charcoal trap for the purpose of gradually reducing the volume of adsorbed nitrogen, water, etc., before attempting to expand the material into a metal receiver such as shown in the drawing.

It was first thought that in order to transfer the heavy gases from an adsorber bed to a collecting bottle, a controlled procedure, such as expansion from the adsorber to the bottle while maintaining a pressure difference between the two, would be required. As a trial, however, it was decided to place the pressure tube next to the large trap and attempt to freeze-out the krypton directly from a slow helium stream without resorting to expansion from the small adsorber. It was found surprisingly simple to retain the gas in the freeze-out tube until at some unknown point the trap closed to gas flow, probably due to water or CO_2 freezing in the inlet tube. However, the stripping operation was easily stopped while a second pressure can was inserted to replace the first. The remaining gas was completely collected in the second bottle.

Assay and Separation of Heavy Gas Mixtures. Considerable attention has already been given to the problem of purification of the fission gases by Brosi, Zeldes and others whose assistance has been obtained in assaying the large krypton samples.

Because of the relative ease in obtaining this isotope in sufficient quantity, it may be used in a trial effort by the Y-12 optical-spectroscopy group under J. R. McNally who with Brosi and others have been interested in determining nuclear spins, especially those of the short-lived xenon isotopes, by spectroscopic methods.

Proposal for Collection of Short-Lived Rare-Gas Isotopes. In order to make further use of the direct adsorption of the fission gases, an all-metal system consisting of the necessary stages of adsorbers, pumps, valves, vacuum containers, and bottles is being designed and studied. A particular problem will be the gamma shielding required for large-scale collection and purification of short-lived xenon isotopes.

Of major interest is the 9.2 hr Xe^{135} which could be prepared by this process in very large quantity compared with the I^{135} method described in previous quarterly reports, provided the required purification and handling can be effected in a correspondingly short time.

HARD GAMMA EMITTERS IN FISSION

M. H. Feldman and H. A. Levy

Measurements of the absorption of hard gamma radiation with deuterium photo-neutrons as detection mechanism were continued.[8] Sets of absorbers of iron, copper and graphite were prepared, and the absorption of the Na^{24} hard γ ray, 2.765 Mev, was studied. The adsorption data are shown in Figs. 8-10. The adsorption coefficients for the three materials are as follows: Fe, 0.266 cm^{-1}; Cu, 0.346 cm^{-1} and C, 0.051 cm^{-1}. These values serve as further calibration points for the determination of γ energies by means of the heavy water detector.

(8) ORNL 286, p. 71.

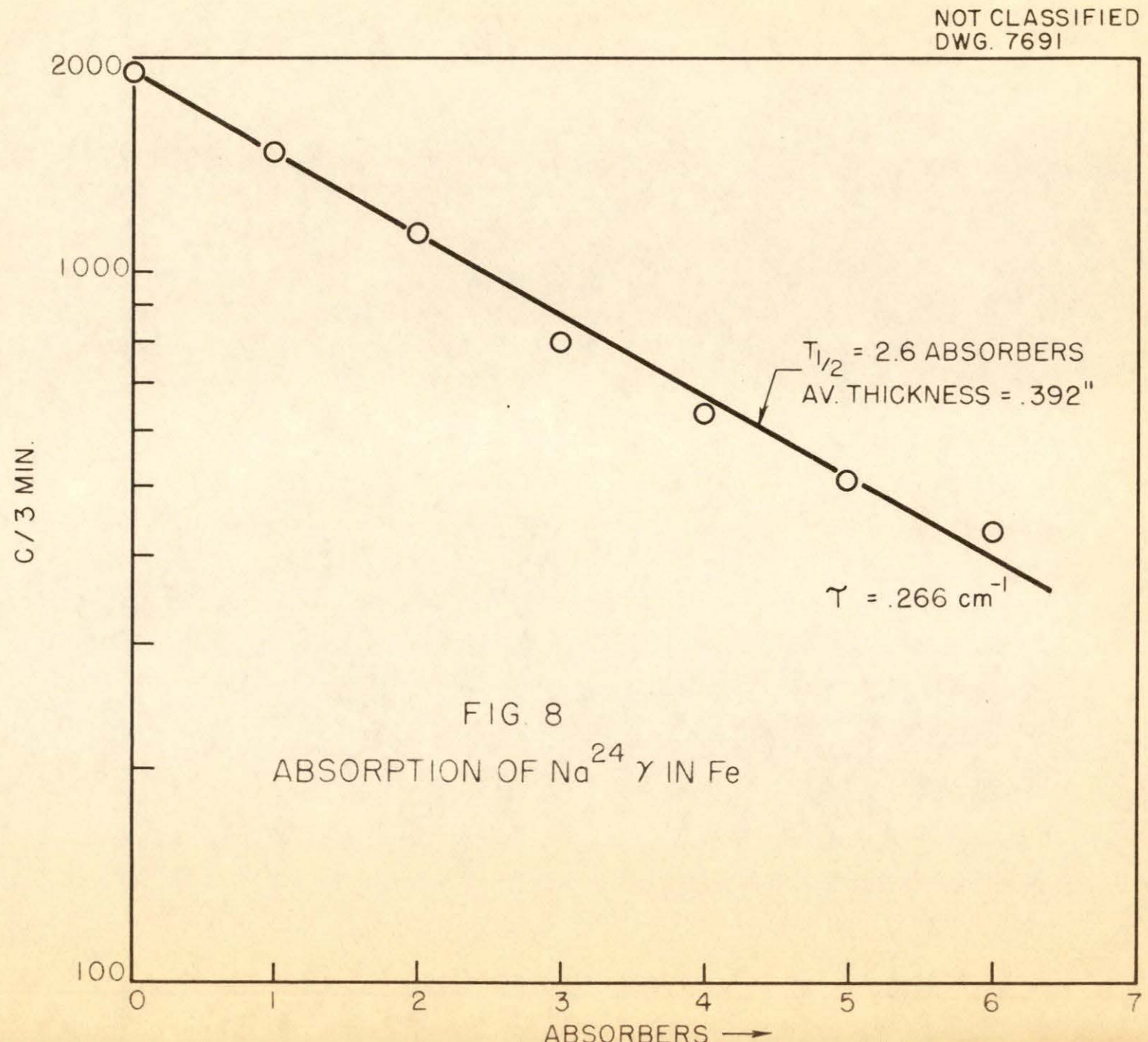


FIG. 8

ABSORPTION OF Na^{24} γ IN Fe

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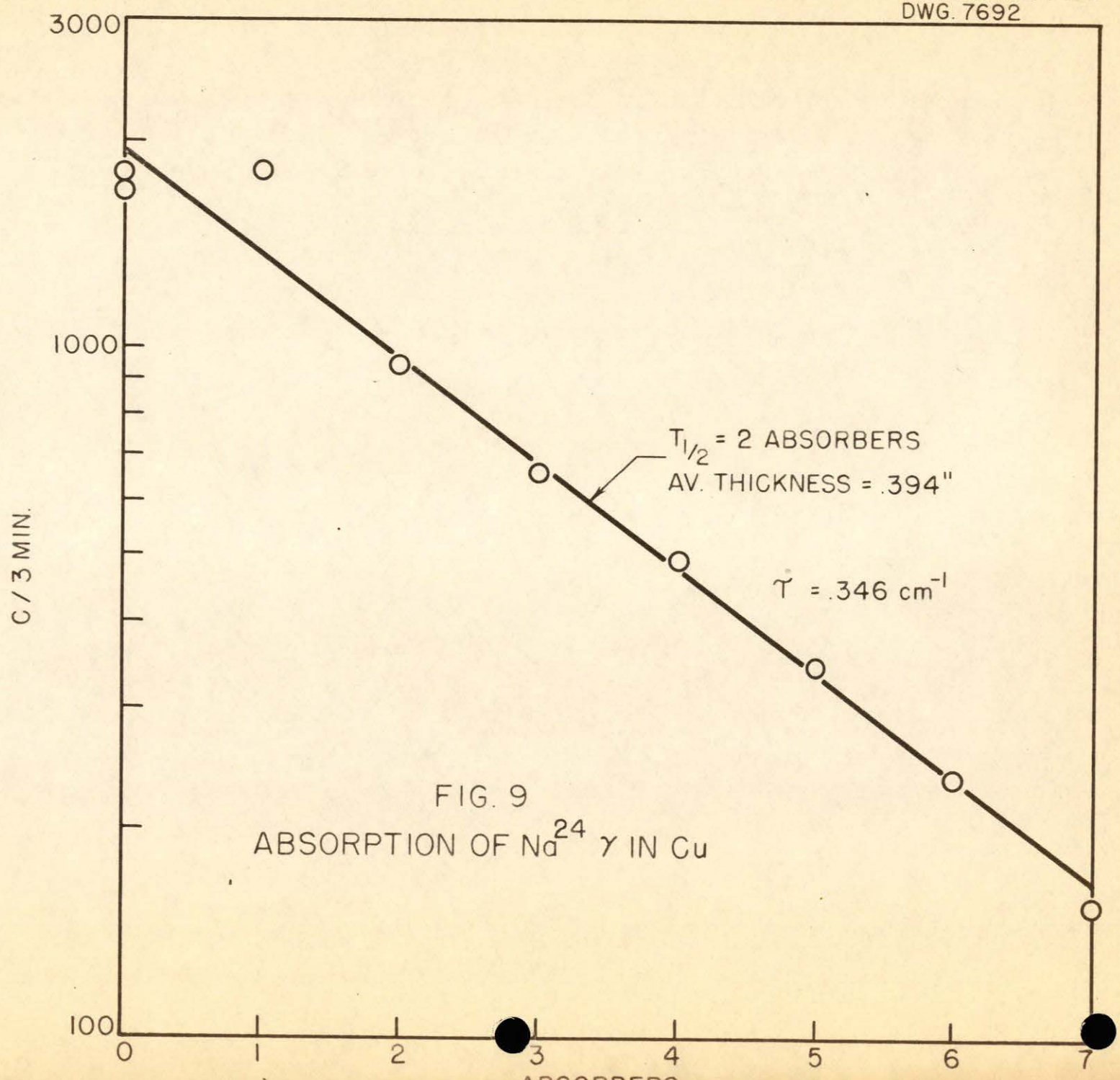


FIG. 9
ABSORPTION OF Na^{24} γ IN Cu

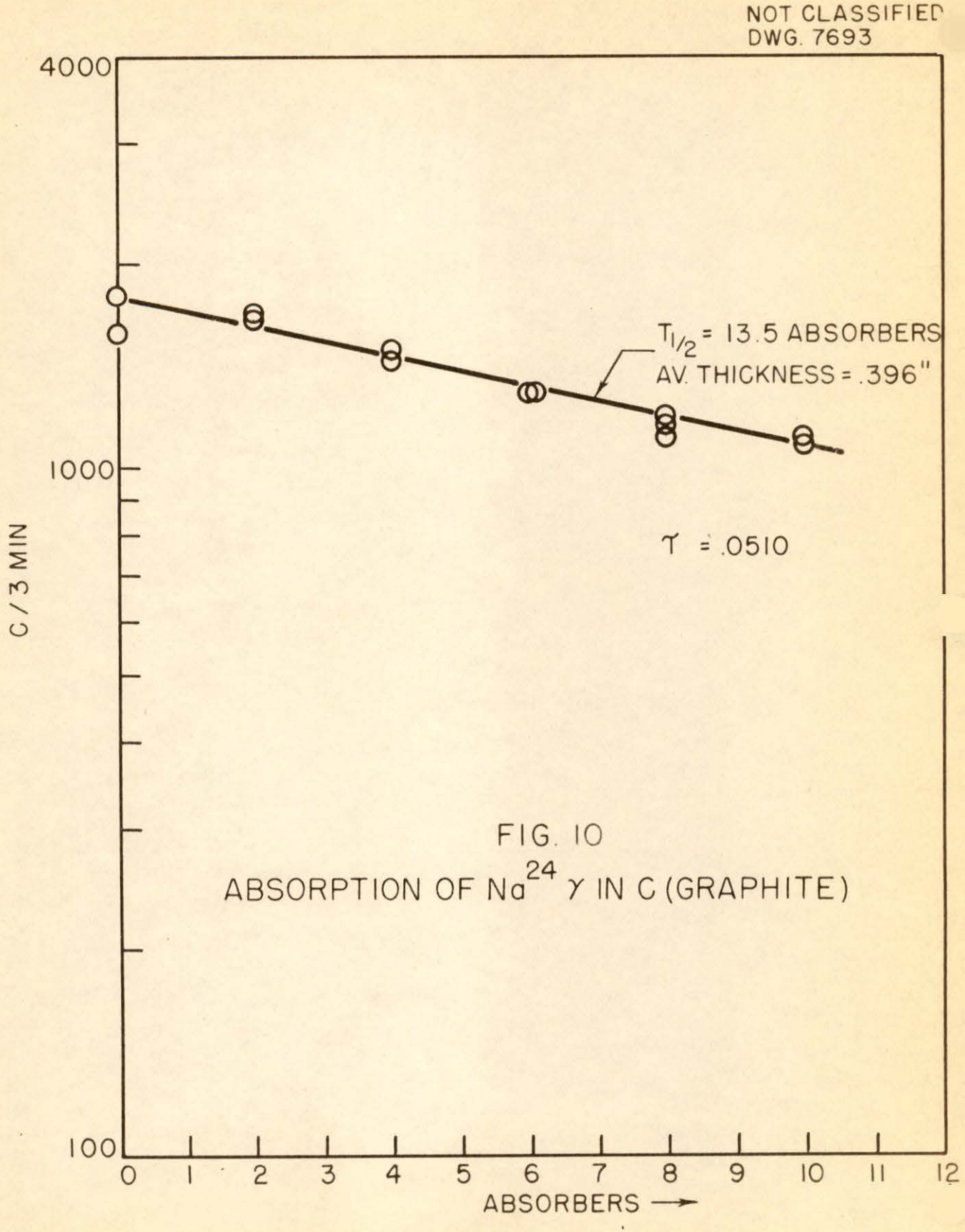


FIG. 10

ABSORPTION OF Na^{24} γ IN C (GRAPHITE)

LIGHTER ELEMENTS

DECAY CONSTANTS OF Ni^{59} AND Ni^{63}

A. R. Brosi and J. C. Griess

Introduction. In measuring the decay of samples of Ni^{59} and Ni^{63} over a period of two and one-half years the Ni^{59}, which decays by electron capture, has shown no decay. This is consistent with the long half-life calculated for this isotope from activation experiments using the cross section of Ni^{58} measured by H. Pomerance. The Ni^{63} (E max ~60 Kev) sample has shown an apparent decay considerably greater than could be expected for an isotope with a half-life of a few hundred years. We estimated this half-life, as did G. Friedlander (Brookhaven National Laboratory), from activation experiments and the adsorption cross section of Ni^{62} given by Pomerance.

A large and uncertain correction for self absorption of the soft radiation was made in our previous estimate of the Ni^{63} half-life. The purpose of the work reported here has been to reduce this and other sources of error involved in the determination of the Ni^{59} and Ni^{63} decay constants.

Decay Constant of Ni^{63}. In preliminary work it was found that reproducible self-absorption curves (activity per mg *versus* mgs/cm^2 of sample) could be obtained by electroplating thin films of nickel on platinum. With a nickel sample of high Ni^{63} specific activity, it was possible to measure the activity when only a monolayer of nickel was deposited. This gave the same value for the activity per mg as the extrapolation of the self adsorption curve to zero mgs/cm^2.

With this assurance that errors from self-absorption could be made negligible, three nickel samples were bombarded with cobalt monitors in the Oak Ridge reactor for 28 days. One of these (K-33a) was enriched in Ni^{58}, a second (J-30a) was enriched in Ni^{62} and a third had the natural isotopic composition. After bombardment, Fe and Cu activities formed by n,α and n,p reactions were removed, and samples of varying thickness were electroplated onto platinum. These samples were counted in a slide chamber proportional counter in which

the counting yield (56%) was known from previous experiments (ORNL 286). The activity with no self-absorption was obtained by extrapolation as described above. The activity in samples prepared from Ni depleted in Ni^{62} (K-33a) was too low for measurement of thin sources. These were compared with natural nickel using "infinitely thick" sources. The data along with 6-12 mass assay data are given in Table I. Within the limits of error of the isotopic assay, the Ni^{63} disintegration rate per mg of Ni^{62} bombarded is a constant. From activation experiments, the best value for the Ni^{62} assay of sample K-33a is 0.165 ± 0.004%.

TABLE I

Comparison of n,γ Yields of Ni^{63} with Ni^{62} Assay

SAMPLE	COUNTS/MIN/mg Ni at 56% COUNTING YIELD	PERCENT Ni^{62}	Ni^{63} Dis/min/mg Ni^{62}
J30a	1.75×10^6	94.25	3.31×10^6
Natural	6.80×10^4	3.66	3.32×10^6
K33a	3.08×10^3	0.13 ± 0.05	$4.2 \pm 1.1 \times 10^6$

From the activation data given in Table 8 and data on the cobalt used as a monitor the half-life of Ni^{63} can be calculated using the equation:

$$T_1 = (\alpha_1 N_1 D_2 T_2)/(\alpha_2 N_2 D_1)$$

Here T is the half-life, α the cross section, N the number of atoms bombarded and D the induced disintegration rate. The subscripts 1 and 2 refer to Ni^{62} n,γ Ni^{63} and Co^{59} n,γ Co^{60} reactions, respectively. The values used to calculate a Ni^{63} half-life and estimated probable errors are given in Table II.

TABLE II

Calculation of Ni^{63} Half-Life

PARAMETER	VALUE	PROBABLE ERROR
α_1	14.8 barns	20%
α_1	34.5 barns	5%
D_1	3.32×10^6 d/m/mg Ni^{62}	5%
D_2	1.31×10^8 d/m/mg Co^{59}	2%
T_2	5.3 yrs	2%

The half-life of Ni^{63} calculated from the data in Table II is 85 ± 20 yrs. This is considerably shorter than previous estimates but still not in agreement with direct decay data which gives a probable half-life of 35 yrs. In addition to rather wide statistical fluctuations the decay data are subject to errors caused by changes in the samples. These are nickel electroplated onto platinum. The activation experiments are subject to the criticism that the neutron energy distribution was different from that used by Pomerance in measuring the cross section. This source of error will be eliminated in experiments now in progress.

Decay Constant of Ni^{59}. When counted with an end window G-M tube, only an X-ray component is observed in activated nickel samples after the 2.6 hr Ni^{65} and 36 hr Ni^{57} have decayed. In order to establish whether the X rays were K X rays of Co originating from electron capture decay of Ni^{59} or K X rays of Ni originating from internal conversion in a metastable state of a Ni isotope, critical absorption measurements were made. Solutions of Co, Fe and Mn were used as absorbers. Measurements were made on a sample of Ni^{59} given us by J. W. Irvine. This sample was produced in the MIT cyclotron by a d,2n reaction on essentially nickel-free cobalt. The ratio of soft β^- to X-ray activity was much lower in this sample than in a second sample which was pile bombarded natural nickel. The MIT sample showed critical absorption by Mn only, indicating essentially pure Co X rays, whereas the pile bombarded nickel showed two components, one critically absorbed by Fe and another by Mn, indicating both Ni and Co X rays. The same result has been obtained with much more decisive data by C. J. Borkowski, using a proportional counter spectrometer.

Because of the low X-ray activity in the samples bombarded 28 days, critical absorption studies could not be made, but spectrometer measurements were made by Borkowski. The data showed that the X-rays in Ni^{58} rich K-33a were almost pure Co K X rays. Both Co and Ni K X rays were found in the natural Ni sample, while the X rays in Ni^{62} rich J-30a were Ni K X rays plus a continuum of harder X-radiation. About 1.6 K X-ray quanta were found per 1000 Ni^{63} β^- disintegrations. This is consistent with the values quoted by Compton and Allison for the efficiency of X-ray production by electron bombardment.

If it is assumed that the total number of X-ray quanta emitted per minute in a sample is equal to a constant times the Ni^{63} activity plus a second constant times the mass of Ni^{58} in the sample, the observed counting rate will be

$$\text{X-ray counts/min} = \beta^- \text{ d/m} \times A_1 \times k_1 + \text{Mgs } Ni^{58} \times A_2 \times k_2$$

Here A_1 and A_2 correct for the absorption in the nickel sample of Ni K X rays and Co K X rays, respectively. The term k_1 is the product of the Ni K X- ray production efficiency of Ni^{63} β^- particles and the counting yield of Ni K X-rays. The term k_2 is the product of the K capture disintegration rate per mg of Ni^{58} bombarded, the fluorescent yield of Co K X rays and the counting yield of Co K X rays. The X-ray counting data on the samples bombarded 28 days are given in Table III.

TABLE III

X-ray Counting Data

SAMPLE	β^- d/m/mg Ni	Mgs Ni	Mgs Ni^{58}	A_1	A_2	X-ray Counts/min
K-33a	5.49×10^3	23.45	23.2	.79	.74	106
Natural Ni	1.21×10^5	29.1	19.7	.74	.69	185
J-30a	3.12×10^6	22.2	0.5	.80	.76	2100

The value for k_2 obtained from these data is 6.0 with a probable error of about 10% because of uncertainties in the analyses of absorption curves. The counting yield of the counter for Co K X rays was determined, using a standard sample whose emission rate was determined within 5% by two independent methods. Using the counting yield of 0.032 and a fluorescent yield for Co K X rays of 0.33, the K capture disintegration rate per mg of Ni^{58} bombarded was found to be 570 ± 85 per minute. Using this disintegration rate, the Ni^{58} cross section of 4.2 barns given by Pomerance and the data on the cobalt monitor given in Table II, a half-life of $1.5 \pm 0.25 \times 10^5$ years is obtained. It should be emphasized that this is a partial half-life for the K electron capture process only. If there is an appreciable fraction of capture from outer shells, as is postulated for high spin changes, the total half-life will be reduced accordingly.

RADIO - ORGANIC CHEMISTRY

SUMMARY

A procedure has been developed for the preparation of ethyl malonate-2-C^{14} in 21% overall yield from ethyl acetate-2-C^{14}. Sodium acetate-2-C^{14} was converted by the action of hot excess triethyl phosphate to ethyl acetate-2-C^{14} in 93% yield. The ethyl acetate was condensed with ethyl oxalate in the presence of sodium ethoxide to give methylene-labeled ethyl oxalacetate (3-ketosuccinic acid-2-C^{14}, diethyl ester) in 53% yield. A vapor-phase decarbonylation at 350° C gave crude diethyl malonate-2-C^{14} in 71% yield. When this series of reactions was carried out upon a microcurie scale, the radiochemical yield of crude diethyl malonate-2-C^{14} was 25%, equivalent to a yield of pure diethyl malonate-2-C^{14} of 21%.

A new method has been developed for the preparation on a macro scale of ethyl acetoacetate-3-C^{14}. The sodium derivative of acetoacetic ester was acetylated with acetyl-1-C^{14} chloride and the resulting diacetylacetic ester hydrolyzed to the above product and acetic acid, each product containing one-half of the initial activity. By this method, 0.765 mc of ethyl acetoacetate-3-C^{14} has been prepared.

Further investigations on the method previously reported for the preparation of formaldehyde[1] have not resulted in significant improvement of yield over that previously reported.

A procedure for the preparation of methylamine in 98% yield and diazomethane in 54% yield from sodium cyanide has been developed, employing conventional procedures adapted to a millimole scale.

A process for the preparation of glycerol-1-C^{14} is being investigated. It starts with β-bromoethyl benzyl ether.

The application to the preparation of acetaldehyde of the process used to prepare formaldehyde[1] has not yet given practicable yields. The pyrolysis of triphenylmethyl ethyl ether has likewise given low yields of acetaldehyde.

Preliminary experiments upon the reduction of acetic acid to ethanol by the action of lithium aluminum hydride have been performed.

The objective of stockpiling about 50 millicuries of C^{14}-labeled Vitamin K is being approached by two methods: (a) a supply of 3-(p-tolyl)-propyl bromide is being built up for use in the synthesis previously reported[2]; (b) an alternate synthesis of Vitamin K is being investigated. It starts with the oxidation of indene to homophthalic acid.

The self-absorption curve of C^{14}-labeled polystyrene is being determined, and the infinite thickness shown to lie between 22-28 mg-cm^2.

(1) ORNL 286, Progress Report, April, May, June 1949, p. 108-110.

(2) ORNL 336, Progress Report, December 1948, January and February 1949, p. 68-73.

Work is in progress upon a synthesis of 5-methylcholanthrene-1-C^{14}.

An apparatus has been constructed to study the effect of prolonged pile irradiation on beryllium nitride, with the purpose of initiating a program for the preparation of concentrated barium carbonate-C^{14} by lengthy irradiation of beryllium nitride in the Hanford pile.

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

1. Ethyl Malonate-2-C^{14} (G. A. Ropp). (a) Discussion: Sodium acetate-2-C^{14} has been heated to 170-220° with pure triethyl phosphate (instead of diethyl sulfate as reported by Sakami, Evans, and Gurin[3] and the resulting mixture has been distilled in vacuum to give a 93% yield of ethyl acetate-2-C^{14}.

Condensation at 70° C of this ester with diethyl oxalate dissolved in a solution of sodium in dry ethanol gave the sodium salt of diethyl oxaloacetate. After removal of excess alcohol, the sodium salt was hydrolyzed at 0° C with dilute sulfuric acid and the crude keto ester extracted with benzene. Removal of the benzene by vacuum distillation gave a product in 53% yield which could be directly decarbonylated by vacuum distilling through a short packed column at 350°[4]. The condensate consisted of crude diethylmalonate in 71% yield.

(b) Experimental: (1) Ethyl Acetate-2-C^{14}. Four milligrams of sodium acetate-2-C^{14} having a specific activity of 24.25 μc per mg were mixed with 0.4018 g (4.90 mmoles) of anhydrous sodium acetate. The mixture was dissolved in 5 ml distilled water, the solution was evaporated to dryness, and the residue was dried several hours at 100-120° at 0.5 micron pressure. One and one-half milliliters of distilled triethyl phosphate and a small piece of glass wool were added to the dried sodium acetate in a 10 ml pearshaped flask, and the mixture was heated one hour under reflux in an oil bath at 170-220°. The reaction mixture was cooled to room temperature and the apparatus sealed to a vacuum line through a trap at -18° and a second trap at -190°. Distillation of the reaction mixture at 70° and a pressure of 0.1-0.01 micron gave 0.400 g (4.54 mmoles, 93%) of ethyl acetate-2-C^{14} in the second trap. A small amount of triethyl phosphate collected in the -18° trap. The vapor pressures

(3) Sakami, Evans, and Gurin, J. Am. Chem. Soc., *69*, 1110 (1947).

(4) Altwegg and Maillard, Ber. *58*, 2186 (1925).

of the ethyl acetate at several temperatures were: 31 mm at 0°, 95 mm at 20°, and 122 mm at 30°. [Lit.[5] gives 119 mm at 30°].

(2) 3-Keto-succinic Acid-2-C^{14}, Diethyl Ester, and Ethyl Malonate-2-C^{14}. Ethyl acetate-2-C^{14}, 0.2862 g (3.26 mmoles), freshly distilled diethyl oxalate, 0.4735 g (3.24 mmoles), and 0.0713 g sodium metal (3.10 mmoles) dissolved in 1.8 ml of absolute ethanol were mixed by magnetic stirring in a closed 50 ml pyrex reaction bulb with detachable fittings as shown in the accompanying sketch (Fig. 11). With the bulb in one position, reagents and water washes could be added from the detachable dropping funnel; with the bulb in a second position, washes could be drawn off into the detachable wash receiver.

The slightly turbid reaction solution was warmed to 70° in the closed bulb and then was allowed to cool slowly to room temperature whereupon the pale yellow sodium salt of diethyl oxalacetate separated. The reaction bulb was attached to a vacuum line and ethanol distilled off at 0.1 micron pressure. The ethanol contained 22.3 μc of activity (26.7% of initial activity). The solid sodium salt remaining was decomposed by the addition of 1.3 ml of 2.85 *N* sulfuric acid and 7.0 ml of benzene followed by thirty minutes stirring in an ice bath. The acid layer was then drawn off into the detachable wash receiver, and the benzene solution was washed three times with 2.5 ml portions of ice water. These washes contained 2.8 μc of activity (3.4%).

Drying of the crude oxalacetic ester was effected by vacuum distillation of the benzene into a liquid nitrogen cooled trap. Another 10 ml portion of dry benzene was added to the concentrate and the distillation was repeated to carry over any remaining water. The combined wet benzene distillates contained 4.0 μc of activity (4.8%). The oxalacetic ester concentrate was washed with dry ether from the reaction bulb into a 10 ml pear-shaped pyrex pot, and the solution was then concentrated by distillation at 5 microns pressure. The residue was 0.3092 g (53% yield based on ethyl acetate) of crude diethyl oxalacetate as a yellow oil.

The crude diethyl oxalacetate was decarbonylated to diethyl malonate by the passage of its vapor through a 7 inch vertical 8 mm pyrex tube filled with glass beads and crushed soft glass. This column was kept at 340-360° by electrically heated jacket. The pot containing the crude oxalacetic ester was connected by a standard taper joint to the bottom of this column and the top

(5) N. A. Lange, Editor, 'Handbook of Chemistry', Handbook Publishers, Sandusky, Ohio, 5th Edit. (1944), p. 1425.

NOT CLASSIFIED
DWG. 7783

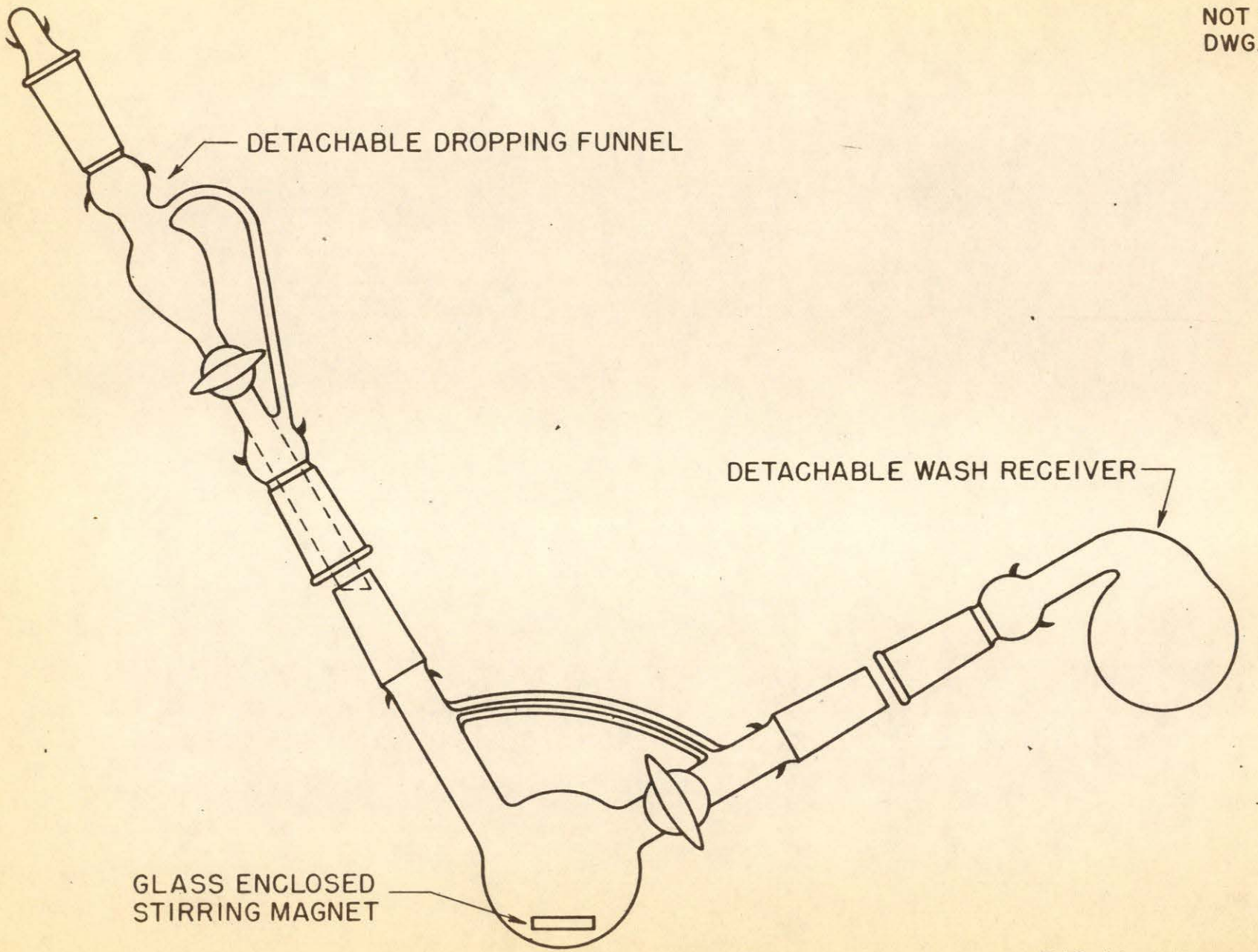


FIG. 11
REACTION BULB AND DETACHABLE PARTS
USED IN OXALACETIC ESTER PREPARATION

of the column was connected through a trap at -190° C to a vacuum line. The temperature of the pot was raised during a one hour period from 72° to 192°, and the pressure during this time of non-condensable gases increased from 0.1 to 150 microns. Crude diethyl malonate 0.1862 g (37.5% by weight based on ethyl acetate), was collected in the -190° C trap. This distillate (crude diethyl malonate) contained 21.0 μc of activity (25%) and the residue contained 12.2 μc (15%). A total of 62.3 μc (75%) of the initial 83.4 μc was thus accounted for.

The yield of pure malonic ester was determined by diluting the above crude product with a known amount of pure ethyl malonate and saponifying the mixture with cold 20% sodium hydroxide. The resulting malonic acid was crystallized, dried and then assayed. Calculation indicated that the above crude product was 83% pure, representing a yield of 17.4 μc (21% from ethyl acetate) of pure ethyl malonate.

2. *Ethyl Acetoacetate-3-C*^{14} *(Carbonyl Labelled AcetoaceticEster. (E. V. Grovenstein*, O. K. Neville).* (a) Discussion: A new method has been developed for the preparation, on a macro scale, of carbonyl-labelled acetoacetic ester. The method involves the acetylation, with acetyl chloride-1-C^{14} of the sodium derivative of acetoacetic ester and the hydrolysis of the resulting diacetylacetic ester to ethyl acetoacetate-3-C^{14} and acetic acid, each containing one-half the initial radioactivity.

$$CH_3C^{14}OCl + (CH_3\overset{\overset{O}{\|}}{C}\text{-}CH\text{-}COOC_2H_5)^- Na^+ \longrightarrow \underset{\underset{C^{14}OCH_3}{|}}{CH_3COCHCOOC_2H_5}$$

$$\xrightarrow[H_2O]{NaOH} CH_3C^{14}OCH_2COOC_2H_5 + CH_3C^{14}OONa \; .$$

By this method, 0.765 mc of acetoacetic ester has been prepared in an over-all radiochemical yield of 20% from acetyl chloride. This yield is superior to that of the only other reported method[6]. The diluted acetic acid is recoverable to the extent of about 75%.

(6) Sakami, Evans and Gurin, J. Am. Chem. Soc. 69, 1110 (1947).

* Participant in ORINS-ORNL Summer Research Program, Dept. of Chemistry, Georgia Inst. of Technology.

(b) Experimental: (1) Ethyl Diacetylacetate-3-C^{14}. To the sodium derivative of acetoacetic ester prepared from 2.30 g of sodium powder and 13 g of ethyl acetoacetate dissolved in 130 ml of ether, was added slowly and with stirring 3.72 g of acetyl chloride-1-C^{14} containing 3.89 mc of activity. The reaction mixture was allowed to stand overnight. The excess sodioacetoacetate was hydrolyzed with 25 ml of water and the aqueous solution was adjusted carefully with dilute sulfuric acid to *p*H 6. The water solution was subjected to continuous ether extraction, and the extracts were combined. From 113.5 ml of ether solution, one milliliter was withdrawn and diluted with 2 ml of pure non-radioactive ethyl diacetylacetate. The copper enolate of this compound, prepared under conditions which prevented contamination with acetoacetic ester, was assayed for radioactivity(7). The yield of ethyl diacetylacetate was found to be 3.52 mc or 91%, based on acetyl chloride.

(2) Ethyl Aceto-1-C^{14}-Acetate. After removal of the ether, the crude diacetylacetate, containing acetoacetic ester was hydrolyzed at 90° for five minutes in 80 ml of 0.625 molar sodium hydroxide solution. The ethyl acetoacetate was removed by continuous extraction, the ether solution was dried, and the solvent was removed. To the product was added 5.06 g of ethyl diacetylacetate as "hold-back" carrier and 30 g of non-radioactive acetoacetic ester. The product was distilled through a 4 ft. Todd column at 20 mm pressure. Two more additions of 10 ml each of ethyl acetoacetate were made during the distillation. The final product weighing 43.87 g contained 0.765 millicuries, or 19.7% of theoretical based on acetyl chloride.

3. *Diazomethane-C^{14}. (A. Russell Jones).* (a) Discussion: Procedures for the preparation of the useful synthetic intermediates methylamine-C^{14}, and diazomethane-C^{14} in yields respectively of 98% and 54% have been developed, although no runs with radioactive materials have yet been made.

Sodium cyanide is catalytically reduced in dilute acid solution to methylamine in 98% yield. The latter, isolated as the hydrochloride, and potassium react quantitatively in water solution at the boiling point to give N-methylurea. This is nitrosated and the N-nitroso-N-methylurea, obtained in 70% yield, is filtered off and purified by elution with anhydrous methanol. Diazomethane is prepared from the nitrosomethylurea in 79% yield.

The procedure has been illustrated with a run starting with 6 mmoles of sodium cyanide in order to obtain yields and melting points without adding any

(7) All radioactive assays were made by wet combustions of liquid or solid samples, and measurement of the ion current produced by the radioactive carbon dioxide.

of the intermediates. However, the procedure has been gone through several times in the manner of a radioactive run: One millimole of sodium cyanide was reduced in 100 ml of dilute acid; 9 mmoles of stock methylamine hydrochloride was added and a single distillation from basic solution concentrated the product.

(b) Experimental: (1) Methylamine Hydrochloride. A mixture of 313 mg (6.07 mmoles) of sodium cyanide (95%, Baker's Analyzed) and 200 mg of platinum oxide was washed into a 500 ml hydrogenation flask with 20 ml of water. The flask was attached to a Hershberg normal-pressure hydrogenation manifold and the system filled with hydrogen. A solution of 6.4 ml of concentrated sulfuric acid in 600 ml of water was added and stirring was begun.

Three hundred and eighty-one ml of hydrogen were absorbed at 27° C and 740 mm pressure. A blank run absorbed 72 ml of hydrogen. The reduction of the cyanide thus required 309 ml (Calculated: 307 ml).

The flask was attached to the distillation apparatus pictured in Fig. 12. Two drops of phenolphthalein solution were added and the contents made basic with 50% potassium hydroxide solution. The flask was heated and the contents stirred (to prevent bumping). Approximately 100 ml of solution were distilled into an ice-cold receiver containing 10 ml of concentrated hydrochloric acid. This flask in turn was connected to the distillation apparatus (Fig. 12), the contents made basic, and approximately 25 ml of solution were distilled into the special reaction flask (Fig. 12a) cooled in ice and containing 5 ml of concentrated hydrochloric acid. (The glass frit was wet with the acid). An aspirator was attached to the stopcock opening and the flask was heated in a 60° air bath while filtered air was drawn over the contents. The white crystalline product, completely dried by evacuating the flask to 0.1 mm, weighed 400 mg, (97.7% yield from sodium cyanide), m.p. 222-225°. Pure methylamine hydrochloride under the same conditions (tube immersed in bath at 200°) melted at 232-233°. A mixture of the two melted at 222-228°.

(2) Methylurea. To the reaction vessel containing the methylamine hydrochloride were added 0.65 g (8.0 mmoles) of potassium cyanate, a magnetic stirrer bar and 5.0 ml of water. The flask was capped, immersed in liquid nitrogen and evacuated. The stopcock was closed and the flask was partly immersed in a boiling-water bath. Stirring and heating were continued for thirty minutes. The flask was cooled, the cap was removed, and the contents evaporated at 60° in a stream of filtered air. The residue was dried at 0.1 mm pressure. Four 10 ml portions of boiling absolute alcohol were used to

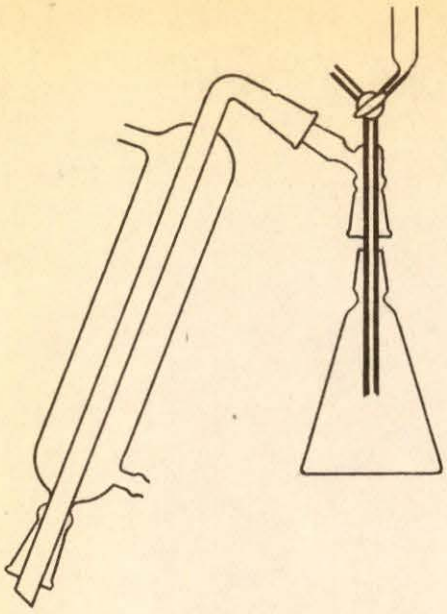


FIG. 12

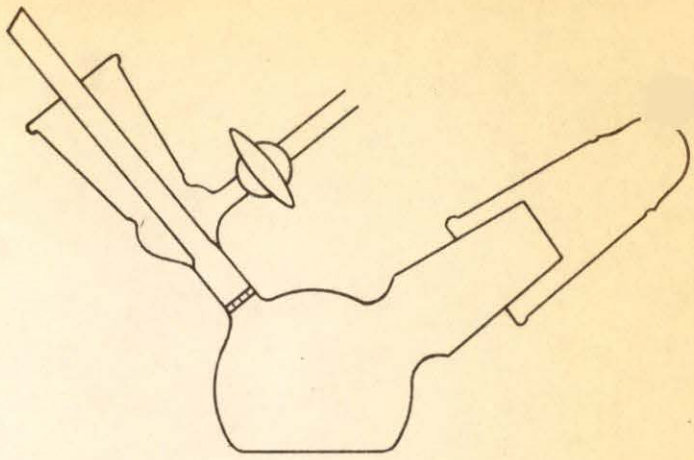


FIG. 12a

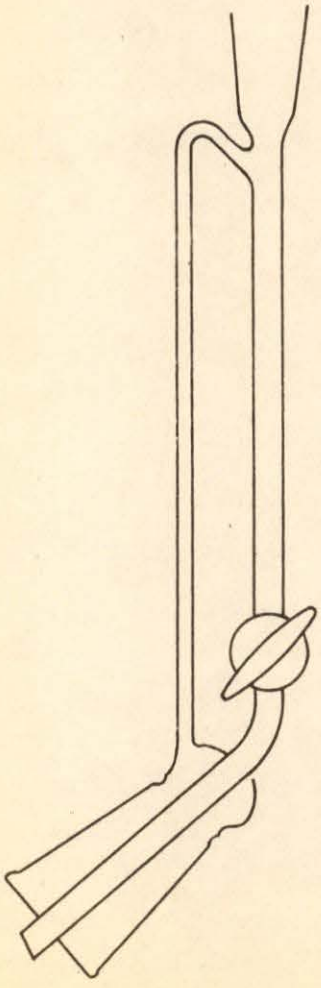


FIG. 12b

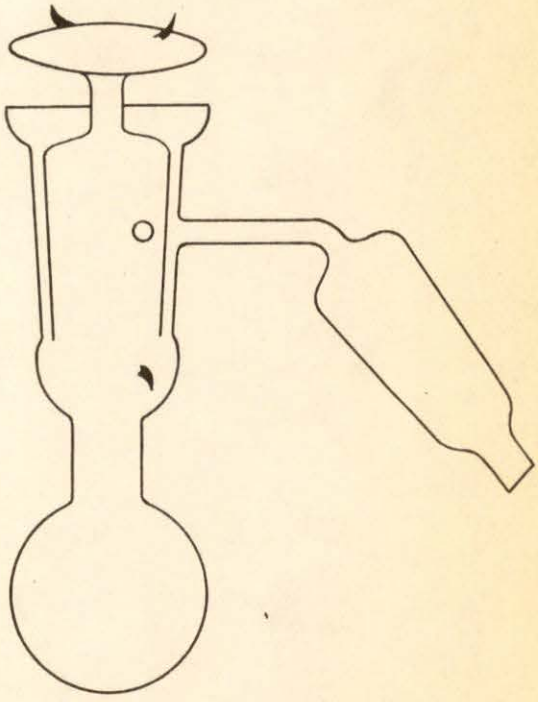


FIG. 12c

elute the methylurea. The methanol solution was treated with Norit and filtered. The filtrate was evaporated in a current of filtered air and solvent was completely removed by evacuating the vessel to 0.1 mm pressure. The white crystalline residue weighed 445 mg (100%), m.p. 80-90°. A mixture of this with authentic methylurea (m.p. 99-102°) melted at 89-98°.

(3) Nitrosomethylurea. The crude methylurea was transferred in methanol solution back into the reaction flask (Fig. 12a) whose contents were then evaporated to dryness. Sodium nitrite, 0.68 g (8 mmoles), and 4.0 ml of water were added; the solution thus formed was stirred vigorously in a -15° bath and an ice-cold mixture of 0.65 g concentrated sulfuric acid and 3 ml of water was slowly added dropwise through the addition funnel (Fig. 12b). The funnel was removed, the flask was inverted, and the contents were suction filtered through the coarse frit. The solid was washed with 1 ml of ice water and then sucked dry. The nitrosomethylurea was then eluted with 10 ml of anhydrous methanol for one minute. This was filtered off and the elution was repeated. The combined light-yellow filtrates were evaporated to dryness below 27° in a current of filtered air. Complete dryness was obtained by evacuation of the bottle at 0.1 mm, at 27°. The off-white fluffy solid weighed 429 mg (69.6% yield from crude methylurea; 68.0% from sodium cyanide).

An 85 mg sample of the nitrosomethylurea was decomposed by refluxing 6 *N* sodium hydroxide with the release of 20.0 ml of gas measured at 28° C and 742 mm pressure. (Calculated nitrogen evolution: 20.6 ml). Since this method of analysis was shown by blanks run with impure and pure nitrosomethylurea to give an accuracy of ±5% or better, a purity of 92% or better is indicated.

(4) Diazomethane. A methanol solution of 327 mg of the nitrosomethylurea prepared above was evaporated in the special flask (Fig. 12c). To the residue was added 25 ml of ether. The flask was cooled in a -15° bath and then 5.0 ml of 50% potassium hydroxide was added. The stopcock plug was quickly inserted and closed and the flask was shaken for 1½ minutes. It was quickly attached to two Dry-Ice cooled U-tube traps in series (each containing 10 ml of ether). and immersed in a 50° water bath. About 20 ml of ether was distilled. The yellow distillate was washed with ether into a flask containing 1.000 g (8.20 mmoles) of benzoic acid and 10 ml of ether. The color disappeared and nitrogen was evolved. No precipitate of ammonium benzoate formed. Back titration of the excess benzoic acid with 0.215 *N* sodium hydroxide required 26.8 cc. A blank of 0.2 cc was obtained. Thus, 5.72 mmoles of acid were present and 2.48 mmoles of diazomethane had been prepared (79% yield for nitrosomethylurea; 54% from sodium cyanide).

4. *Formaldehyde-C^{14} (W. J. Skraba).* (a) Discussion: A method for the preparation of formaldehyde-C^{14} in 60% yields by the hydrolysis of monochloromethyl-C^{14} acetate has been previously reported[1]; 19 mc's were prepared by this method. Further studies were undertaken in an attempt to increase the yield of formaldehyde. The methods tried were:

(a) Bromination of Methyl Acetate. Methyl acetate was treated with gaseous bromine in an evacuated vessel. The bromination was incomplete even after 48 hours.

(b) Chlorination of methyl chloroacetate gave approximately the same yield as methyl acetate.

(c) Chlorination of dimethyl oxalate proceeded readily but hydrolysis of the chloroester gave a low yield of formaldehyde.

5. *Glycerol-1-C^{14} (J. G. Burr).* (a) Discussion: The attempted synthesis of this intermediate is in progress along the line indicated by the following sequence of equations:

$$C_6H_5CH_2OCH_2CH_2Br \xrightarrow[C^{14}O_2]{Mg} C_6H_5CH_2OCH_2CH_2C^{14}OOH$$

I IIA

$$C_6H_5CH_2ONa + ClCH_2CH_2COOC_2H_5 \xrightarrow[\text{steps}]{2} IIB$$

$$IIA \xrightarrow[PCl_3]{Br_2} CH_2Br + HOCH_2CHBrC^{14}OOH$$

IIIA

$$III \xrightarrow{Ag_2O} HOCH_2CHOHC^{14}OOH \xrightarrow{LiAlH_4} HOCH_2CHOHC^{14}H_2OH$$

IV

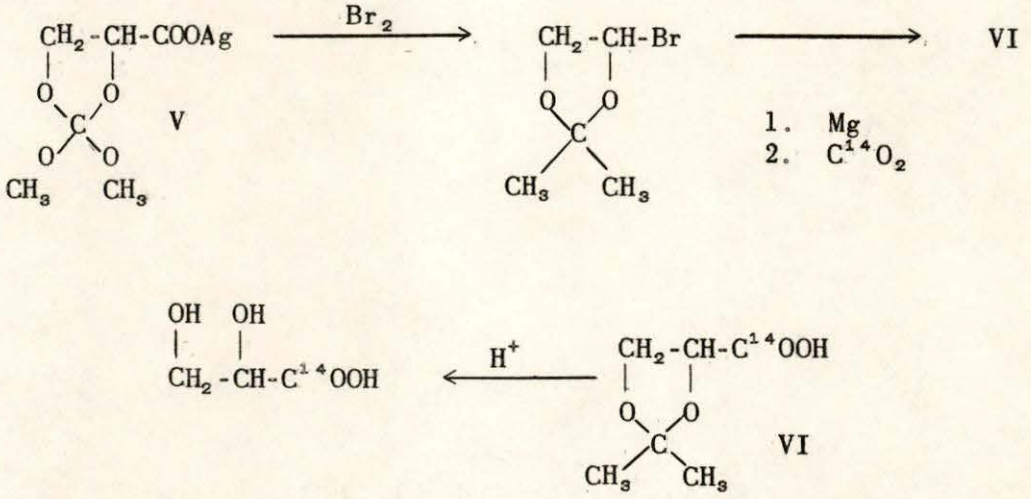
Inactive β-benzyloxypropionic acid (IIB) has been prepared as a crystalline solid melting at 26-28° by the reaction of sodium benzyloxide with ethyl-β-chloropropionate. The synthesis of the active acid (IIA), however, will be carried out by carbonation of the Grignard reagent prepared from β-bromoethyl benzyl ether (I), prepared by the method of Clemo and Perkin[8].

The inactive acid (IIB) reacts with bromine in the presence of phosphorus trichloride to give a 62% yield of benzyl bromide (identified as the β-naphthol

(8) Clemo and Perkin, J. Chem. Soc. *121*, 642 (1923).

benzyl ether) and a 50% yield of liquid, water-soluble halogen-containing acid which it is hoped larger scale runs will show to be the desired acid (IIIB). This acid can be converted to glyceric acid by treatment with moist silver oxide[9].

An earlier approach to this problem which did not prove fruitful is illustrated by the following equations:



The potassium salt of (V) was prepared by the alkaline permanganate oxidation of isopropylidine glycerol[10] which itself was prepared by the method of Newman and Renoll[11]. Although silver glycerate is a known, if unstable, substance[12] the silver salt of isopropylidine glyceric acid (V) proved to be too unstable for isolation; nor could suitable lead or mercury salts be prepared.

(b) Experimental: (1) β-Benzyloxypropionic Acid. A solution of 7 g (0.30 moles) of sodium in 100 ml of benzyl alcohol diluted with an equal volume of benzene was prepared by overnight heating. This solution was heated to boiling and a solution of 37.4 g (0.27 mole) of ethyl β-chloropropionate in benzene was added dropwise. Within one-half hour the mixture became extremely viscous so it was cut with 100 ml of benzene. This suspension was stirred and

(9) Beckurts and Otto, Berichte *18*, 236; Lossen and Kowski, Ann. *342*, 135.

(10) Reichstein, et. al., Helv. Chim. Acta. *18*, 598 (1935).

(11) Newman and Renoll, J. Am. Chem. Soc. *67*, 1621 (1945).

(12) Franklin and Appleyard, J. Chem. Soc. *63*, 296 (1893).

refluxed for six hours, and was then hydrolyzed with 100 ml of water. The benzene layer was washed with water and dilute hydrochloric acid. The aqueous layer was diluted and extracted with ether. The combined ether and benzene solution was dried and concentrated. The residue was heated under vacuum until it began to distill at 101°, showing the absence of unreacted propionate ester. This residue was then dissolved in 500 ml of ethanol, and a solution of 12 g (0.30 moles) of sodium hydroxide in 20 ml of water was added. Saponification was completed by refluxing the solution for two hours. The alkaline solution was poured into water, and the aqueous-alcohol mixture extracted with ether, and then acidified. Ether extraction of the acidified solution gave a product which was recovered by evaporation of the ether. Upon distillation of the residue, 22.4 g of a water-white oil boiling at 153-156° at 2 mm pressure was recovered. This oil slowly crystallized upon standing. Redistillation gave 15.3 g of a colorless oil boiling at 158-159° at 2 mm. This oil crystallized almost immediately to a solid which melted at 26-28°. Neutralization equivalent: Calculated for $C_{10}H_{12}O_3$, 180; Found: 184.

(2) α-Bromohydroacrylic Acid. β-benzyloxypropionic acid, 3.0 g (16.7 mmoles), was placed in a dry flask and warmed with 1.5 ml of bromine and 10 drops of phosphorus trichloride. The initially vigorous reaction soon moderated, and the mixture was heated at 100° for one and one-half hours. It was then cooled and shaken with strong potassium carbonate solution. The heavy yellow oil which remained undissolved was extracted with ether. The carbonate solution was acidified, and then submitted to continuous ether extraction for twenty-four hours. The ether extract was acidified and concentrated under vacuum at 100°. The residue weighed 1.40 g (50%), and was a viscous syrup. It gave a strong Beilstein test for the presence of halogen. Recovery of the carbonate-insoluble fraction gave 1.76 (62%) of a reddish oil. When this oil was heated with potassium hydroxide and β-naphthol, it gave an alkali-insoluble product which upon recrystallization melted at 95-98°. [Lit.[13] for the similar derivative from benzyl halides is 99°].

6. *Acetaldehyde (W. J. Skraba).* Two methods of preparation were tried:

(a) A method similar to that of the preparation of formaldehyde. Ethanol was esterified with acetyl chloride and the product was chlorinated in an evacuated vessel. The chlorinated product on hydrolysis gave a low yield of acetaldehyde.

(13) Characterization of Organic Compounds, F. Wild, Cambridge, 1947, p. 48.

(b) Pyrolysis of triphenylmethyl ethyl ether

$$(C_6H_5)_3CCl + C_2H_5OH \longrightarrow (C_6H_5)_3COC_2H_5 + \text{pyridine hydrochloride}$$

$$(C_6H_5)_3COC_2H_5 \xrightarrow{300\text{-}400^\circ} CH_3CHO$$

Triphenyl methyl chloride was treated with ethanol in the presence of pyridine hydrochloride and benzene. The mixture after stirring (magnetic bar) for 48 hours was distilled to remove the solvent and unreacted ethanol and pyridine. Water was then added and the mixture stirred until all the water soluble material dissolved. Benzene was added and the two phases after mixing thoroughly were separated in a Brown extractor. The benzene phase containing the triphenyl-methyl ethyl ether was dried and part of the solid decomposed. The yield of acetaldehyde was low as determined by preparation of dimedone derivative.

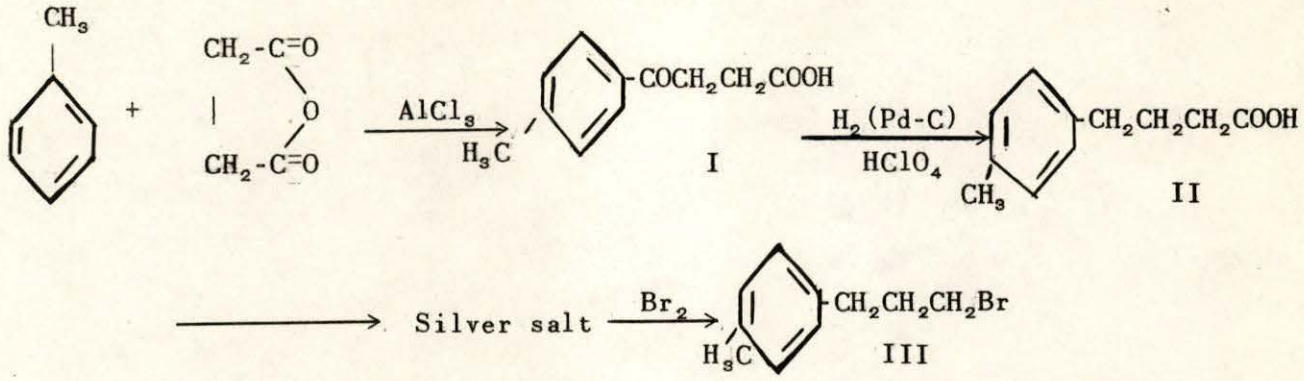
7. Ethanol (W. J. Skraba). Preliminary experiments on the preparation of ethanol by reduction of acetic acid with lithium aluminum hydride are being performed.

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

1. Synthetic Vitamin K (Carbon-14 Labeled 2-Methyl-1,4-Naphtho-quinone) (C. J. Collins, D. N. Hess, and R. G. Mansfield). (a) Discussion: The problem of stockpiling approximately 50 millicuries of carbon-14 labeled synthetic vitamin K is being approached by two separated routes:

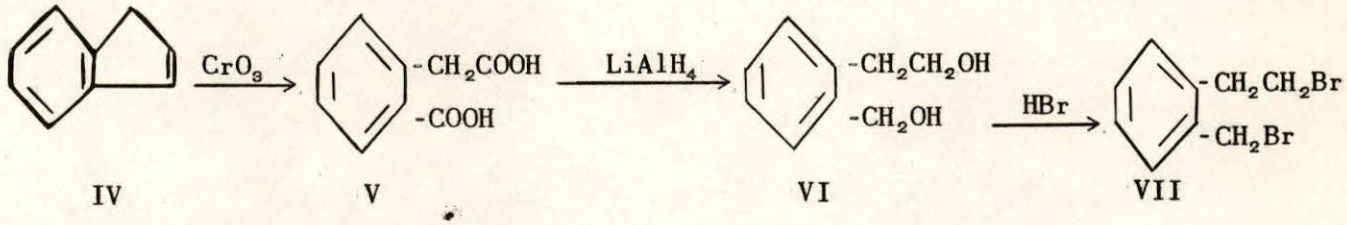
(a) A supply of β-(p-tolyl)-propyl bromide (III) is being built up prior to its use in a synthesis previously described[14]. An alternate synthesis of this bromide is being employed.

(14) ORNL 336, Progress Report, December 1948, January, February 1949, p. 68-73.

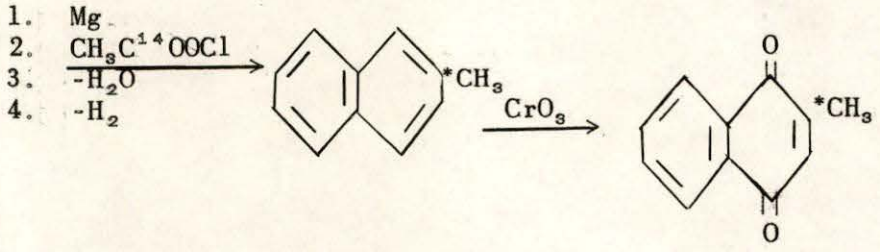


The preparation of compounds I and II, and the conversion of II to its silver salt have proceeded smoothly. The bromination of the silver salt of II, however, has led to 28-46% yields of the bromide (III). The improvement of the yield of this latter reaction is under investigation.

(b) An alternate synthesis of labeled 2-methylnaphthalene (VIII)is under investigation. The proposed reaction series follows:



IV V VI VII



VIII IX

The oxidation[15] of indene (IV) has given 40-45% yields of homophthalic acid (V). The lithium aluminum hydride reduction of V has been performed in ether solution to yield VI in low yield. Present efforts are directed toward improving this yield before preparation of the dibromide (VII).

(b) Experimental; (1) β-(p-Methyl) benzoylpropionic Acid (I). A conventional Friedel-Crafts reaction (with the exception of a nitrogen sweep) using 0.34 moles of succinic anhydride, 2.25 moles of toluene, and 0.75 moles of $AlCl_3$ resulted in a 76% yield of acid (I) melting at 129-130°.

(2) γ-(p-Tolyl) Butyric Acid (II). Hydrogenation of the methyl benzoyl propionic acid was carried out in a manner described[16] by Kindler and coworkers for similar compounds, in two batches of ca. 20 gms each, using 150 ml glacial acetic acid, 5 drops perchloric acid, and Pd-C catalyst amounting to ¾ the total weight of methyl benzoylpropionic acid. A 2½ hour reaction time for the first batch gave a yield of 73%. The second batch was allowed to proceed for 19 hours; the yield was 94%. The product on crystallization from the glacial acetic acid by addition of water melted at 56-58°.

(3) γ-(p-Tolyl) Butyric Acid, Silver Salt. p-Tolyl butyric acid and ammonium hydroxide in equivalent amounts were dissolved in ethyl alcohol. An equivalent quantity of silver nitrate solution (100 gm/100 ml) was added dropwise with vigorous stirring. The silver salt precipitated as a white solid. By reworking the filtrate from this, the total yield can be made to approach 100%. Assay of the silver salt by ignition indicates 100% purity.

(4) Homophthalic Acid (V). Indene was oxidized by the procedure of Fieser and Pichet[15]. A modification of their procedure was to purify the indene by passage through a column of alumina, rather than by distillation. Several runs produced consistent yields of 40-45% homophthalic acid, m.p. 173-176°.

(5) β-(o-Methylolphenyl) Ethanol (VI). Homophthalic acid (V), 19 gms, was placed in a Soxhlet Extractor, and slowly dissolved in the ether condensate of a solution of 20 gms of lithium aluminum hydride in 500 cc dry ether. The solution of all of the acid required one and one-quarter hours. The mixture was heated under reflux and additional fifteen minutes, and then worked up in the usual fashion. Distillation yielded 3.2 gms of a colorless oil, presumably VI. Yield, 20%. The p-nitrobenzoyl ether melted at 130-131.5°.

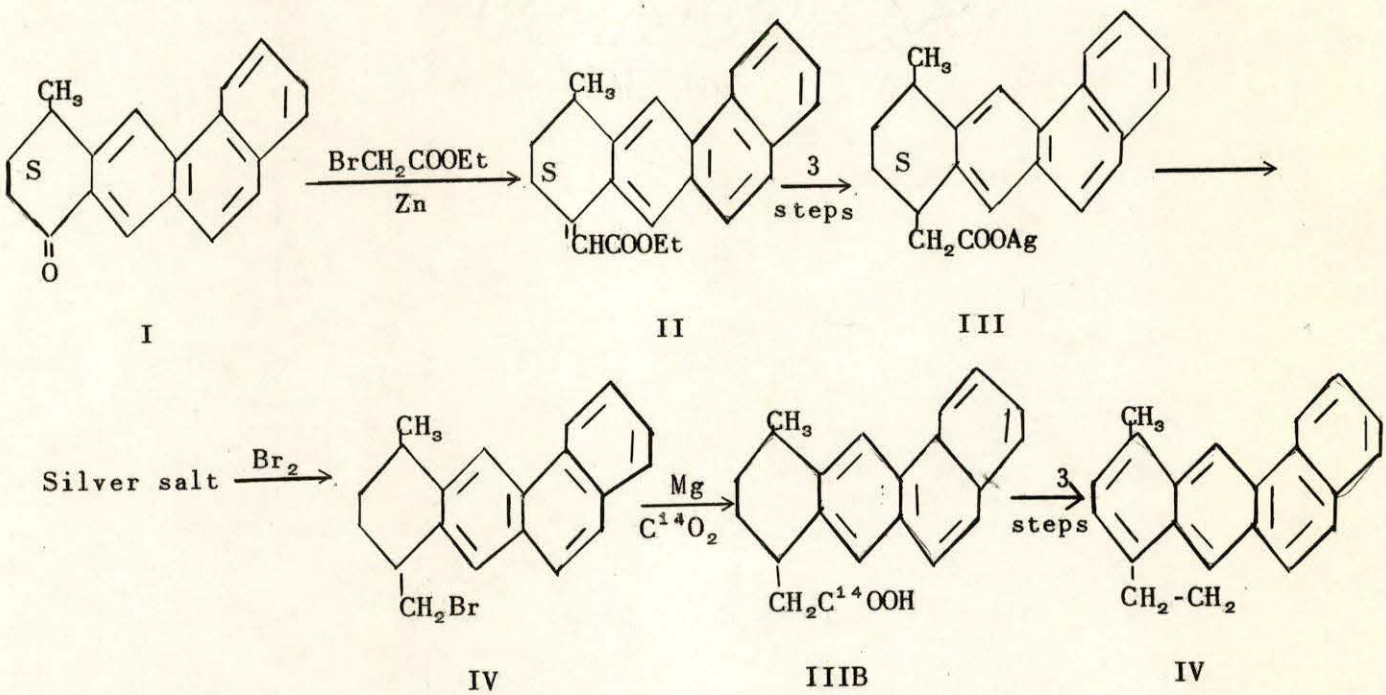
(15) Fieser and Pichet, J. Am. Chem. Soc. *68*, 2578 (1946).

(16) Kindler and Dschi-yin Kwok: Ann. *554*, 9 (1943).

2. *Self Absorption Curve of Radioactive Polystyrene. (O. K. Neville, W. J. Skraba, E. V. Grovenstein*).* Although the self-absorption curve of barium carbonate-C^{14} has been published by several workers[17,18,19,20], no similar data have been reported for other carbon containing compounds. As part of the general problem of the preparation of polystyrene counting standards, a self-absorption curve of polystyrene-C^{14} is being determined. Although the work is not yet complete, it appears that the infinite thickness lies between 22 mg/cm^2 and 28 mg/cm^2.

The counting samples were prepared by dissolving polystyrene-C^{14} of known specific activity in successively larger amounts of methylene chloride as solvent and spreading equal aliquots from the various dilutions over equal areas of mercury. The samples of various thicknesses after drying slowly overnight were free of solvent and quite stable. A disc of 18.5 mm diameter was cut from each film. The thickness was measured with a micrometer, and the weight of each sample was determined, prior to mounting on an aluminum disc. The samples were counted in a (shielded) converted I.D.L. alpha proportional counter having a geometry of about 50% and a background of 32 cts/min.

3. *5-Methylcholanthrene-1-C^{14} (J. G. Burr).* (a) Discussion: The synthesis of labeled methyl cholanthrene is being undertaken according to the following scheme:



(17) Yankwich, Rollefson, Norris, J. Chem. Phys. *14*, 131 (1946).

(18) W. B. Leslie, MonC 173.

(19) Armstrong and Schubert, Anal. Chem. *20*, 270 (1948).

(20) Haissinsky and Pullman, J. Phys. Radium *8*, 33 (1947).

* Participant in ORINS-ORNL Summer Research Program, Dept. of Chemistry, Georgia Inst. of Tech.

The ketone I was prepared by the method of Riegel and Burr[21]. A Reformatski reaction with ethyl bromoacetate, followed by dehydration, hydrogenation, and saponification gave the free acid (III), which melted at 145-146°. The silver salt of this acid (III) reacts with bromine to give a neutral product (IV) and a larger quantity of acidic substance (recovered acid III); but conditions have not yet been worked out which give the maximum yield of halide (IV).

(b) Experimental: (1) 11-Methyl-8,9,10,11-tetrahydrobenz(a)anthracene-8-acetic Acid (III). A solution of 5.0 g of the ketone (I) in a mixture of 50 ml of benzene and 50 ml of ether was prepared. To this was added 7.5 ml of ethyl bromoacetate, 10 g of dry acid-washed zinc, and 0.5 g of iodine. Upon heating this mixture, a reaction started immediately and was completed by heating and stirring over-night. The reaction solution was hydrolyzed with dilute hydrochloric acid, and the unwashed organic layer was concentrated and the residue heated *in vacuo* on the steam bath, thus effecting dehydration of the tertiary hydroxyl group. The dark brown residue was evaporatively distilled to give 5.74 g (100%) of a pale yellow gum, presumably the ester (II). Upon hydrogenation at atmospheric pressure with a platinum catalyst, this ester took up 85% of the theoretical amount of hydrogen. The hydrogenated ester was saponified by refluxing it under nitrogen with a solution of 1.5 g of potassium hydroxide in ethanol. The acidic material recovered from the hydrolysis weighed 4.80 g and was a solid. Several crystallizations from dilute alcohol gave 1.4 g of III as pale tan shining plates which melted at 145-146°.

The silver salt (III A) was prepared and ignited to silver. Calculated for $C_{21}H_{19}O_2Ag$: Ag, 27.1%; Found: Ag, 27.0%.

PREPARATION OF C^{14}

Gas Formation During Irradiation of Beryllium Nitride (A. J. Weinberger). (a) Discussion: When cans of Be_3N_2 are irradiated in a pile, gases are produced. A previous measurement of the pressures and composition of the gases produced in slugs canned at Argonne National Laboratory and containing Argonne-prepared nitride was made[22,23]. It was thought desirable to test in a similar

(21) Riegel and Burr, J. Am. Chem. Soc. *70*, 1073 (1948).

(22) Memo from R. B. Briggs to M. C. Leverett, 'Tests on Beryllium Nitride Slugs', Nov. 11, 1946.

(23) C. D. Bopp, O. Sisman, W. K. Stromquist, 'Pressure Developed in Beryllium Nitride Slugs', ORNL Report, August 11, 1947.

manner the slugs canned at Oak Ridge National Laboratory and containing Be_3N_2 prepared by Clifton Products Co. These measurements are now being made.

(b) Experimental: An apparatus (Fig. 13) was set up for this purpose. It consists of two main parts, the slug puncturing chamber (A) with its manometer (B) and the analytical system which comprises the remainder of Fig. 13.

The slug puncturing chamber is a nickel plated brass tube into which a slug fits snugly. The chamber is sealed with a flange plate secured with 8 Allen-head bolts and gasketed with two concentric rubber "O" rings which have V shaped seats in the plate and the chamber. The space between the "O" rings can be evacuated and connected to a small volume mercury manometer (A1). This arrangement reduces time spent finding leaks.

To the slug chamber is attached a stainless steel bellows-sealed rod with a removable hardened steel needle point. The rod has a stainless steel fulcrum at the chamber end of the bellows. When the rod is moved up and down, the needle point scratches holes through the two aluminum walls of the slug.

The manometer (B) contains three calibrated bulbs which can be filled with mercury. A mercury plug valve (B_4), consisting of a spare between two fine porosity centered glass discs, which can be filled with or emptied of mercury, permits pressure equalization on the manometer arms; this is necessary before they can be drained of mercury to allow gas passage.

The analytical system contains a manometer (C), a trap (C1) which can be immersed in liquid nitrogen or other baths, a storage reservoir (D) containing calibrated bulbs (D1)(D2)(D3)(D4) and a Toepler pump (D5). On the two mercury sealed ground glass joints (D6), various pipettes can be mounted. In Fig. 13 is shown the palladium valve pipette (D7) with its manometer (D8), its Toepler pump (D9) and its reservoir (D10). The palladium valve is heated by turns of nichrome wire and is insulated with asbestos. A thermometer well in the top is made to contain a small 0-300° C thermometer.

The slug chamber is shielded with lead bricks. Various pieces of long handled equipment are used during the insertion and removal of a slug from the puncturing chamber.

A thermometer hung above (D) is used to determine the temperatures of the gases. The small Hg manometer (C2) is convenient but not necessary.

The detailed operation of this apparatus will be discussed in the completion report for this problem.

(c) Results: This method of analysis supposes that no gases having an appreciable vapor pressure at liquid nitrogen temperatures are present other

NOT CLASSIFIED
DWG. 7960

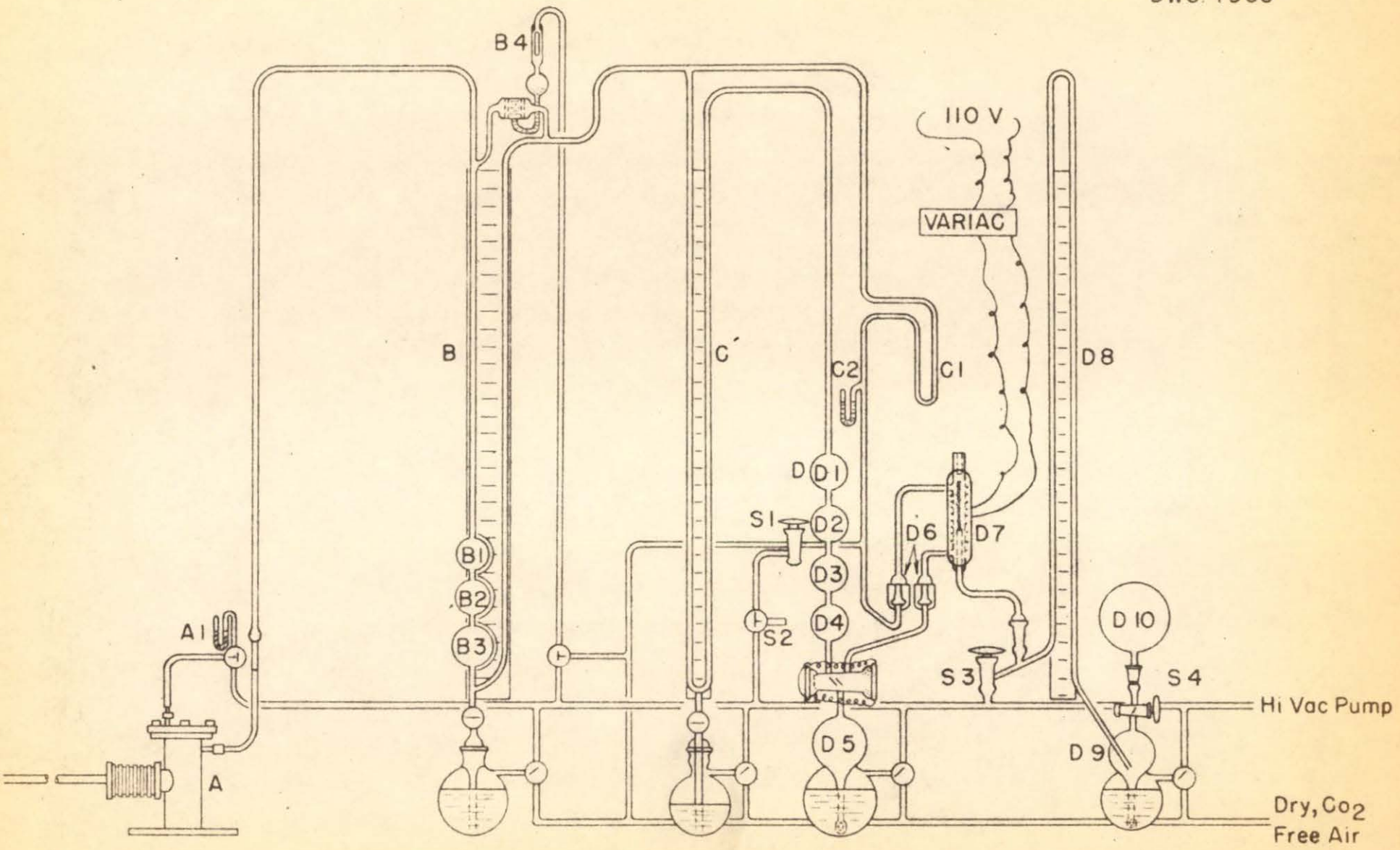


FIG. 13
APPARATUS USED TO DETERMINE THE PRESSURE AND
COMPOSITION OF THE GASES PRODUCED IN IRRADIATED Be_3N_2 SLUGS

than oxygen, nitrogen, hydrogen and argon, and that the hydrogen and oxygen are quantitatively converted to water on the palladium valve. Several experiments with known mixtures of air and purified hydrogen have shown the latter premise to be true at least within the limits of accuracy of the apparatus and the methods.

Typical results, obtained on slug 13-15-359, are shown in the accompanying table.

TABLE I

Analysis of Gas from Irradiated Be_3N_2

Free volume of chamber containing slug unpunctured	82.6 ml.
Free volume of chamber containing slug with outer can punctured	-----
Free volume of chamber containing slug with both cans punctured	113.0
Free volume of inner can	30 ml.
Pressure of inner can gas at 576.5 ml. and 30° C.	299.4 mm.
Pressure of inner can gas at 30 ml. and 30° C.	557 mm. or 0.73 atmos
Analysis of inner can gas	
H_2O	1.8%
H_2	87.7%
N_2 + A	8.9%
O_2	0.1%
Other gases condensable in liquid nitrogen.	0.2%
Analysis of gas between inner and outer cans	
Fraction condensable in liquid nitrogen	86.8%
Fraction not condensable in liquid nitrogen	13.2%

The water found in the inner can gas may have been part of the gas between the can walls which was not completely removed.

CHEMISTRY OF SEPARATION PROCESSES

VOLATILITY STUDIES

P. Agron and E. G. Bohlmann

The general objectives of this program have undergone some changes during the past quarter. Initially a study of fission product fluorides was contemplated. However, considerable effort is already being devoted to such investigations at other installations. From a long range point of view, the real advantage of the systems and compounds which have usually been considered for volatility applications lies in the possibility of direct use as reactor fuel or blanket material. Thus a program of studies designed to establish the properties of systems which might be useful in such applications seems of considerable interest. Such a program is now being initiated.

An obvious first choice for investigation was the possibility of utilizing a solution of thorium fluoride in anhydrous hydrofluoric acid (deuterated) as a blanket. There was little reason to hope that thorium fluoride would be sufficiently soluble for such an application. However, since no data could be found in the literature, an investigation was instituted. Preliminary data obtained in relatively crude experiments indicate that this pessimistic prognostication was correct; no appreciable solubility was observed in the temperature range 26° C to 70° C. Further studies of this and other systems are contemplated.

SOLVENT-EXTRACTION PRINCIPLES AND APPLICATION

EXTRACTION OF $Th(NO_3)_4$ INTO TRIBUTYL PHOSPHATE-HEXANE

O. E. Myers and R. W. Stoughton

The simplified system $Th(NO_3)_4$ (aq)-Bu_3PO_4 (hexane) has been chosen as a starting point in a study of the fundamental chemistry involved in the butyl phosphate extraction of thorium. The nature of the chemical species responsible for the extraction is to be determined.

Tributyl phosphate, obtained from the semi-works, was distilled at a pressure of 6 mm Hg. The fraction boiling in the range 140-142° C (uncorr.) was retained and dried over calcium sulfate. A 0.551 *f* solution in dry hexane showed no acidity on titration with sodium hydroxide (acidity not greater than 0.00015 *f*). The amount of mono- and dibutyl phosphate present may be considered negligible. The hexane used was also obtained from the semi-works and was dried over calcium sulfate.

A 5.00 ml aliquot of thorium nitrate solution was mixed with 5.00 ml of tributyl phosphate in hexane in a 15 ml centrifuge cone placed in a mechanical agitator in a thermostat-controlled water bath at 25.00 ± 0.05° C. Violent shaking was continued for 1½ hour for the experiments reported, although only very small discrepancies were noted when these runs were compared with runs which were shaken for ¼ hour.

Aliquots of both the aqueous and organic phases were analyzed for thorium by a volumetric method which involves the back-titration of a known amount of standard 1.0 *f* NaOH with standard 0.1 *f* HCl after removal of the precipitated hydrous thorium oxide. This method gives results which agree with those of a gravimetric method (pptn. of ThO_2 by excess NH_4OH solution) to within 0.2%. The reported distribution coefficients D_a^o are the ratios of the observed thorium concentrations in the two phases (i.e., organic/aqueous).

Run 20 was performed in order to test the possibility of non-equilibrium in this system. The initial conditions were those of Run 1. After 1½ hour shaking the aqueous phase was replaced with fresh solution and the shaking was

repeated. (This procedure was suggested by E. G. Bohlmann.) No anomalous behavior was observed within the limits of experimental error. This indicates that no adverse rate-phenomena need be considered.

From a graph showing log D_a^o *vs* log $Th(NO_3)_4(aq)$ for a given concentration of tributyl phosphate (Fig. 14) it is seen that a definite maximum occurs which seems to be shifted to lower thorium concentrations at higher phosphate concentrations.

Figure 15 shows the ratio of butyl phosphate molecules to thorium atoms in the organic phase as a function of the final aqueous thorium nitrate concentration. This ratio approaches 3 at high thorium concentration, in agreement with observations by Overholt and DeLozier (FLS-71, 6/14/49).

TABLE I

Distribution of Thorium between Nitrate Solution and Bu_3PO_4

NO.	INITIAL $Th(NO_3)_{4aq}$	FINAL $Th(NO_3)_{4aq}$	FINAL $Th(IV)_{org}$	MATERIAL BALANCE	$\bar{D}_a^o$	$\frac{Bu_3PO_4}{Th(IV)_{org}}$	f Bu_3PO_4
1	1.460	1.309	0.149	99.8%	0.114	3.70	0.551
2	1.170	1.031	0.144	100.3	0.140	3.82	
3	1.170	1.035	0.145	100.9	0.140	3.80	
4	0.878	0.762	0.118	100.2	0.155	4.67	
5	0.878	0.760	0.118	100.0	0.155	4.67	
6	0.585	0.512	0.076	100.4	0.148	7.25	
7	0.585	0.513	0.077	100.8	0.149	7.15	
8	0.438	0.386	0.049	99.3	0.127	11.2	
9	0.438	0.390	0.049	100.2	0.126	11.2	
10	0.292	0.273	0.021_6	100.7	0.079	25.5	
11	0.292	0.273	0.022_1	100.8	0.081	24.9	
12	0.144	0.145	0.003_7	103.2	0.025_5	(149)	
13	0.144	0.144	0.003_4	102.2	0.023_5	(162)	
14	0.438	0.414	0.022_8	99.7	0.055	14.5	0.330
15	0.438	0.414	0.022_8	99.7	0.055	14.5	
16	0.585	0.552	0.039_3	101.4	0.071	8.4	
17	0.878	9.814	0.067_2	100.4	0.083	4.91	
18	1.460	1.374	0.099	100.8	0.072	3.33	
19	1.460	1.341	0.099	98.5	0.074	3.33	
20	see text	1.423	0.164	-	0.115	3.36	0.551
21	1.460	0.971	0.509	101.4	0.523	3.60	1.833
22	0.878	0.520	0.356	100.0	0.684	5.15	
23	0.730	0.428	0.301	100.0	0.702	6.09	
24	0.438	0.273	0.167	100.4	0.612	11.0	
25	0.292	0.203	0.089_8	100.3	0.440	20.5	
26	0.146	0.127_4	0.023_1	103.1	(0.181)	79.3	

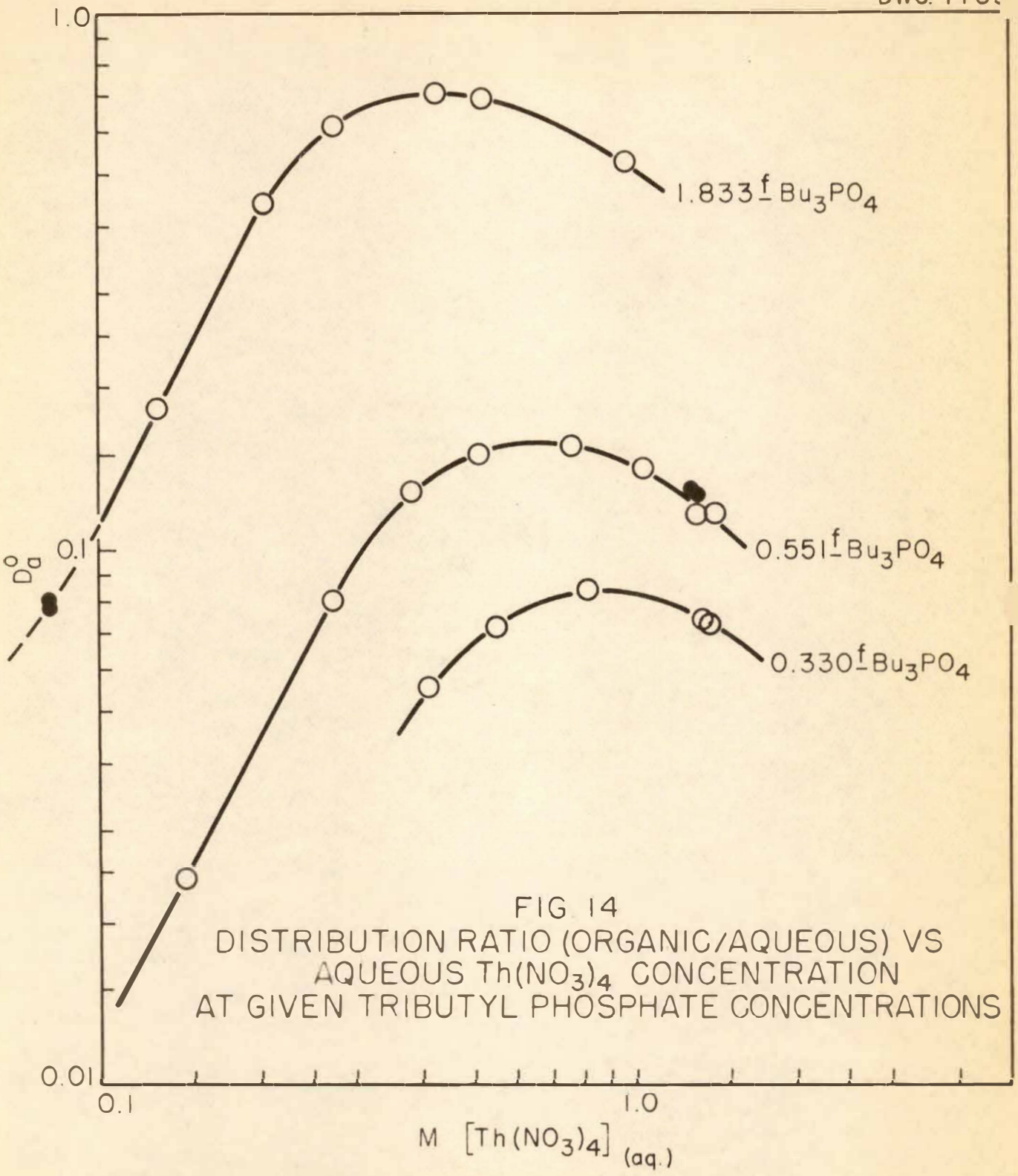


FIG 14
DISTRIBUTION RATIO (ORGANIC/AQUEOUS) VS
AQUEOUS $Th(NO_3)_4$ CONCENTRATION
AT GIVEN TRIBUTYL PHOSPHATE CONCENTRATIONS

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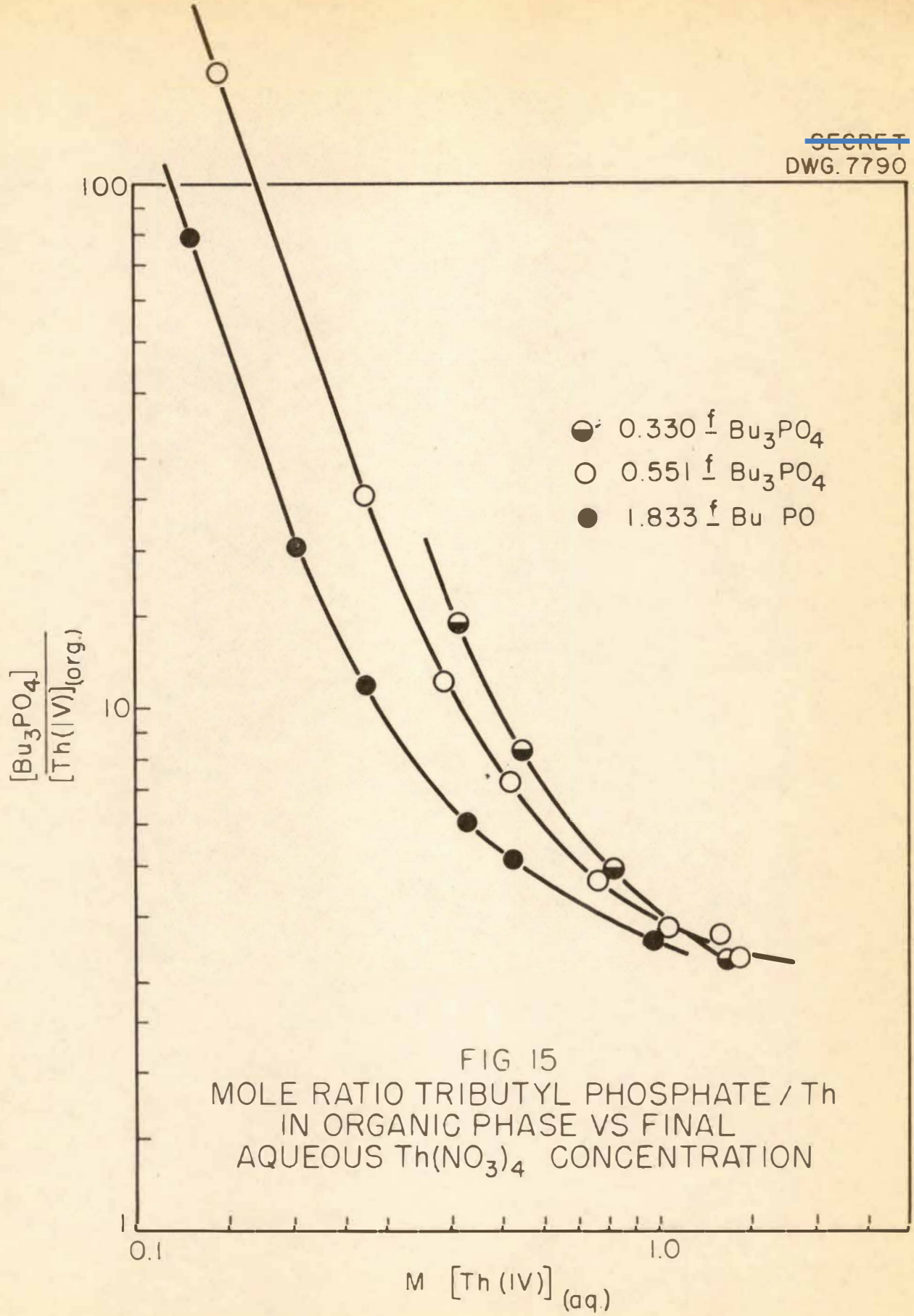

FIG 15
MOLE RATIO TRIBUTYL PHOSPHATE / Th
IN ORGANIC PHASE VS FINAL
AQUEOUS $Th(NO_3)_4$ CONCENTRATION

EXTRACTION OF ZIRCONIUM AND HAFNIUM INTO TTA-BENZENE

J. P. McBride and R. W. Stoughton

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

$$M(OH)^{+n}_{4-n\ A} + mHT_B + (4-m)X^-_A \rightleftharpoons MT_m(OH)_{4-m\ B} + (m+n-4)H^+ + (4-n)H_2O$$

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

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

Where a single metallic species in each phase in predominant, the expression becomes

$$K = \frac{(DR_{(B/A)})(H^+)^{m+n-4}}{(HT)^m(X^-)^{4-m}}$$

where $DR_{(B/A)}$ refers to the distribution ratio of the metal, benzene over aqueous.

Work at this Laboratory indicates that the extraction of Hf from 0.5 to 3.5 *M* HNO_3 may be represented to a close approximation by the equation

$$Hf(OH)^{+3}_A + 4HT_B \rightleftharpoons HfT_{4B} + 3H^+_A + H_2O \quad (1)$$

(1) J. P. McBride, ORNL-303.

A recent report from Knolls Laboratory postulates a third power acid dependence but a second power TTA dependence for Hf extraction from dilute HNO_3 (up to 1 *M*) which increases to approximately fourth power as the acidity increases.[2] The initial work reported below shows fourth power TTA dependence for extractions from 1 *M* HNO_3, in agreement with previous work at this Laboratory.

An investigation of the extraction of Hf from HCl solutions by TTA carried out here has shown the extractions from such solutions to be unexpectedly complicated and that more than one metallic species is extracted, one or more of which contains chloride (cf. previous quarterly report). A study of the extraction of Zr from HCl solutions, presented below, shows similar complications.

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

Two stock solutions of Hf^{181} tracer were prepared. For the first, 47.8 mg of pile-irradiated hafnium (as hafnium oxychloride) were dissolved in concentrated HCl and the resulting solution was diluted to 25 ml 10 *M* in HCl. For the other, 15.9 mg of the irradiated hafnium was dissolved in perchloric acid, the resulting solution being fumed twice to dryness, before the residue was taken up in approximately 11 *M* HNO_3. The hafnium concentrations in the two tracer solutions were about the same.

Two series of experiments were run to determine the TTA dependence for extractions from 1 *M* HNO_3. In one, benzene solutions of the desired TTA concentrations were prepared by diluting a 0.0200 *M* TTA-benzene solution containing tracer with benzene and a TTA-benzene solution. The 0.0200 *M* TTA-benzene tracer solution has been prepared by equilibrating a 0.0205 *M* TTA-benzene solution with an equal volume of the diluted Hf tracer-HCl stock solution. In the second series, a similar group of organic solutions was prepared using a 0.0200 *M* TTA-benzene solution prepared as above but using the diluted Hf-HNO_3 stock solution. The solutions thus prepared (2 to 4 ml in volume) were then equilibrated in pyrex tubes for 3 hours at room temperature (34° C) with equal volumes (org = aq) of a 1 *M* HNO_3 solution.

The Zr^{95} tracer used in the study of Zr extraction from HCl solutions was prepared from a 0.5% oxalic acid solution containing fission product Zr, by treatment with $KMnO_4$ at ca. 95° C. This treatment destroyed the oxalate and caused MnO_2 to precipitate, whereby the Nb^{95} was carried from solution. The supernatant was diluted and the tracer Zr extracted into a TTA-benzene solution.

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

The benzene solution was then washed several times with dilute HCl and the tracer, stripped into concentrated HCl. The extraction cycle was repeated and the resultant HCl solution used as a stock tracer solution.

The TTA-benzene solutions used in the Zr extractions were prepared as in the case of Hf. A 0.0200 *M* TTA benzene solution which had been prepared by equilibrating a 0.0205 *M* TTA solution with an equal volume of the diluted Zr-HCl tracer stock solution was diluted with benzene and with a TTA-benzene solution to the desired TTA concentrations. An adsorption curve run on the tracer product of this treatment showed it to contain no Nb. The TTA-benzene solutions (2 to 4 ml in volume) were then equilibrated in pyrex tubes for 1½ hours at room temperature with the appropriate chloride solutions.

The Hf or Zr activity in the various phases was determined by drying an aliquot on a 1 in. watch glass, mounting (with a cellophane cover) on an aluminum card and counting without inserting an absorber between the sample and G-M tube. Where the addition of salts to the aqueous phase rendered direct evaporation unfeasible, an aliquot of the aqueous phase was extracted with a benzene solution containing TTA in such large excess as to extract all the tracer, and then an aliquot of the resulting benzene solution was counted.

3. Dependence of Hf Extraction from 1 M HNO_3 on TTA Activity. As pointed out in the introduction, a decrepancy exists between the data obtained here and at Knolls on the dependence of Hf extraction from dilute HNO_3 on TTA activity. The experimental procedures followed were similar except in the preparation and handling of the Hf^{181} tracer. In the work here the Hf tracer was prepared from irradiated Hf (as HfO_2) which was dissolved in HF-HNO_3, fumed repeatedly with $HClO_4$, extracted into TTA-benzene, and eventually stripped into 10 *M* HNO_3. Tracer was introduced into the various experiments by extracting the diluted tracer stock solution with TTA-benzene and adding aliquots of the resulting benzene solutions to the organic phases of the extraction runs. At Knolls the Hf tracer from the $HClO_4$ fumings was taken up in an HCl solution which was subsequently converted to an HNO_3 solution, presumably by fuming with concentrated HNO_3 for most runs. In the others, the activity was extracted directly into TTA-benzene from the HCl solution and the resulting benzene solution then used as a stock solution for the activity. In view of the fact that Hf extraction data obtained here indicate the presence of an extractable chloro-TTA complex of Hf it was felt that the discrepancy between the Knolls and ORNL data might be due to the use of HCl in the preparation of the tracer. Hence, two series of extractions from 0.96 *M* HNO_3 were run in which the tracer was

introduced into the organic phases in one case by an initial extraction from an HCl tracer stock solution and in the other by extraction from an HNO_3 tracer stock solution (cf. Experimental Section).

Table 1 gives the data obtained. Column one shows the TTA concentrations corrected for aqueous solubility assuming a distribution ratio (benzene over aqueous) of 40. Columns two and three list the TTA activity coefficients and calculated activities using the data of King and Reas.[3] Column four gives the common logarithms of the TTA activities; column five gives the distribution ratios obtained with the tracer extracted from an HCl solution, and column six, those obtained with the tracer extracted from an HNO_3 solution.

Figure 16 illustrates the data presented in Table 1, showing a plot of log $DR_{(B/A)}$ *vs* log (TTA). As indicated in the introduction the distribution ratio (benzene over aqueous) may be represented by

$$DR_{(B/A)} = [K_{(HT)}m]/[(H^+)^{m+n-4}]$$

Hence a plot of log $DR_{(B/A)}$ *vs* log (TTA) at constant acidity should yield a straight line whose slope, *m*, represents the number of TTA radicals associated with the metal in the organic phase. The slope of 3.8 found, checks the value obtained in ORNL-303 for extraction from 1 *M* HNO_3 but does not give any information as to the reason for the discrepancy between the ORNL data and that obtained at Knolls. It is still possible that an explanation of the disagreement lies in the preparation of the tracer and that the method used above does not duplicate the Knolls preparation exactly enough to reproduce these results. It is also possible that the Hf species in related experiments were in different states of hydrolysis so that the rates of approach to equilibrium or the apparent equilibria attained were sufficiently different so as to produce a TTA dependence at variance with the above result.

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

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FIG. 16
DEPENDENCE OF Hf EXTRACTION
FROM 0.96 M HNO_3 ON TTA ACTIVITY

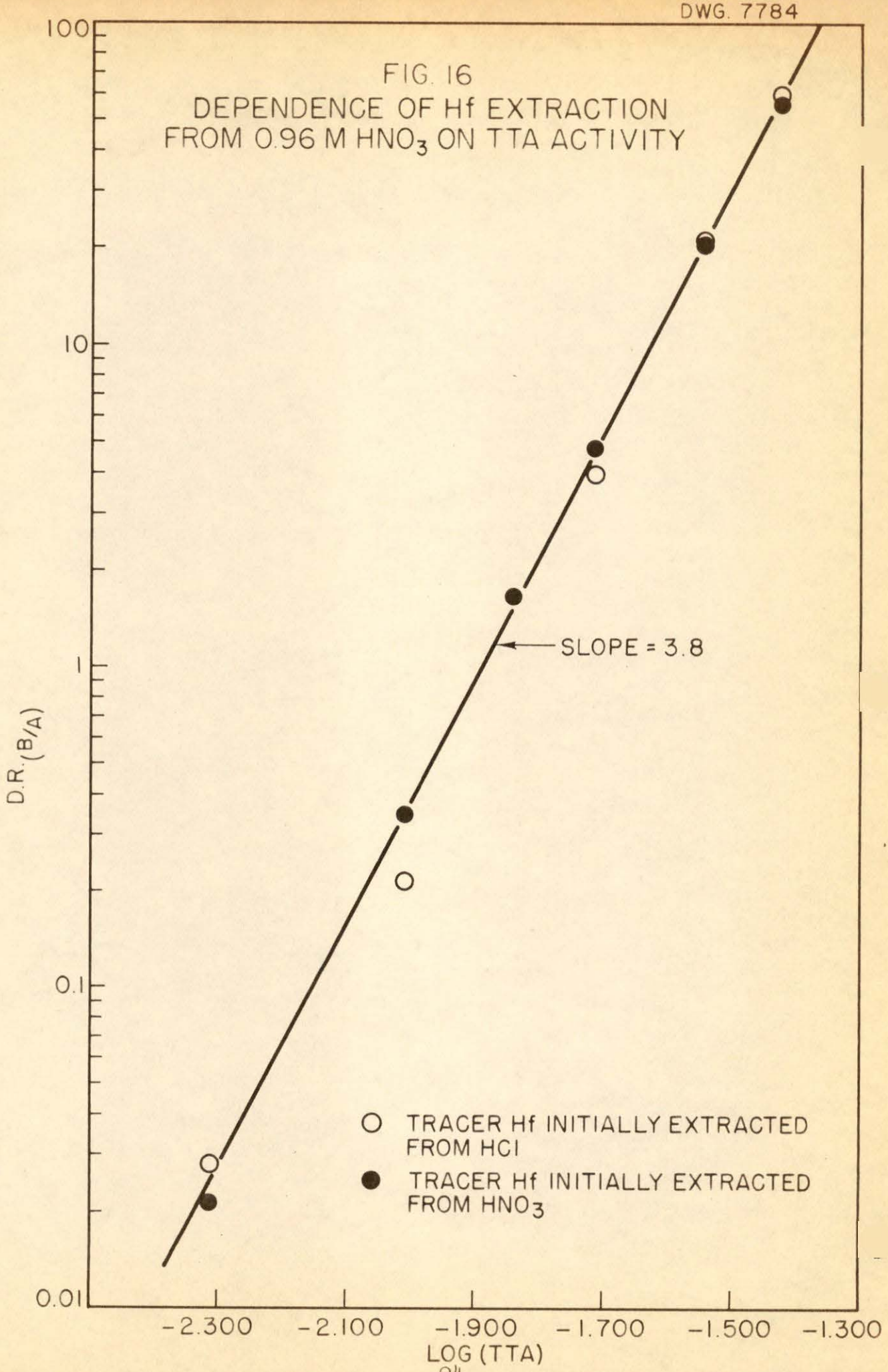

TABLE I

Dependence of Hf Extraction from 0.96 M HNO_3 on TTA Activity

M TTA	f_c(TTA)	(TTA)	log(TTA)	$DR_{(Hf-HCl)}$	$DR_{(Hf-HNO_3)}$
0.0049	0.998	0.0049	-2.310	0.028	0.021
0.0098	0.996	0.0098	-2.009	0.215	0.346
0.0146	0.991	0.0145	-1.839	1.65	1.66
0.0195	0.985	0.0192	-1.717	4.00	4.81
0.0293	0.977	0.0286	-1.544	21.5	21.1
0.0390	0.967	0.0377	-1.424	59.4	55.5

4. *The Extraction of Zr from HCl Solutions.* Figure 17 illustrates data obtained for Zr extraction from 0.496, 0.739, 1.15, and 1.96 *M* HCl solutions as a function of TTA activity. Log $DR_{(B/A)}$ is plotted against log (TTA). The TTA activities were calculated as above by the use of the activity coefficients of King and Reas, after correcting the TTA concentrations for aqueous solubility. The TTA dependence is seen to vary from 1.5 to 2 for the more dilute TTA solutions to 3.3 to 3.6 at the higher concentrations. As in the case of Hf extraction from HCl solutions the presence of more than one metallic species in the benzene phase is demonstrated and since a TTA dependence greatly less than four seems peculiar to the HCl system an extractable chloride species is indicated.

The same data are plotted in Fig. 18 as a function of hydrogen ion "activity" at constant TTA activities. The hydrogen ion "activities" were estimated using the semi-empirical activity coefficients obtained in ORNL-303 and the preceding quarterly report for use in TTA extraction calculations. The solid line through each set of four points gives the approximate fit taking all acid solutions into account. An examination of Figs. 17 and 18, however, shows the data for the 0.5 *M* solutions to be less self-consistent than the data for the higher acidities, and it is felt that hydrolysis phenomena at 0.5 *M* acid affect the extractions in a less reproducible manner. Hence, the broken lines of Fig. 18, drawn through the three points of higher acidity only, give what is considered to be the acid dependence for the higher acidities. The

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FIG. 17
DEPENDENCE OF Zr EXTRACTION FROM HCl SOLUTIONS ON TTA ACTIVITY

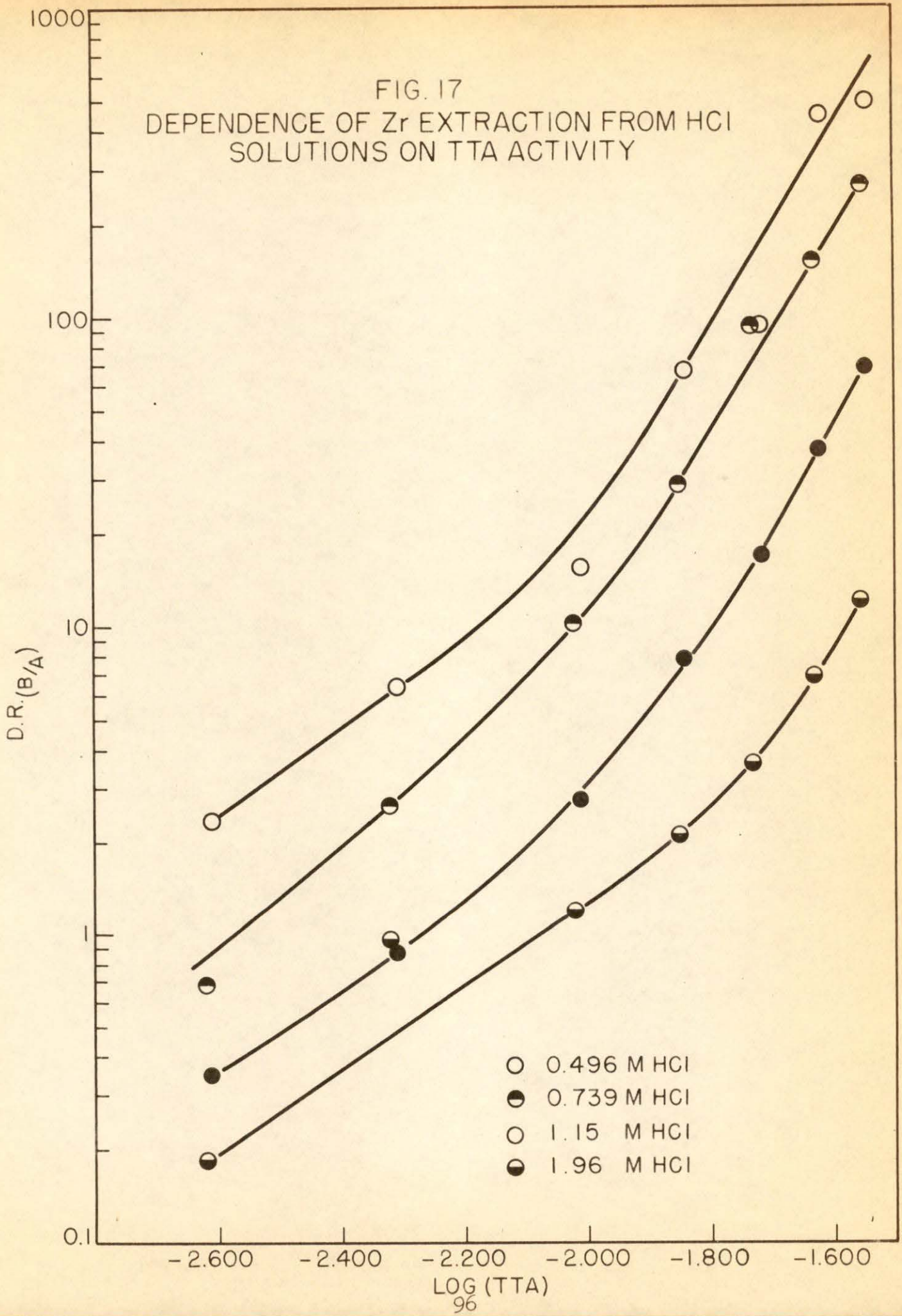

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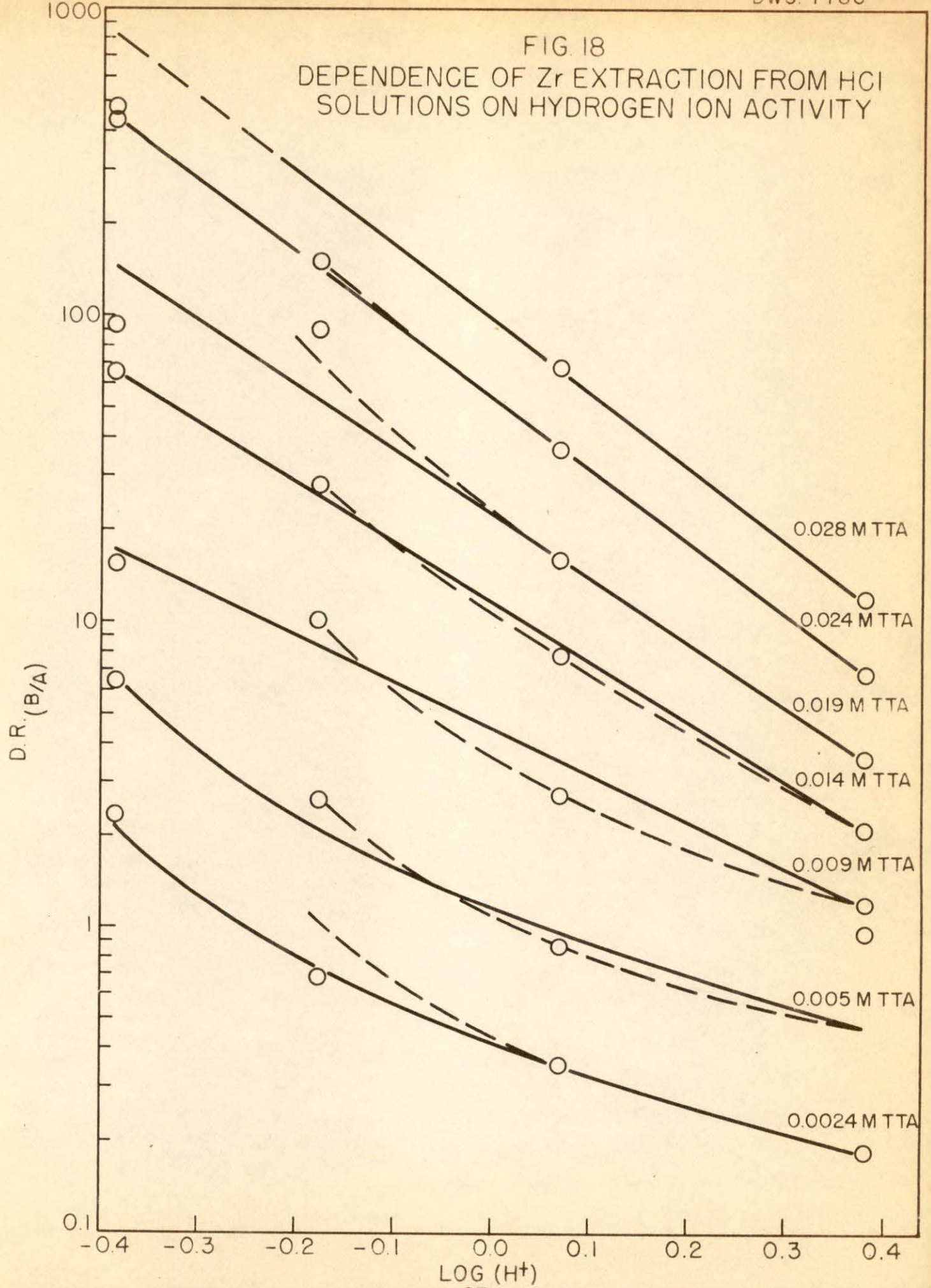
FIG. 18
DEPENDENCE OF Zr EXTRACTION FROM HCl SOLUTIONS ON HYDROGEN ION ACTIVITY



dependence of the distribution ratio on acidity is seen also to be a function of TTA concentration in that the log-log plot has a slope of 0.9 at high acidity and low TTA concentration, which increases to a value (slope) of 2.4 for the highest TTA concentration.

As previously stated the extraction from HNO_3 media is represented by the equation

$$ZrOH_A^{+3} + 4HT_B = ZrT_{4B} + 3H_A^+ + H_2O_A$$

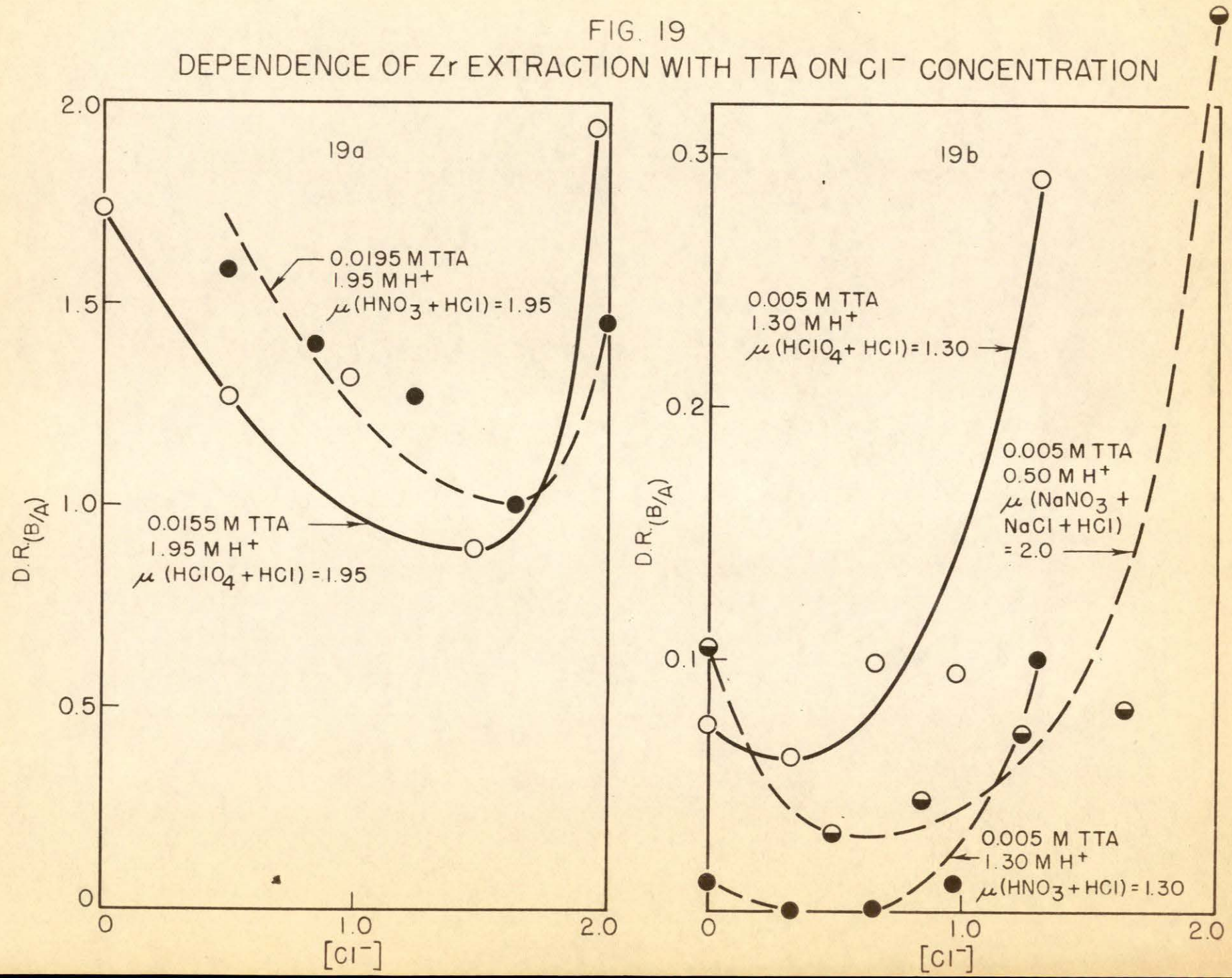
In HCl media there is evidence for more complexing in the aqueous phase than is the case in HNO_3 media. If the additional complexes are of the form $ZrCl^{+3}$ or $ZrCl_2^{+2}$, it is expected that the apparent acid dependence would be at least 3 at all acidities for all TTA concentrations. Actually a dependence approaching first power or less is found at the lower TTA concentrations. Hence, it is assumed that one (or more) metallic species containing chloride is being extracted. Since there is no detectable extraction of Hf under similar conditions when TTA is absent, it is concluded that the complex (or complexes) must contain both TTA anion and chloride.

Several series of experiments were run to determine extraction dependence on chloride concentration at constant acidity and TTA activity. The aqueous solutions in these series of runs were made up by mixing nitrate and chloride solutions to give solutions of constant ionic strength (for any one series of experiments) with varying chloride concentration. A second group of experiments were run using an analogous group of aqueous solutions made up by mixing perchlorate and chloride solutions of the proper concentrations.

The tracer used in the nitrate runs was obtained from a TTA-benzene solution containing tracer which had stood for several days and was purified from Nb by simply equilibrating with a dilute acid solution. The distribution values obtained were low by a small factor, presumably because of some remaining Nb impurity. The tracer for the perchlorate runs was freshly prepared and introduced into the various experiments as given in the experimental section.

Figure 19 illustrates the data. The conditions for the various runs are indicated beside each curve. The dotted lines illustrate the nitrate data which is included mainly to show the position of the minima which appear in the curves. Although all curves showed some inconsistency it can be concluded that one or more aqueous chloride complexes of Zr are formed and that one or more

FIG. 19
DEPENDENCE OF Zr EXTRACTION WITH TTA ON Cl^- CONCENTRATION



chloride containing complexes are extracted. The sharp increase in extraction with increasing chloride concentration indicates that chloride enters the extraction expression to a high power.

Although the data obtained with the perchlorate-chloride system at 0.5 *M* acidity showed an increase in extraction with increasing chloride concentration, it was not consistent and is not included in Fig. 19. It has been pointed out above that runs performed at 0.5 *M* acidity are less reproducible presumably because of hydrolysis phenomena in the aqueous phase. The data obtained in the chloride dependency runs showed less self-consistency as a rule than would be anticipated from previous experience and it may be that the rate of approach to equilibrium is slower than anticipated. Some difficulty was encountered also with absorption of tracer on the walls of the pyrex tubes used for the extractions. In general, a material balance of 93 to 94% could be expected in the presence of a significant concentration of chloride. Since no difficulty was experienced in the pure nitrate and pure perchlorate systems in this regard, this phenomena seems peculiar to chloride systems. These points will be investigated and chloride dependence over a larger range of chloride concentrations determined.

5. *Conclusions.* It seems evident that the Zr species that are extracted by TTA from HNO_3 and HCl are not all identical and that in the case of HCl solutions more than one species, one or more of which contains chloride, are extracted. In addition, an aqueous chloride complex is indicated. Hence, in interpreting the extraction data, a minimum of four species (and perhaps more) are needed. A further study of the extraction mechanism will necessitate the use of experimental conditions which permit the effect of each species on the extraction to be determined independently of the others. Future work planned includes the use of Cl^{36} tracer as a means of determining the composition of the extractable chloride species. In addition, a spectrophotometric study is being considered as a means of studying the species formed in extraction mixtures and variations which are produced with changing conditions. A third approach would be the use of another organic-soluble complexing agent which does not form an extractable chloride species with the metal in order to study chloride complexing in the aqueous phase alone. It is possible also that the same result could be achieved by the use of another solvent for the TTA.

ELECTRODEPOSITION

M. L. Lietzke and R. W. Stoughton

ELECTRODEPOSITION FROM FUSED ETHYL PYRIDINIUM BROMIDE

The electrodeposition of aluminum and several other metals from a plating bath consisting of salts of the metals dissolved in fused ethyl pyridinium bromide or chloride has been reported recently.[4] Hence it seemed desirable to attempt the deposition of aluminum on a uranium cathode from a bath of this type. The ethyl pyridinium bromide used was prepared by reacting ethyl bromide with pyridine. From the fused bath a grey adherent deposit of aluminum could be obtained on copper but not on uranium even though the surface had been carefully treated as recommended by Grey and Wehrmann.[5] Another plating bath containing toluene was also unsuccessful.

When zirconium oxychloride was dissolved in the fused ethyl pyridinium bromide and the solution electrolyzed, a dark grey to brownish deposit was obtained. Spectrographic analysis showed the plate was zirconium. Since the plate was very thin, it was impossible to decide whether it was metallic or a lower oxide.

A motor generator is being set up so that further studies can be made with the fused ethyl pyridinium bromide bath. The conductivity of some of the solutions is so low that an electroanalyzer is inadequate as a D.C. source.

CO-DEPOSITION OF URANIUM WITH IRON, COBALT, AND NICKEL FROM AQUEOUS MEDIA

Since tungsten can be co-deposited with iron, cobalt, and nickel, it seemed desirable to determine whether uranium could be co-deposited with these metals in the same manner. A series of alkaline baths containing citrate as a

(4) F. H. Hurley, U.S. Patent 2446, 331; T. P. Wier, Jr. and F. H. Hurley, U. S. Patent 2446, 349.

(5) A. G. Gray and R. F. Wehrmann, CT-1793.

complexing agent was prepared. Uranium was added as uranium (IV) sulfate and the iron, cobalt, or nickel as the double ammonium sulfates. Silvery metallic deposits were obtained which, however, contained at the most only 0.6% uranium (with iron).

A saturated carbonate bath was also tried. Preliminary work with a Hull cell showed that bright silvery deposits of all three metals could be prepared from a bath of this type. When uranium alone (added as uranyl acetate) was present in the carbonate bath a brownish, thin, non-metallic appearing deposit was obtained down to 33 amp/ft^2. At lower current densities the plate showed colored interference bands. When iron and uranium or nickel and uranium were tried, non-adherent, very thin deposits were obtained, showing that uranium in the batch inhibited the deposition of iron and nickel.

The bath containing cobalt and uranium, however, behaved differently. The Hull cell cathode showed dull grey, shining black, and tarnished silvery deposits at different current densities. Quantitative runs made under various conditions gave deposits that were silvery at first, then rapidly darkened to a dull dark grey color. The plates, which were made on copper cathodes, weighed from 10 to 33 mg (area of cathode 8.3 mm^2 each side). Analysis of the plates showed they contained as much as 42.5% uranium. However, the cobalt and uranium together made up only 75-85% of the plate weight. Hence it seems probable that oxides were present in the deposit, although it was impossible to decide what they might be. As a result of this work it appears that deposition of uranium from a saturated carbonate solution is favored by the presence of cobalt-ion.

FUNDAMENTAL STUDIES ON PARTITION EQUILIBRIA

G. E. Boyd and Q. V. Larson

An exact thermodynamic treatment of ion-exchange equilibria has been made, assuming a Gibbs-Donnan mechanism to determine the distribution of electrolytes between the exchanger and an aqueous solution. Two general equations have been derived, special cases of which for uni-univalent electrolytes are:

$$\text{(I)} \qquad RT \ln K_a = \pi(\bar{v}_{M_1} - \bar{v}_{M_2})$$

$$\text{(II)} \qquad \ln \frac{[m_{\pm MX}]_R}{[m_{\pm MX}]_W} + \ln \frac{(f_{\pm MX})_R^2 \; (f_{H_2O})_W^2}{(f_{\pm MX})_W^2 \; (f_{H_2O})_R^2} = \frac{\pi}{RT} (2\bar{v}_{H_2O} - \bar{v}_{M+} - \bar{v}_{X-})$$

Equation (I) governs the exchange between two univalent cations (or anions) where K_a is the thermodynamic equilibrium constant, π, the swelling pressure exerted by the exchanger, and $\bar{v}_{M_1}$ and $\bar{v}_{M_2}$ are the relative partial molal volumes at infinite dilution (assuming ion incompressibility) of the ions M_1 and M_2, respectively.

Equation (II) describes the distribution of a neutral electrolyte, MX, between the exchanger and aqueous phases where $m_\pm$ is the mean molality, $f_\pm$ the mean activity coefficient, and the other symbols are as described for Equation (I).

Both these equations show the dependence of the equilibrium partition upon the swelling pressure, π, which is determined by the elastic constants of the exchanger (and by the ionic strength of the aqueous phase), and upon hydrated ion size as indicated by the partial molal volume terms. Thus, according to (I) the smaller ion will be enriched in the exchanger, and this enrichment will

be greater the greater the bulk elastic modulus of the exchanger. Equation (II) predicts the variation of the amounts of diffusible anion, X^-, in the exchanger as a function of π, $\bar{v}_{M+}$ and $\bar{v}_{X^-}$, respectively.

The experimental work during the past quarter has been concerned with the verification of the Gibbs-Donnan requirement of diffusible *anions* in the exchanger, and with a detailed study of (II). By using exchange polymers of varying cross-linking, it has been possible to vary π, holding all other conditions constant, and to observe changes in the amounts of $(HCl)_R$ inside the exchanger. The quantities $\bar{v}_{M+}$ and $\bar{v}_{X^-}$ have been varied at constant cross linking by comparing the distribution of HCl with LiCl, and of HCl with HBr. Good general agreement was observed, although certain details remain to be clarified. The method of activation analysis was employed throughout to determine the quantities of diffusible anions inside. Accurate moisture contents of the exchanger in equilibrium with various concentrations of electrolyte in the aqueous phase were determined by titration with Karl Fischer reagent. (We wish to thank Mr. A. D. Horton and Dr. M. T. Kelley of the Analytical Group for these determinations.)

SEPARATIONS OF THE FIFTH, SIXTH AND SEVENTH GROUP ANIONS

R. W. Atteberry and G. E. Boyd

Studies on the separation of the halides reported last quarter (ORNL 286, p. 131) have been continued in order to develop a more rapid fractionation than was possible using 1 *M* Na_2CO_3 with a Dowex A-1 column. The difficulty with this system arises from the high selectivity exhibited by A-1 as reflected in the large K_d values observed. Since the volume at which an elution peak occurs (F_{max} in units of free column volumes) is related to the distribution coefficient, K_d by: $F_{max} = C = K_d(m/V)$ where (m/V) is the mass to volume ratio for the exchange column, a large K_d requires that the elution peak be retarded until large volumes have passed through the bed. Essentially, then, K_d must be lowered, or else be changed readily by adjustment of *p*H, concentration, etc., if a convenient separations technique is to be evolved. In the specific problem of effecting a rapid, efficient fraction of F^-, Cl^-, Br^- and I^- ions we are

further limited by the instability of the latter ion towards oxidation by dissolved oxygen. This limitation has required that the *p*H be maintained at or above 9 at all times, or else that some added stabilizing reagent be present.

In the exploratory experimental work, several new anion exchangers were examined and brief mention of them may illustrate the general approach in the development of an ion-exchange separations scheme. First, it was hoped that a lower halide selectivity could be obtained using Dowex A-2, since *p*H titration curves had revealed this polymer to behave as a somewhat weaker base than either A-1 or Amberlite IRA-400. Actually, however, in the 1 *M* carbonate system very little if any improvement was realized. Next, the degree of cross-linking A-2 was varied, using 1, 2, 4 and 6% cross-linked preparations. Here, the lowest selectivity should be exhibited by the least cross-linked material, and hence it was considered that possibly a sufficiently low K_d could be achieved with the 1% preparation. Although a distinct improvement was realized in the carbonate system, still the selectivity was too large. Next, a weak base exchanger was employed together with an $NH_4OH + NH_4NO_3$ buffer. Good control of the K_d could be achieved in this system by varying the *p*H at constant nitrate concentration, but, unfortunately, in this case the selectivity was too low and could only be raised into a usable range by dropping below a *p*H of 7. Alternatively to effecting a displacement elution either by OH^- and/or $CO_3^=$ or NO_3^-, a complexing elution using $Hg(NO_3)_2$ was demonstrated. Here the separation depends upon the formation of $HgX_4^=$ complex ions, and, as was anticipated the order of elution was $I^- > Br^- > Cl^-$ which is the reverse of the sequence obtained with displacement. Rather poor separations were realized using $Hg(NO_3)_2$, however, and further, the K_d values appeared to be extremely dependent upon the Hg(II) concentration. Presently, studies are in progress using A-2 and $NaOH + NaH_2PO_4$ buffers wherein a *p*H dependent displacement elution will be conducted.

A preliminary investigation has indicated the possibility of a chromatographic separation of Mo, Tc and Re using anion exchangers. Thus, using 1 *M* Na_2SO_4 with Amberlite IRA-400 K_d values of 74, 850 and 1350 for these respective elements were observed. Again, a lower selectivity, particularly for Tc, is to be desired. An increase in the $SO_4^=$ ion concentration caused some but not a sufficient reduction in K_d. The effect of a number of other displacing anions was investigated. One molar NH_4F, NaCl and KSCN solutions gave 3200, 400 and 6.7 as K_d values respectively for the distribution of ReO_4^- ion.

Further studies with varying concentrations of the latter reagent have revealed that a rapid, convenient separation of Re from Tc might be feasible using SCN^- + OH^- ions.

SEPARATION OF PROTACTINIUM, NIOBIUM AND TANTALUM BY ANION EXCHANGE

George E. Moore and Kurt A. Kraus

In the previous quarterly report[6] a number of separations of metal ions by anion exchange were described. Work on such separations has continued using the same metal ions previously discussed. Since this work primarily involved extension of the studies described and since it generally confirmed the conclusions previously reached, they will not be discussed at this time except for the extremely striking separation of the triad Nb-Ta-Pa. A typical separation is illustrated in Fig. 20. The pertinent experimental conditions were: Dowex-1 resin, cooumn length: 12.5 cm, column cross section 0.0226 cm^2, eluent: 0.05 *M* HF-9.0 *M* HCl, flowrate ca. 0.3 $ml/cm^2/min$. It may be noticed that the elution order is Pa, Nb, Ta.

A few other conditions where separation can be achieved, can be found from Table 4, where the elution constants R[7] of Nb, Ta, and Pa are given at a number of HF concentrations in 9.0 *M* HCl. Similar studies are now being carried out at lower chloride concentrations.

The ease of separation on Nb and Ta is particularly surprising since the separation of the adjacent elements Zr and Hf under similar conditions is very poor.[6][8] Furthermore Nb and Ta have practically the same size[9], at least in the complex fluorides K_2XF_7. The difference in their behavior may be due to comparatively large differences in the polarizability of the ions (this would be more important for the more highly charged fifth group elements than for those in the fourth group) causing considerable differences in chloride complex constants. However, differences due to primary coulombic effects on the stability of the fluoride complexes cannot be entirely eliminated. For these highly complexed materials the product of a considerable number of complex constants is involved which could cause considerable differences in the concentrations of the most heavily complexed species even if the individual complex constants differ only by a few percent.

(6) K. A. Kraus and G. E. Moore, Report ORNL 286 (September 1949).

(7) R is the distance in cm a band travels when 1 ml of eluent is passed through a column of 1 cm^2 cross-sectional area. See also previous quarterly report.[6]

(8) K. A. Kraus and G. E. Moore, J. Am. Chem. Soc. *71*, 3263 (1949).

(9) J. L. Hoard, J. Am. Chem. Soc. *61*, 1252 (1939).

TABLE 4

Elution Constants of Nb, Ta and Pa in HF-HCl Mixtures (9 M HCl, Dowex-1)

M HF	ELUTION CONSTANT		
	Nb	Ta	Pa
.01	.0062	.0077	-
.02	.019	.013	.81
.05	.07	.005	.5-1
.1	.23	.0051	.9
.18	.26	.0035	-
.5	ca .06	-	1.53
1.0	.027	-	-

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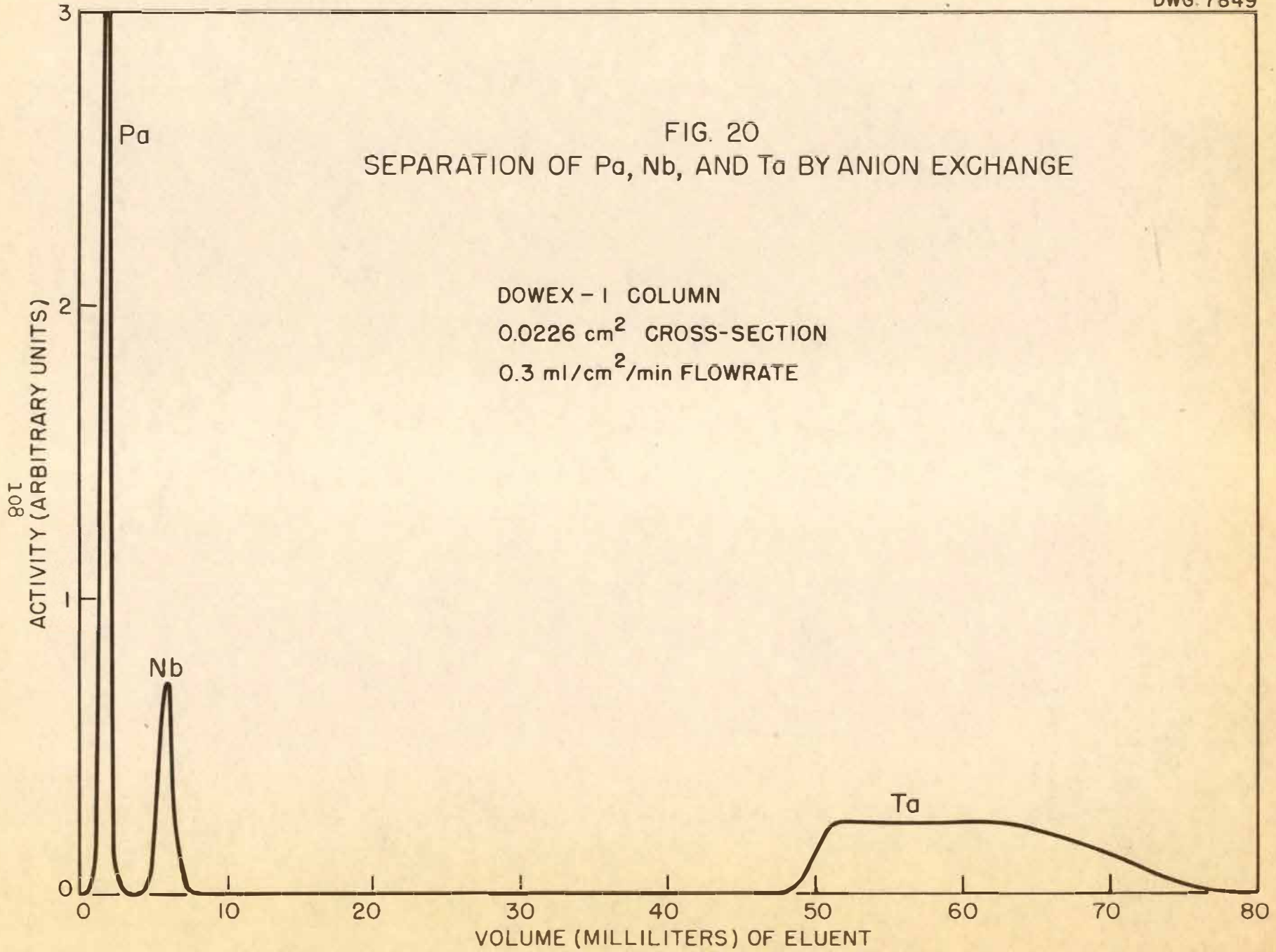

FISSION PRODUCT SEPARATIONS

RaLa PROCESS AND SEPARATION OF FISSION RARE EARTHS

C. E. Higgins and W. H. Baldwin

Work on the RaLa process and the separation of fission product rare earths was suspended during this quarter as all available manpower was needed for the Zr-Cb work.

SEPARATION OF Zr-Nb FROM REDOX PROCESS WASTES

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

Ten column runs at high activity level have demonstrated the feasibility of the proposed silica gel process for removal of fission Zr and Nb from the Redox Process Waste Solution IAW. The proposed process shows an 80-85% yield. Laboratory results indicate that this yield can be substantially increased by operation at higher temperatures (e.g., 70° C) or at slower flow rates.

A feasibility report covering all work to date on the separation of fission zirconium and niobium from Redox waste solutions has been written and issued separately. The report is entitled "Feasibility Report on Recovery of Fission Zr and Cb from Redox Process Waste Solutions Using Silica Gel", and the Central Files number is 49-9-178.

CHEMICAL PHYSICS

MICROWAVE SPECTROSCOPY

Ralph Livingston

Upon completion of measurements on I^{129} as described in the last quarterly report (ORNL 286), the equipment was dismantled and new equipment constructed for remote control operation. A barricaded hood in a concrete room in the 706-D building will be used for the remote control experiments. First work will be on I^{131}, but the same equipment should be suitable for measurements on other iodine isotopes. The electromagnet for observing Zeeman splittings of the methyl iodide hyperfine structure will be included so that, if conditions are favorable, the magnetic moment as well as spin and quadrupole moment will be measured. Cooperative work with Walter Gordy at Duke University has also been underway on measurements of antimony deuteride, SbD_3. The first rotational transition of SbD_3 in the microwave region has been searched for but not yet found.

Remote Control Equipment. A number of remote control devices have been constructed and will be described in fuller detail at a later time. The main portions of the remote controlled high vacuum system consisting of three stopcocks and a trap has been completed. The glassware has been rigidly mounted to a brass plate by casting the stopcocks in place with a low melting alloy. Flexible shaft drives are used to actuate the stopcocks. Adjustable limit stops are built in at the stopcocks so that backlash in the drive mechanism is of no consequence. Lifts for raising and lowering Dewar flasks have also been completed. Flexible shaft drives are used, and the mechanical motion is obtained with a rack and pinion gear. A simple glass blowing operation, sealing off a tube, will be done with a special cross fire burner that has been completed.

The wave guide cell, coiled and placed between the pole pieces of a magnet, will be cooled to approximately -70° by circulating cooled trichlorethylene over the cell. The cooling liquid is circulated with a centrifugal pump through a heat exchanger coil immersed in a dry ice bath and then to the wave guide cell. A preliminary flow system has performed satisfactorily and is now being built into final form. The coiled wave guide cell in being mounted in the annular space of a can made from two concentric cylinders. The space in the hollow core of the can will be occupied by a proton resonance probe for measuring the intensity of the magnetic field. Proton resonance equipment (amplitude method) has been built and tested, but further electronic work is required. A

substance other than water will probably be used as the proton sample since the probe will be at a low temperature. A variety of possible substances were tested at room and dry ice temperatures. Of these, an ethanol or an ethanol-water mixture appeared most feasible.

Antimony Deuteride. Antimony deuteride was synthesized by the action of deutero-sulfuric acid on an antimony zinc alloy. The deutero-sulfuric acid was prepared by adding heavy water to SO_3 which had been obtained by distillation from fuming sulfuric acid. A mossy 50% antimony zinc alloy was used. The product stibine was dried over calcium chloride and phosphorus pentoxide and then condensed in a liquid nitrogen-cooled trap. A vacuum system transfer of the SbD_3 to two ampoules of approximately 300 ml volume was then made. The ampoules were filled to an absolute pressure of about 2 cm of mercury. The stibine could be seen as a white solid when the ampoules were cooled in liquid nitrogen. The samples were transported to Duke University and microwave spectrometer observations started in the 3 mm wave length region. After a few days, a dark gray deposit, presumably antimony, formed inside the ampoules. The samples were frozen in liquid nitrogen and pumped on to remove deuterium before more stibine was used from them. Although noticeable decomposition took place in a few days, a sufficient amount of sample was on hand for a few weeks work. The first rotational transition of SbD_3 has not yet been observed. Gordy and his group are now working on spectrometer developments. Gilliam, at Duke, is working on a frequency standard system to be used in the iodine work.

NEUTRON DIFFRACTION STUDIES

*H. A. Levy and S. W. Peterson**

Neutron diffraction methods of crystal structure determination have been shown to be particularly applicable to the problem of locating hydrogen atoms or ions in a crystal. This makes available a powerful tool for the study of hydrogen-bonded structures. The present investigation of hydrogen-containing compounds by the neutron diffraction method was undertaken with the idea of contributing to the solution of a number of structural and valence problems involving hydrogen bonds.

Potassium hydrogen fluoride was chosen for the first experimental work because of its relatively simple structure and because of its fundamental importance. KHF_2 has been shown by Bozarth[1] to crystallize in the tetragonal system with NH_4Cl-type of arrangement of potassium atoms and bifluoride dumbbells. The bifluoride dumbbells lie in planes perpendicular to the tetragonal axis. Hydrogen atoms were presumed to be located between the two fluorine atoms forming the dumbbell thus giving HF_2^- — ions. Helmholz and Rogers[2] confirmed the interatomic distances found by Bozarth.

EXPERIMENTAL

1. Single crystals of KHF_2 about $1 \times 1 \times 0.2$ cm in size were grown from aqueous solution by evaporation in a desiccator over sulfuric acid. Laue type neutron diffraction photographs were taken using an indium foil and X-ray film mounted in a cassette, a technique previously demonstrated by Shull and Wollan[3] with large NACl crystals. Long exposures were found necessary with the available crystals resulting in rather bad darkening of the film. The patterns obtained were not defined sharply enough to be useful. The difficulties are attributed to the large diffuse scattering cross section of hydrogen, high background radiation around the pile and to the use of crystals which were much

* Participant in ORINS-ORNL Research Program, Dept. of Chemistry, Vanderbilt University.

(1) R. M. Bozarth, J. Am. Chem. Soc. *45*, 2128 (1923).

(2) L. Helmholz and M. T. Rogers, J. Am. Chem. Soc. *61*, 2590 (1939).

(3) E. O. Wollan and C. G. Shull, Nucleonics *3*, 8, (1948).

below optimum size. In view of the difficulties the accumulation of structurally useful data by the Laue method does not seem feasible at present.

2. Deuterated KHF_2 was prepared by dissolving recrystallized KHF_2 in 99.8% D_2O, allowing the exchange to occur, and removing excess D_2O by evaporation. It was found necessary to carry out the process in plastic containers and in an atmosphere of nitrogen in a dry box. With the presently available apparatus, the most highly deuterated sample that has been obtained was found by neutron transmission measurements to have a deuterium content 92% of theoretical. Neutron spectrometer data have been obtained, with the cooperation of Shull and Strauser of the Physics Division, on a powder sample of KDF_2 (85% D) over a 20° range of scattering angle. Preliminary comparisons of experimental neutron scattering intensities with theoretically calculated values for a range of hydrogen parameters gives strong indication that the hydrogen atoms in KHF_2 are centrally located between pairs of fluorine atoms forming bifluoride ions. Additional measurements on powder samples of both KHF_2 and KDF_2 are planned in order to obtain further confirmation.

3. It appears that neutron spectrometer measurements on large single crystals will be very valuable in structural studies such as these. In this case deuterated material is not essential. Hence apparatus is now being developed for growing monocrystals by a slow controlled cooling process. The method should be applicable to a large variety of crystalline substances.

EXPERIMENTS WITH MOLECULAR BEAMS

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

As previously described, it is intended to study the reaction

$$K + Br_2 = KBr + Br$$

by a molecular beam technique, using neutron activation to measure bromine and the surface ionization gage to measure potassium. It appears feasible to measure directly the cross sections for scattering and for reaction, quantities which have been previously obtained only indirectly. This experiment is also to be regarded as a trial of the feasibility of the general idea of using molecular beam methods to study a number of fundamental aspects of chemical kinetics. It is believed that the possibilities of the method have been extended by the availability of neutron activation for the measurement of minute amounts of a number of elements.

Preliminary experiments directed toward testing components and learning techniques have been concluded, and the metal apparatus for the first experiments has been completed, assembled and tested. It is expected that actual scattering experiments will begin in the following quarter.

CALORIMETRY OF RADIOACTIVITY

G. H. Jenks and F. H. Sweeton

A calorimeter, designed and constructed by this group, was described in the last quarterly report[4]. The calorimeter, which was planned to operate at the temperature of liquid helium, was expected to be useful in measuring very low rates of evolution of heat. Two tests of the sensitivity and accuracy of this instrument have now been carried out.

The data obtained in the first of these tests are presented in Table 1. The energy input, measured electrically, is given in column 2. The duration of the observation and the rate of helium gas evolution observed are listed in columns 4 and 5, respectively. The difference between the pressure of helium vapor which was maintained in the calorimeter and that maintained in the calorimeter bath is listed in column 3. Column 6 contains a list of gas evolution rate values computed from the equation:

$$R = 2.023\ W \times 10^{6} + 0.093$$

where

R = rate of helium gas evolution,
W = energy input in watts.

The absolute and percentage deviations of the measured and computed rates are shown in the last two columns.

The above equation represents the least squares straight line relating the data obtained in the first seven observations. ΔP was the same for each of these observations and thus the deviations listed in column 7 should be a direct measure of the sensitivity of the calorimeter. For this set of data, the greatest deviation from the line was ±0.006 rate units, corresponding to a maximum uncertainty in the amount of heat entering the calorimeter of about 2.5×10^{-6} cal/hr.

(4) ORNL 286, p. 171, June 30, 1949.

In addition to furnishing information on the sensitivity of the calorimeter, the data obtained from the first seven observations also established the value for the background evolution of helium at $\Delta P = 0.13$ mm. This value, found either by reference to the equation relating the data or by examining a plot of the data (line 1, Fig. 21), was 0.093 rate units. The background rates at two other values of ΔP, 0.9 mm and 2.1 mm, were determined in the other measurements listed. These were found to be 0.097 and 0.110 rate units, respectively.

The above background rates, which correspond to about 3.5×10^{-5} cal/hr flowing into the calorimeter from its surroundings, were considerably higher than anticipated. However, the variation of the background rate with change in ΔP was only about one tenth of the amount expected if all of the background arose from conduction of heat from the bath into the calorimeter. This indicated that some region outside of the bath was the source of the background heat.

The most likely mechanism by which heat could have been transported to the calorimeter from a region outside the bath was thermal radiation along the ¼ in. tubing connecting the calorimeter jacket with an external vacuum system. In order to determine if radiation down this tube did account for the large background, some additional radiation shielding was placed in the tube and a second determination of the background carried out. The data obtained in this determination are listed in Table 2 and are shown graphically in line 2 of Fig. 21.

As can be seen from the graph, the background rates obtained in this case were appreciably smaller than the previous values. Unfortunately, however, not much information concerning the fraction of the background originating in the bath was available. This was due to a partial clogging which existed in the 25 mil tubing connecting the calorimeter with the pressure control system. The clog, which consisted of frozen air, caused a pressure drop to occur along the tube, even at the very low flow rates used in this work. Because of this pressure drop, the observed values for ΔP recorded in Table 2 may differ from the true value by as much as one or two mm. Although not conclusive, the results of this test indicate that the background can be made much smaller if it is desired to do so.

If no further calibration studies are carried out, the uncertainly in the determination of the energy of a source will arise entirely from the uncertainty in the value for the background. However, even if a maximum value for this uncertainty is assumed, it is still possible to measure accurately very low

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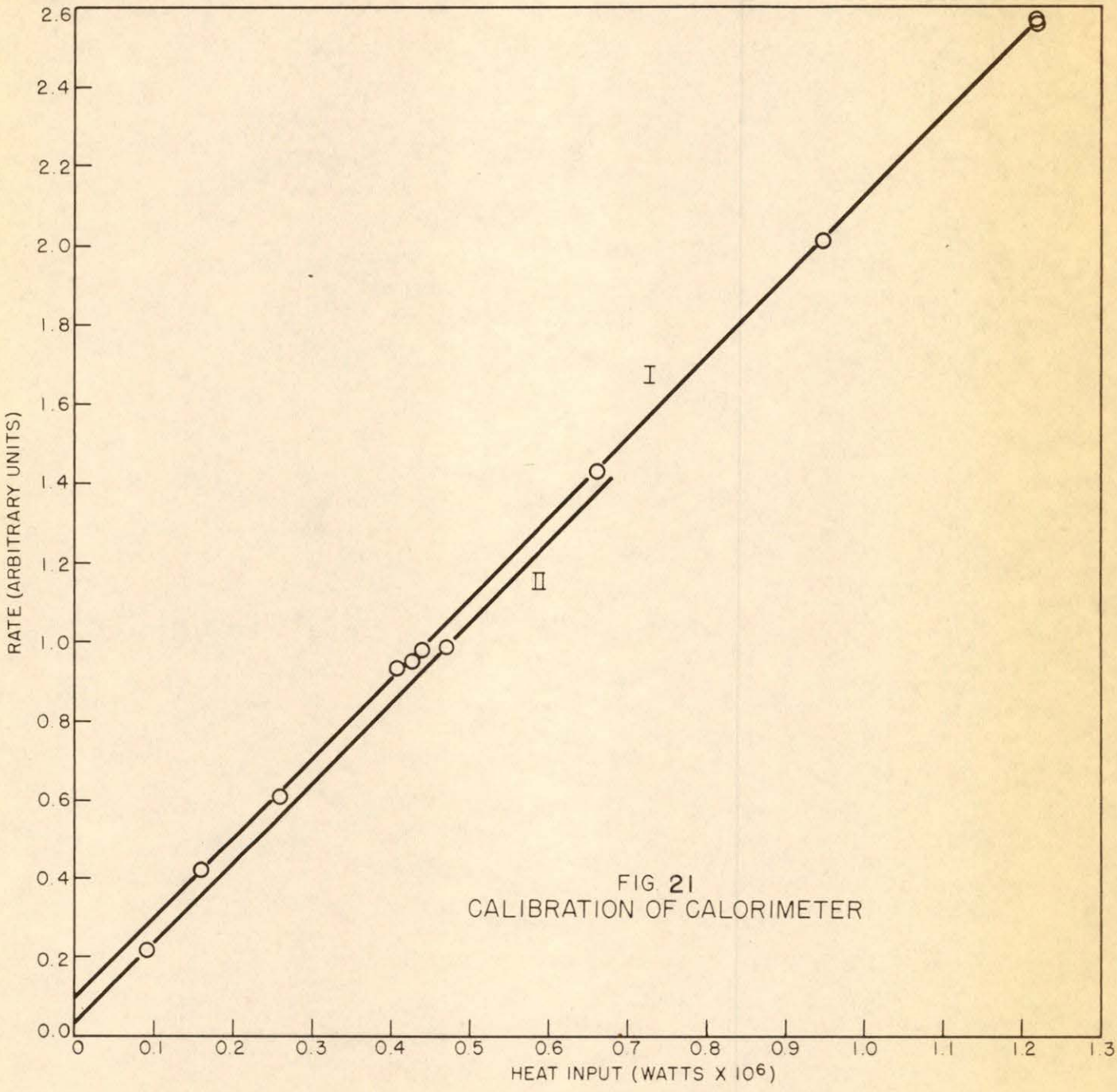

FIG. 21
CALIBRATION OF CALORIMETER

TABLE 1

Calibration of Liquid Helium Calorimeter

OBSERVATION NUMBER	WATTS x 10^6	ΔP mm of Hg	LENGTH OF OBSERVATION (minutes)	RATE OF He GAS FORMATION (Arbitrary units)		DEVIATION	DEVIATION (Percent)
				Observed	Calculated		
1	0.1595	.13	59	0.422	.416	+ .006	1.4
2	0.2586	.13	61	0.610	.616	- .006	1.0
3	0.4266	.13	48	0.950	.956	- .006	0.6
4	0.4392	.13	60	0.980	.981	- .001	0.1
5	0.6596	.13	48	1.432	1.427	+ .005	0.3
6	0.9980	.13	34	2.113	2.112	- .001	0.0
7	1.219	.13	20	2.561	2.559	+ .003	0.1
8	0.1595	0.9	52	0.420	0.416	+ .004	
9	0.4061	2.1	32	0.933	0.914	+ .019	
10	1.217	2.1	31	2.57	2.555	+ .016	

TABLE 2

Calibration of Liquid Helium Calorimeter with Further Radiation Shielding

WATTS x 10^6	ΔP mm of Hg	LENGTH OF OBSERVATION (minutes)	RATE OF He GAS FORMATION (arbitrary units)
0.0928	3.2	44	0.216
0.0928	2.0	45	0.218
0.4704	1.2	65	0.982

rates of heat evolution. Thus the maximum spread in the background values which have been measured is about $\pm 2 \times 10^{-5}$ cal/hr. Taking this spread as the uncertainty, heat inputs of 2×10^{-8} cal/hr or 5×10^{-7} cal/sec can be determined to within 1% in a very short period.

RADIATION CHEMISTRY

RADIATION CHEMISTRY - GENERAL

J. W. Boyle, J. A. Ghormley, C. J. Hochanadel,

D. M. Richardson and E. H. Taylor

The Van de Graaff generator began to operate satisfactorily about the middle of September, producing ~ 2 Mev electrons at currents up to 300 micro amperes. When the machine is operating properly, the voltage and current are stable to about 1%. Most of the quarter was spent in setting up apparatus for use in radiation chemistry studies in the new laboratory of the Van de Graaff building. Initial experiments have been performed using the X-ray beam from the machine.

In addition to the Van de Graaff machine, it is planned to use Co^{60} as a source of gamma rays in radiation chemistry studies. This will provide a dependable and constant source of fairly high intensity gamma radiation of known energy. The design for a lead shield to house ~ 300 curies of cobalt, with facilities for exposing a wide variety of samples, has been completed. The source should be ready for use within two months.

DECOMPOSITION OF AQUEOUS SOLUTIONS OF FISSIONABLE MATERIALS

J. W. Boyle

A satisfactory run was made in the pile with the high pressure bomb mentioned in the last quarterly report[1], checking quite closely work done in capillary tubes by E. Shapiro several years ago and showing both methods to be feasible and practical.

A type #309 stainless steel bomb 1 in. ID × 2 in. long with 3/8 in. walls was connected to a P10-5MG-350 Statham transducer with a ¼ in. tapered pipe thread joint previously tinned with 75-25 solder, the total assembly having a volume of about 29.3 cc. 11.6 cc of 0.028 *M* UO_2SO_4 (enrichment 83.5% in U^{235}) was placed in a quartz liner and the bomb sealed at atmospheric pressure with a screw cap against three 5 mil metal diaphragms giving a leakless seal up to about 3000 pounds per sq. in. The sample was irradiated in hole #12 for 5 days at 65° C, receiving a total pile irradiation of 409 MWH and giving rise to a pressure of 1535 pounds/in^2 at the time of removal. The temperature and pressure were recorded continuously during this time.

Figure 22 gives the plot of megawatt hours versus pressure, each point on the curve being taken from the pressure recording at the time of pile power change. This means that the pile power was constant between points on the curve. At about 253 MWH, the pile was shut down for 1 hour at which time extra gas was liberated, giving the break in the otherwise smooth curve. The reason for this is not understood.

Also plotted on this graph are three points from Shapiro's data. These points were obtained by taking the total gas in his ampoules and calculating the pressure by assuming conditions similar to the present experiment. The corrections and assumptions consisted of the following: (1) A liquid phase—gas phase ratio of 11.6/12.6 as in the present experiment was assumed; (2) A temperature correction from 102° C to 65° C was made on the gas present; (3) A correction factor 5.5/3.92 for uranium 235 concentration was made. (It is assumed that essentially all the gas production is due to the fission process taking place in solution. Thus, the gas production will be directly proportional to the number of U^{235} atoms present.); (4) A decrease of 37% due to the slow neutron absorption in the walls of the bomb was applied. This value was calculated from the well known relationship $I = I_0 e^{-\Sigma X}$[2]. In this equation I_0 and I are the incident and emergent neutron intensity. Σ is the absorption

(1) ORNL 286.

(2) The Science and Engineering of Nuclear Power, Addison Wesley Press, p. 14-15.

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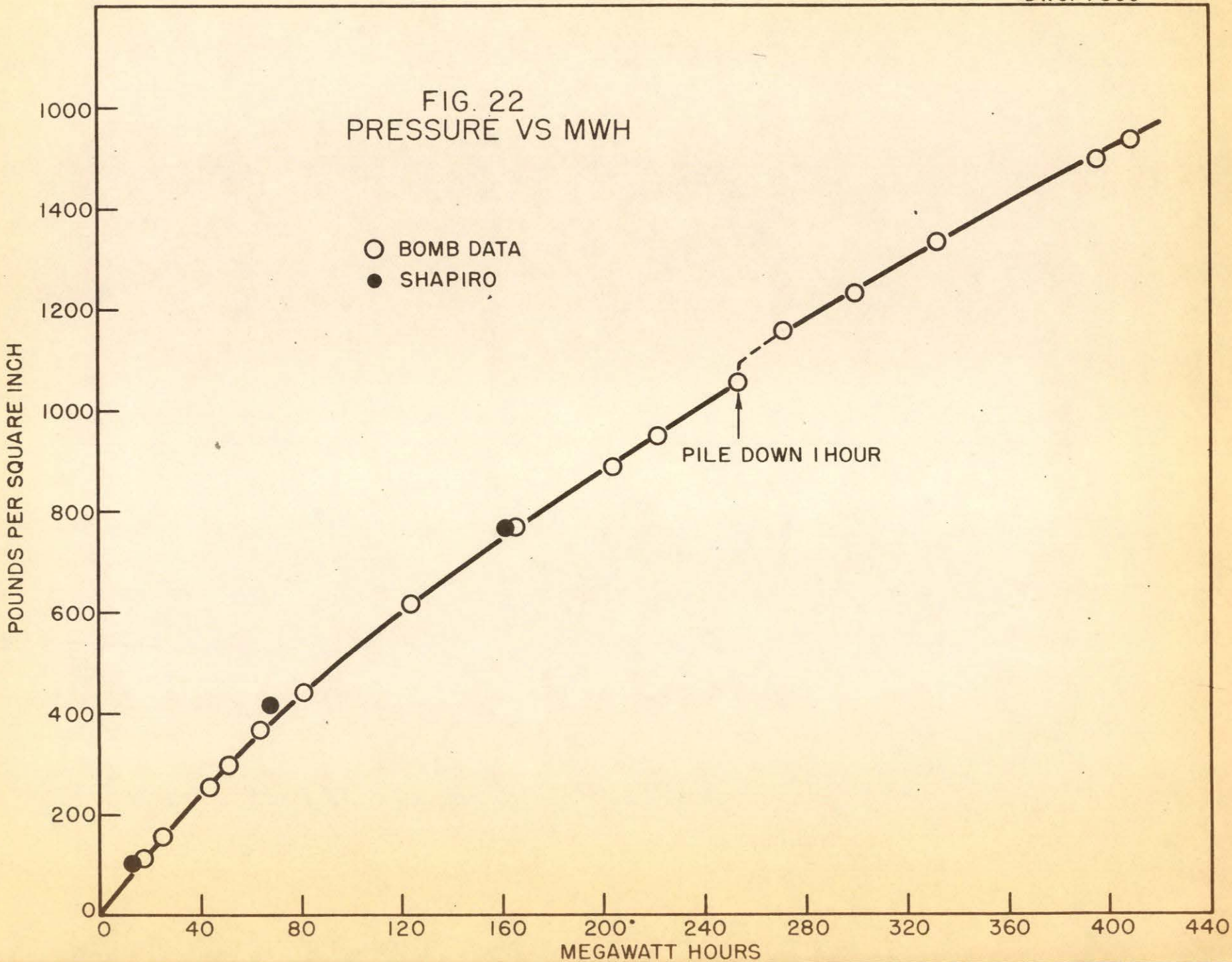

cross section per cc of material which is equal to the sum of the macroscopic absorption cross sections $\alpha_a N$ of the component elements making up #309 stainless steel. The scattering cross sections α_s are neglected as it is assumed that on the average the number of neutrons scattered out of the sample will be equal to the number scattered into the sample and vice versa. Thus $\Sigma = \alpha_1 N_1 + \alpha_2 N_2 - - - - \alpha_n N_n$ where α_1, $\alpha_2 - - - \alpha_n$ are the microscopic absorption cross sections of the elements present and N_1, $N_2 - - - - N_n$ are the respective number of atoms of these same elements present in one cc of #309 stainless steel. X is the equivalent thickness (cm) of the bomb. For the actual calculation of I, the bomb was assumed to be a cylinder of 1¾ in. OD × 2¾ in. long with 3/8 in. wall thickness, and the neutrons were assumed to be going uniformly in all directions. I, then, is a rough integration over all angles of the incident neutrons and not a true mathematical integration.

It is seen that the agreement is very good considering the wide differences in the two methods. This close agreement indicates several things which will have to be checked. First, it appears that the gas production is altered very little by the addition of 0.7 N free H_2SO_4 as this experiment has no free acid whereas Shapiro's tubes had 0.7 N free H_2SO_4 present. Second, the effect on rate of pressure build-up of the increased temperature of Shapiro's tubes of 102° C instead of 65° is negligible. Third, pressure has very little or no effect on the back reaction, since in Shapiro's tubes of the greatest radiation dose, pressure of 8600 lbs per sq in. was obtained. The greatest radiation dose on any of Shapiro's ampoules was 160.6 MWH. However, he obtained very high pressures due to the large liquid phase—gas phase ratio present in his ampoules. If the pressure had any appreciable effect, one would expect his last point to be low with respect to the curve.

Upon consideration of the above data, it seems reasonable to expect that the pressure in the bomb would build up to as high a value as obtained in the capillary tubes if left in the pile long enough. As the capillary tubes were still increasing in pressure even at 8600 lbs/in^2 one would expect similar bomb pressures to result before equilibrium would be reached.

As was expected, all the uranium precipitated as hydrated UO_4 during the radiation of the bomb. The precipitate was canary yellow and the supernatant was water white. The precipitate was analyzed in a vacuum line using a gasometric method as worked out in detail by Leininger, Hunt and Koshland[3] and shown to UO_4. Upon heating UO_4 in a closed system to above 820° C for 75 minutes and allowing to cool, UO_4 is converted quantitatively to U_3O_8.

(3) CN 3424.

$$3UO_4 (820^\circ\ C/75\ min)\ U_3O_8 + 2O_2$$

The O_2 obtained was 1% lower than the calculated amount from the above reaction. The accuracy of the analysis was estimated to be within about 1%. There was also a few per cent of acid gas measured which was not identified.

A spot test was made for $SO_3^=$ in the supernatant by the auto-oxidation of $Ni(OH)_2$[4] with benzidine as indicator. A negative test resulted.

The *p*H of the supernatant was measured with a Beckman *p*H meter and found to be 1.46. This is very close to the calculated *p*H, assuming all the SO_4 was liberated as H_2SO_4 when the UO_4 precipitated.

The precipitation of UO_4 can be prevented by the addition of a small amount of free H_2SO_4 as shown by Shapiro's work.

(4) Qualitative Analysis by Spot Tests, 3rd Edition, F. Feigl, p. 233.

STORED ENERGY FROM IONIZING RADIATION IN IONIC CRYSTALS

J. A. Ghormley (with H. A. Levy)

INTRODUCTION AND PROSPECTIVE PROGRAM

This work was started with the objective of obtaining information about the amount and nature of energy that may be stored as physical or chemical changes within ionic solids subjected to ionizing radiation. Four types of measurement have been considered: heat of solution, chemical analysis of products after dissolving, thermoluminescence, and specific heat. Preliminary experiments on the first three are reported here.

The stored energy in irradiated crystals at room temperature can be determined by measuring the heat of solution and comparing this with the heat of solution of similar unirradiated crystals. A chemical analysis of the solution and any gas evolved on dissolving would also be necessary. Stored energy (or loss of energy) involved in the chemical changes could then be calculated from the heats of formation of the products.

A direct method for measuring stored energy released below room temperature would be to irradiate at a low temperature, then measure the heat required to bring the sample to room temperature. The same sample could be cooled again with no irradiation and the specific heat measurements repeated. The heat input required to bring the sample to room temperature after irradiation would be less than that with no irradiation and the specific heat measurements repeated. The heat input required to bring the sample to room temperature after irradiation would be less than that with no irradiation by an amount equal to the stored energy released. In addition, the rate of release of stored energy as a function of temperature would permit calculation of activation energies for rate determining steps in the processes for release of the energy.

Another type of investigation which should yield information about the quantity of stored energy as well as the mechanism for its storage and release is the study of thermoluminescence. This field has received considerable attention in recent years in connection with investigations of phosphors, and has been applied to "pure" solids particularly by Kats[5] in his study of

(5) Kats, M. L., Zhur. Eksptl. Teoret. Fiz. 18, 501 (1948).

thermoluminescence of NaCl, KCl, and KBr exposed to X rays at liquid air temperatures. It would be of interest to determine the relationship between the various color centers produced in alkali halides, the nature of which appear to be fairly well known[6], and peaks in the glow curves (thermoluminescence intensity *vs* temperature at constant rate of temperature increase). It is hoped to start measurements soon on absorption spectra after each peak in the glow curve for a number of alkali halides irradiated with X rays at temperatures down to about 4° K. We hope it will be possible to determine by change in absorption spectra and the amount and spectral distribution of thermoluminescence in a given temperature range not only the activation energy required to initiate release of stored energy but also the magnitude of the stored energy. Apparatus is being designed for measurement of emission spectra of thermoluminescence in the ultraviolet by means of an electron multiplier phototube at liquid nitrogen temperature and a Beckman spectrophotometer.

HEAT OF SOLUTION MEASUREMENTS ON PILE-IRRADIATED BARIUM NITRATE

Experimental. Reagent grade barium nitrate was sealed into a silica tube and placed in hole 12 of the pile for 9 days at 30° C. An adiabatic twin calorimeter was tried first for heat of solution measurements, but was unsatisfactory because the irradiated salt in one Dewar dissolved faster than the unirradiated salt in the other. In the single isothermal calorimeter finally used, 1.8057 g of barium nitrate contained in a platinum gauze basket was dissolved in 50 ml of water in a 200 ml Dewar. Stirring was accomplished by moving the basket up and down at a rate of 100 strokes per minute and amplitude of 15 mm. Temperature was measured by a 10 junction thermopile with the reference junction in another Dewar of water at the same temperature as the constant temperature batch, 30° C. As the salt dissolved, heat was supplied to the solution by a resistance heater to maintain its temperature constant. The heater was turned on and off manually about 20 times during the dissolving of each sample, and the total heating time was measured by means of two electric stop clocks connected with the heater switch. For each time the clocks were turned on and off, a correction of 0.03 and 0.06 seconds respectively for the two clocks had to be added to obtain the correct total time. Heater current was recorded with a Speedomax recorder and remained constant during each run. Total time required for dissolving a sample was about 30 minutes, and the temperature was followed for an additional 90 minutes to find the correction for heat leakage and heat supplied by the stirrer.

(6) Seitz, F., Rev. Mod. Phys. 18, 384 (1946).

Results and Discussions. Heats of solution per mole of unirradiated $Ba(NO_3)_2$ in four determinations were -8801, -8735, -8809, and -8830 cal.; for the irradiated salt, the values -8568, -8587 and -8593 were obtained. The average values are -8794 and -8583 respectively, and their difference is 211 cal. This value does not directly give the energy stored during irradiation, however, since the solutions resulting from dissolving the unirradiated and irradiated salts are chemically different. Thus a permanganate titration of one solution from a calorimeter run on irradiated salt indicated that 3.0% of the nitrate had been converted to nitrite. Previous studies[7] of $Ba(NO_3)_2$ under electron bombardment have shown that a quantity of O_2 gas roughly equivalent to the nitrite formed is liberated when the irradiated salt is dissolved, together with a much smaller amount of H_2, and that the solution is slightly alkaline. For the purpose of calculating the stored energy, we here assume that 0.015 mole of O_2 was evolved on solution for each mole $Ba(NO_3)_2$ irradiated, ignoring the contribution of H_2 and other minor products. We must then add to the observed 211 cal, the difference in heats of formation of 0.03 mole $Ba(NO_3)_2$ (aq) and 0.03 mole $Ba(NO_2)_2$ (aq) + 0.015 mole O_2(g), namely 1.450 kcal, to yield the total stored energy, 1.661 kcal per mole of $Ba(NO_3)_2$.

We will now discuss briefly the evidence bearing on the manner in which this energy is stored in the irradiated crystal. If the chemical products found on electron bombardment are assumed to be representative of the present experiments, it is clear that the major reaction taking place must be the conversion of nitrate ion to nitrite and oxygen. The energy accounted for by this change may be estimated from heat of formation data to be 1.485 kcal, which value should be corrected by a presumably small contribution representing the heat of mixed crystal formation. Further, it appears that the oxygen must appear in the crystal as largely molecular rather than atomic oxygen, for the stored energy involved in 0.03 mole atomic oxygen would be of the order of 3.55 kcal, much greater than the 176 cal. left unaccounted for by nitrite formation. This consideration sets an upper limit of ~5% to the fraction of atomic oxygen present.

The presence of H_2 and OH^- in the products of the electron-bombarded material[7] suggests that some of the remaining stored energy may be associated with neutral Ba atoms, or more likely singly positive Ba^+ ions. An equivalent quantity of electron deficient species would have to be formed simultaneously, and this latter would have to dissolve without yielding acid. Neutral NO_3, giving gaseous NO and O_2, for example, would behave in this way.

(7) Allen, A. O. and J. A. Ghormley, J. Chem. Phys. 15, 208 (1947).

The total stored energy, 1.66 kcal/mole, is doubtless a very small fraction of the total energy absorbed from the ionizing radiation. Thus the electron studies[7] showed that about 5.2×10^3 kcal was required to produce 0.03 mole $Ba(NO_2)_2$ from $Ba(NO_3)_2$; if a similar figure applies to pile-bombardment, the fraction of energy absorbed and not released as heat or light soon after the end of bombardment is ~0.03%.

A measurement of the heat of solution of the irradiated salt after annealing at 300° C for one hour gave 8571 cal, and after similar treatment the heat of solution of unirradiated salt was -8836 cal. In neither case was any significant change observed in the heat of solution. The irradiated salt consisted of transparent yellow crystals when removed from the pile, but after heating to 300°, the crystals were white and opaque. This color change appears to be the same as that observed by Lees[8] for sodium nitrate.

THERMOLUMINESCENCE OF IRRADIATED ALKALI HALIDES

In some preliminary measurements of the thermoluminescence single crystals of LiF, KCl, NACl and KBr were exposed to X rays from the Van de Graaff generator and glow curves were recorded by means of a 1P21 photomultiplier connected with a vacuum-tube voltmeter and recorder. Tin-foil wrapped samples were irradiated in a Dewar of liquid nitrogen, then, after removal of the foil, were transferred to the top of a copper block in an unsilvered pyrex Dewar. Imbedded in the copper block were a resistance heater and a thermocouple junction. No attempt was made to adjust the rate of heating to give a constant rate of temperature increase.

Figure 23 shows thermoluminescence of a crystal of lithium fluoride after 45 minutes exposure to X rays. The peak appearing at 1370° K is about a hundred times higher than most other peaks observed, and may result from the release of "self-trapped" electrons. According to calculations by Markham and Seitz[9] such traps in lithium fluoride would be stable at liquid nitrogen temperature. It is possible that nearly every electron getting into the conduction band at this temperature would become "self-trapped"; hence it is conceivable that as much as half of the energy absorbed from ionizing radiations in lithium fluoride at liquid nitrogen temperature would be released only at higher temperatures.

Lithium fluoride crystals irradiated at liquid nitrogen temperature for two minutes in the pile were pale yellow while still at liquid nitrogen temperature and then turned blue-green during light emission on warming to room

(8) Lees, R. B., ANL 4288, Section 2.6.

(9) Markham, J. J., and F. Seitz, Phys. Rev. 74, 1014 (1948).

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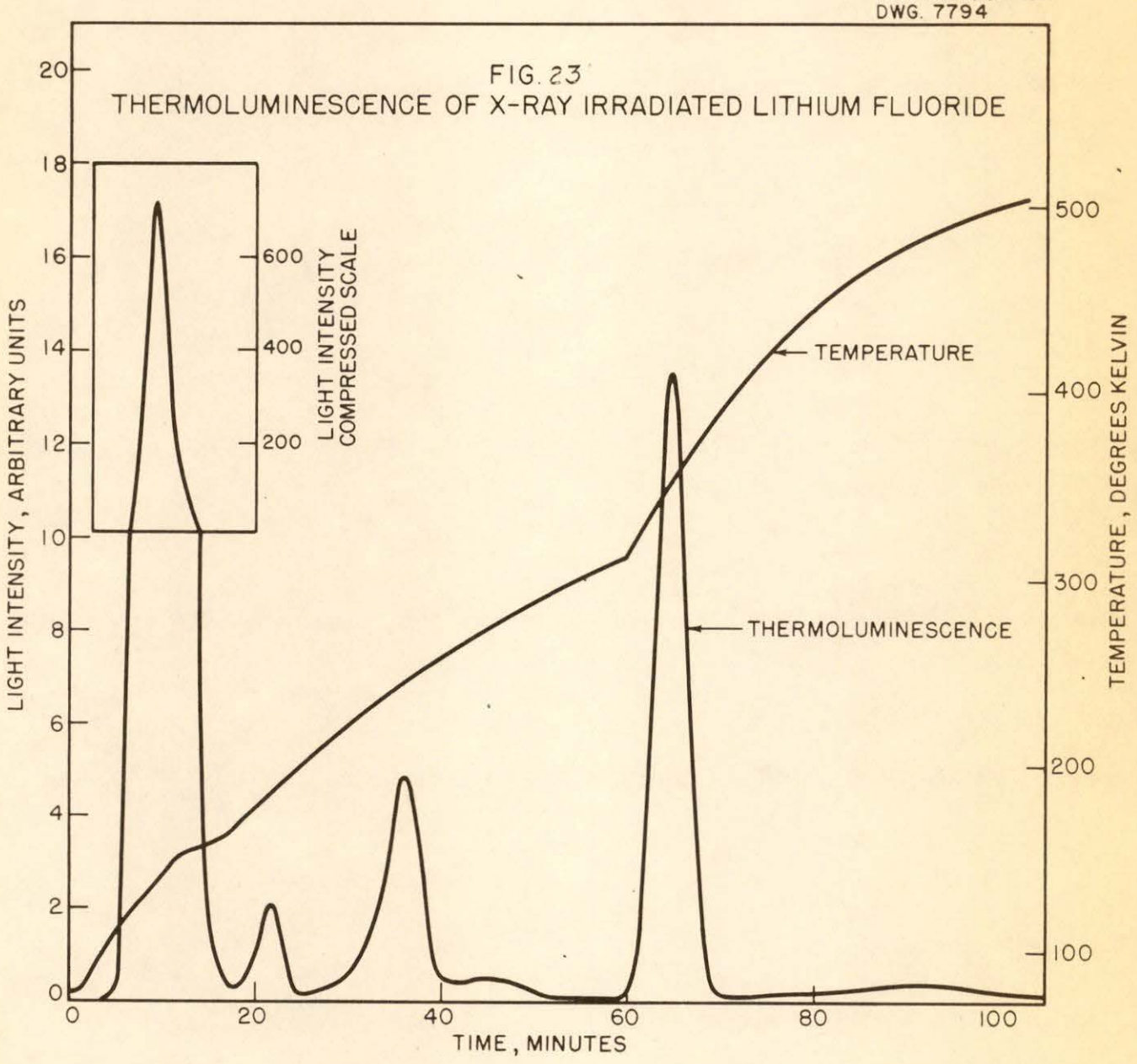
FIG. 23
THERMOLUMINESCENCE OF X-RAY IRRADIATED LITHIUM FLUORIDE



temperature. The crystals were yellow again after a few hours at room temperature. Similar color changes in electron irradiated lithium fluoride have been reported by Casler and Pringsheim[10] who observed that the blue-green color was produced by an absorption band that disappeared in a few hours at room temperature. The stability of this absorption band appears to be the same as that of the centers resulting in the glow curve peak at just above room temperature. The appearance of the blue color may be associated with the glow curve peak at 137° K. The need for measuring absorption spectra at low temperatures is indicated.

Change in the glow curve of potassium chloride by exposure to visible light has been reported by Kats and Andryanov[11]. Our measurements of thermoluminescence of sodium chloride before and after long exposure to room light is shown in Fig. 24. The peaks at 159° K and 230° K were completely eliminated by two hours exposure to room light while in a Dewar of liquid nitrogen, but the peak at 500° K remained unchanged. In the crystal exposed to room light for only about one minute, luminescence was observed while the sample was still surrounded by liquid nitrogen. This luminescence is attributed to centers, which would give rise to a peak in the glow curve below liquid nitrogen temperatures.

Crystals of potassium chloride and potassium bromide gave glow curve peaks similar in magnitude to those observed for sodium chloride. Sodium nitrate under similar conditions gave no measurable thermoluminescence.

During one X-ray irradiation, crystals were supported in the Dewar of liquid nitrogen by a wad of cheesecloth which was found to be light blue after irradiation. Thermoluminescence was observed during warming to room temperature and the cheesecloth became colorless. The same phenomenon was observed with bleached cotton.

(10) Casler, R., and P. Pringsheim, ANL 4288, Section 2.7.

(11) Kats, M. L., and A. S. Andryanov, Doklady, Akad. Nauk. S.S.S.R. 61, 817 (1949).

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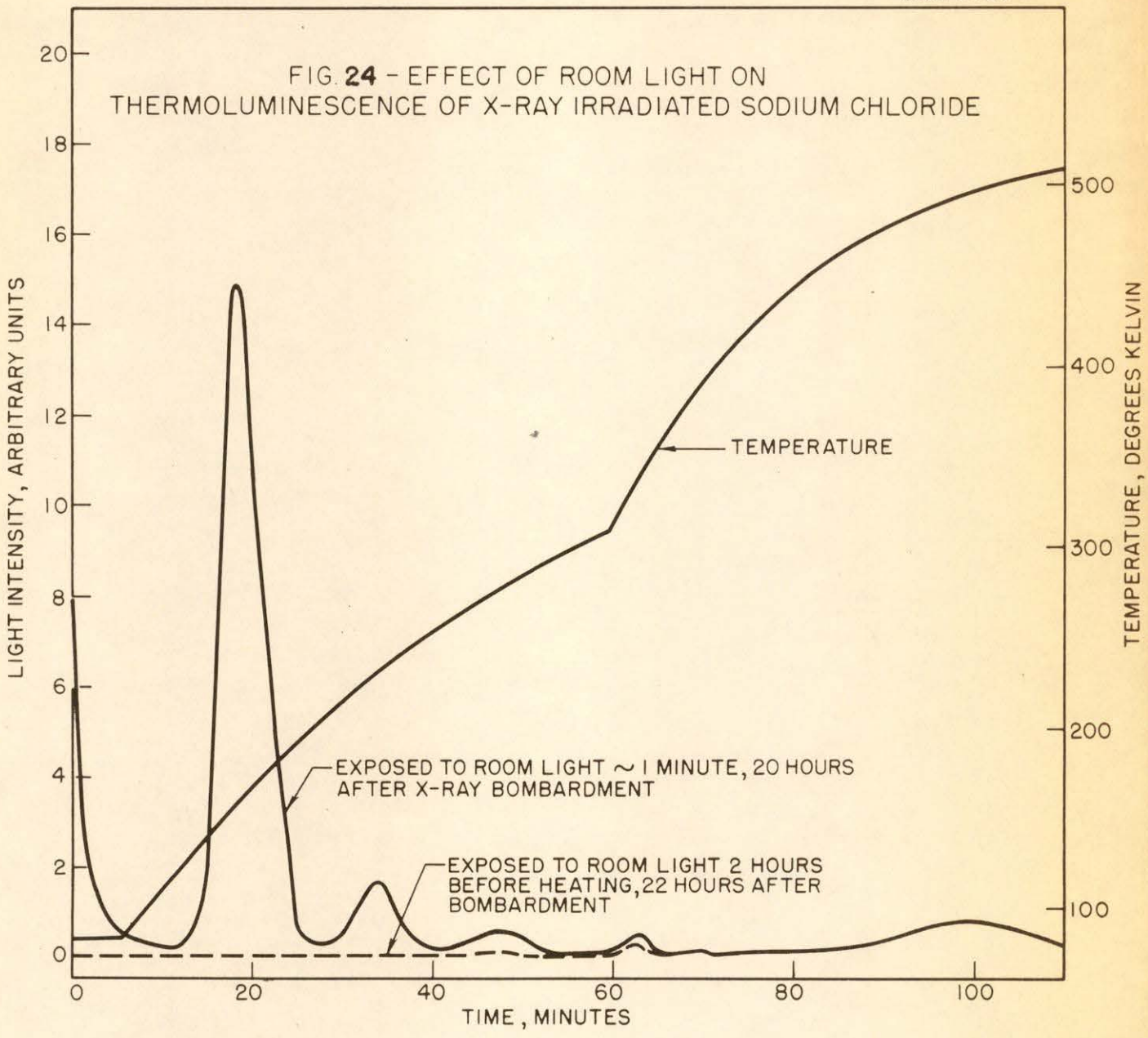
FIG. 24 - EFFECT OF ROOM LIGHT ON THERMOLUMINESCENCE OF X-RAY IRRADIATED SODIUM CHLORIDE



PHYSICAL MEASUREMENTS AND INSTRUMENTATION

OPTICAL AND ELECTRON MICROSCROPY

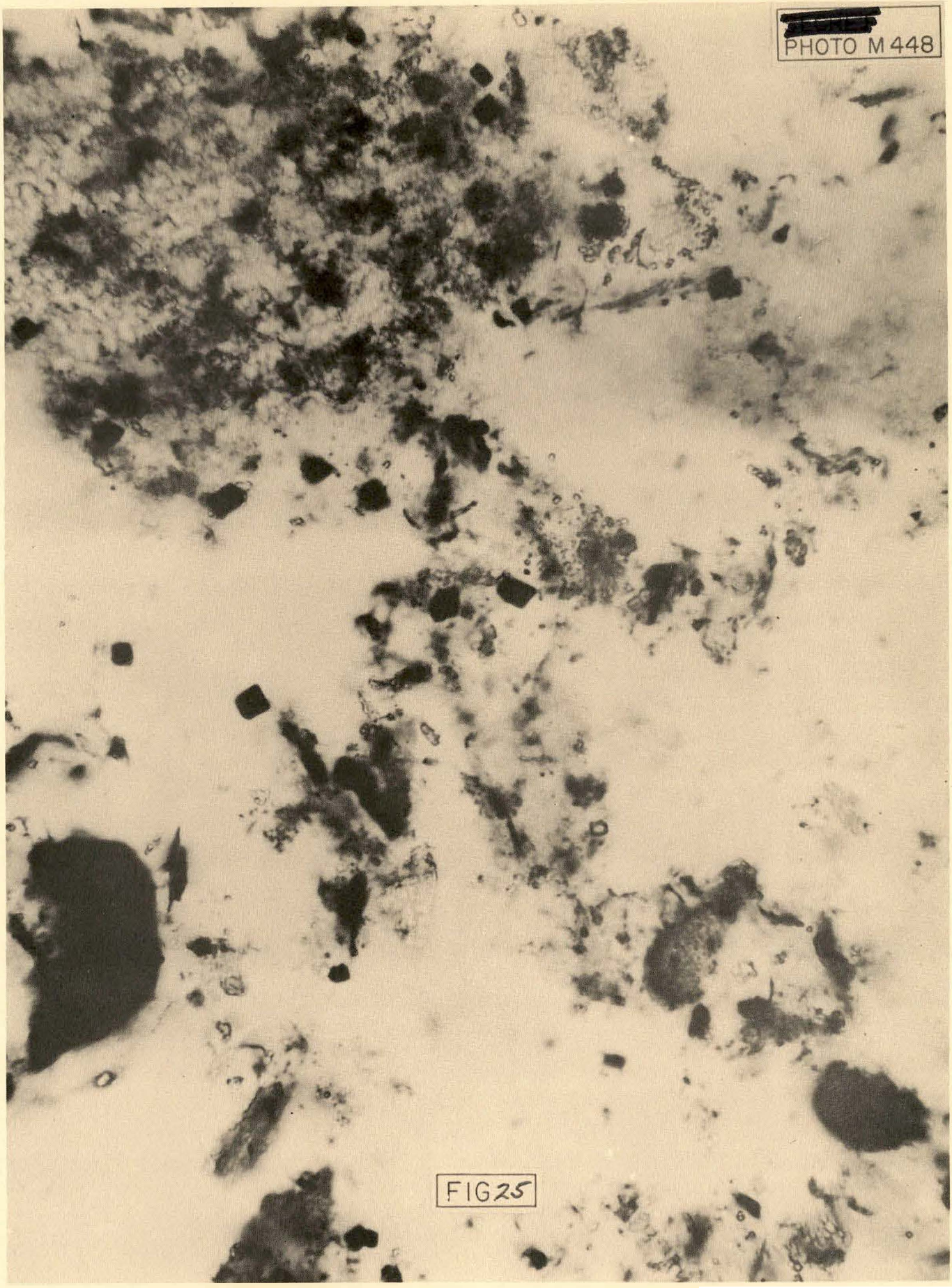
T. E. Willmarth, F. D. McNeer, B. I. Gary

In addition to the usual co-operative work on a variety of problems, best reported as a part of those problems, the following observations on beryllium appear to be of some independent interest.

Microstructure of Beryllium. Continuing the work on the miscrostructure of beryllium reported in CF 49-3-207, a microscopic study has been made of the residue remaining after the volatilization of a sample of beryllium with hydrogen chloride gas at a temperature of 600° C according to the procedure set up by the National Bureau of Standards for the quantitative analysis of beryllium metal and oxide (Report No. A 2949 NBS-C-100). The beryllium sample used was a segment of a bar that had been found to contain a high percentage of beryllium oxide and beryllium carbide by X-ray and metallographic examination. It was assumed that a better determination of the form and size range of impurities appearing as inclusions in the beryllium metal could be made from the residue of a whole piece of metal rather than from the examination of a single plane made previously with the metallograph.

The material in the residue was dispersed and examined at medium and high power with the optical microscope. Dispersions were also made and observed with the electron microscope. Two crystal forms and an amorphous appearing material were noted (Fig. 25).

One type of crystal was off-white in color, translucent, and rod-like in shape when lying in a horizontal position, and roughly hexagonal when on end. Twinning was frequently observed. These crystals had the same form as those previously identified as beryllium oxide by X-ray and optical examination. The size range as measured, 3 to 8 microns in length, ½ to 3 microns in diameter, agrees with the previously reported measurements. The other type of crystal present appeared to be dark grey, opaque, and apparently cubic in form. These crystallites resembled those previously identified as beryllium carbide in the metallographic examination. They were fairly uniform in shape and size with a range of 4 to 12 microns, but the bulk of the material was between 9 and 12 microns. The remaining material in the residue appeared amorphous with the



optical microscope. Electron micrographs showed the material to be in the form of very thin films, probably representing oxide from exposed surfaces of the sample.

If carbon is present in the residue in the combined form, Be_2C, as apparently it is from the observations made thus far, the ignition of the residue at 1200° C in the National Bureau of Standards procedure, which follows the volatilization of the beryllium metal, would fail to eliminate or convert the carbon present. Therefore, the percentage of BeO determined in this way would be in error.

Further work is contemplated on this problem in collaboration wm th W. Wolkowitz.

INSTRUMENTS FOR DETECTION OF RADIATIONS

PROPORTIONAL COUNTER SPECTROMETER

C. J. Borkowski

The use of a proportional counter with high gas amplification for the determination of beta and X-ray energies below 200 Kev was first suggested by the author in MonN 311, March, 1947. Since that time the work of Curran *et al* and Kirkwood *et al* has shown that the method gives good resolution for X rays and correct end points for the maximum energy of beta spectra.

Using a proportional counter with a beryllium side window and filled to a pressure of two atmospheres with 90% argon and 10% methane, X-ray photo-electron peaks have been obtained with a half-width of 17% at 6.87 Kev-(Co X ray). Figure 26 shows a typical peak produced by X rays from Ni^{59} which decays by K-capture. A second small peak is observed at about 4 Kev and is due to the fact that the fluorescent yield in argon is about 7% which means that in 7% of the interactions the total energy dissipated by the electrons will be 3 Kev lower due to the escape of the argon K X ray. In 93% of the interactions the 3 Kev argon X ray is internally converted producing auger electrons and thus the total energy of the incident X ray (6.87 Kev in this case) is expended in producing ions in the gas.

The resolution at 7 Kev is sufficiently good to resolve the K X rays of adjoining elements in this part of the periodic table. Figure 27 shows the photo-electron peaks produced by X rays from Fe^{55} Mn X ray) Ni^{59} (Co X ray) Zn^{65} (Cu X ray).

Figure 28 shows the cobalt X rays from Ni^{59} and the nickel X rays produced by the bombardment of the soft beta (60 Kev max) from Ni^{63} on the nickel salt present in the sample. The latter sample contained several million dis/min of Ni^{63}. The broad peak *C* is a sample containing both Ni^{59} and Ni^{63}. The relative amounts of Co X rays and Ni X rays can be estimated in this broad peak.

The photo-electron peaks produced by X rays from various elements serve as energy calibration points for the proportional counter spectrometer.

A large proportional counter 4 inches in diameter and 12 inches long having a 50% geometry for solid samples has been designed to obtain the beta spectra

FIG 26

X-RAY PEAKS FROM Ni^{59}

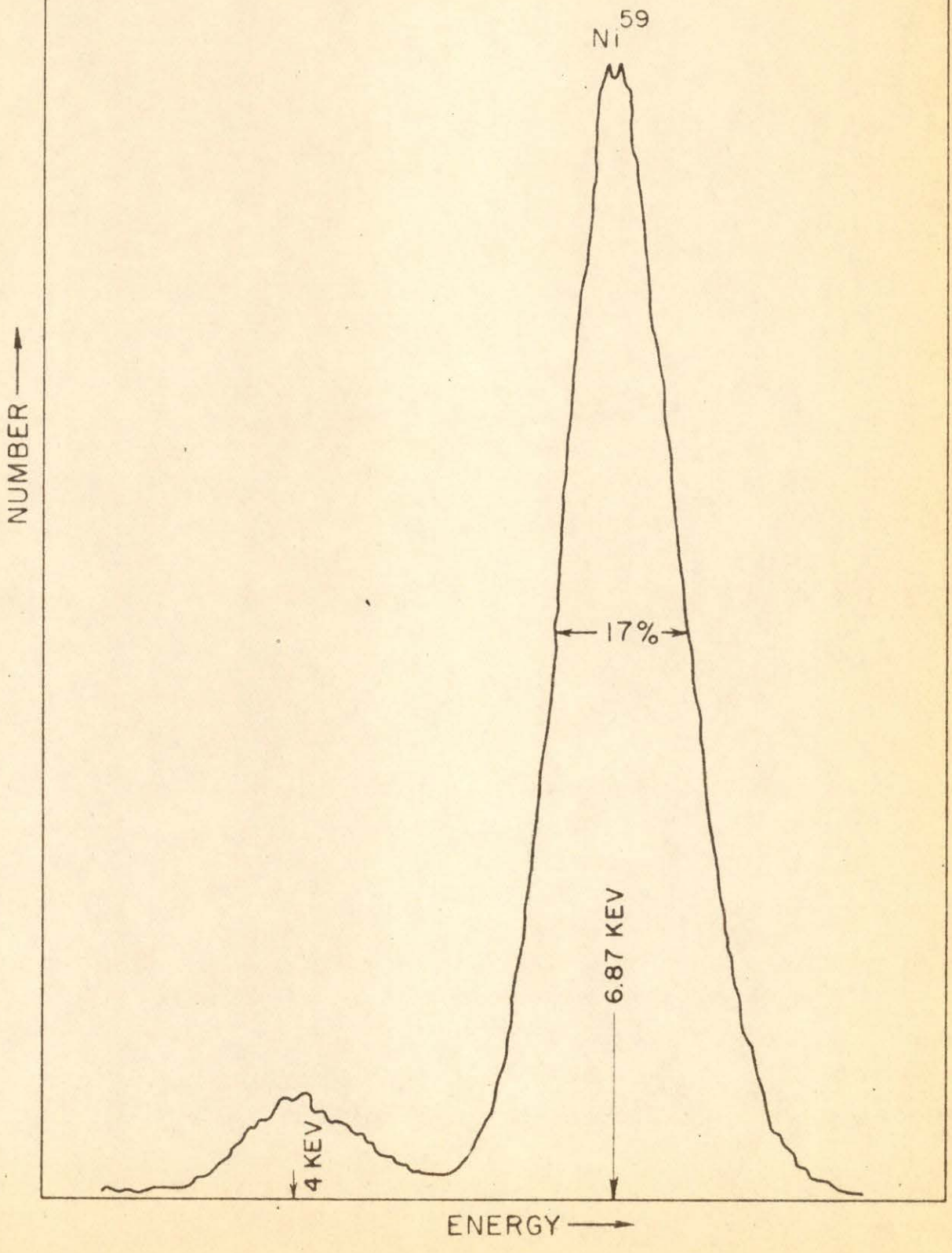


FIG. 27

X-RAY PEAKS FROM Ni^{59}, Fe^{55}, Zn^{65}

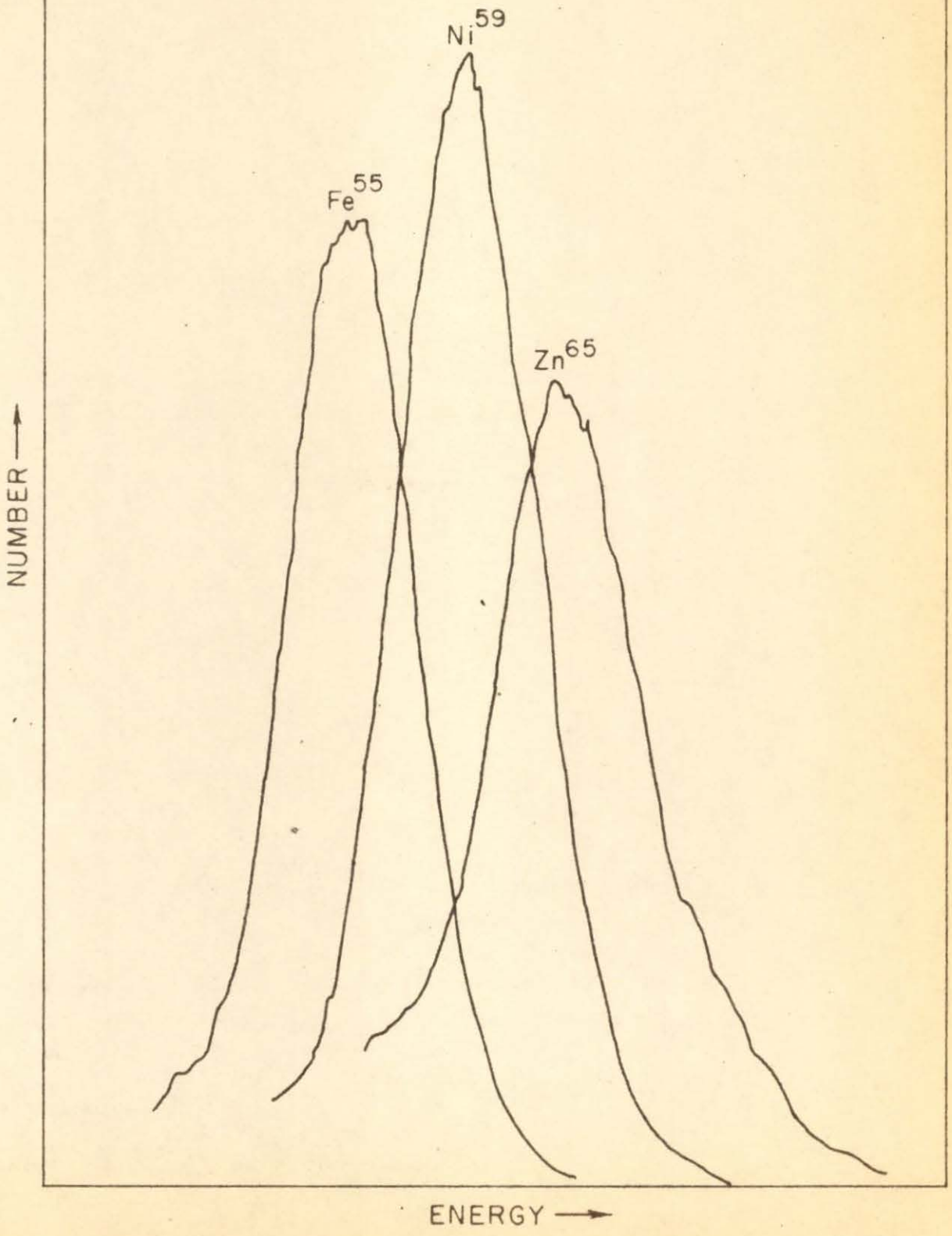
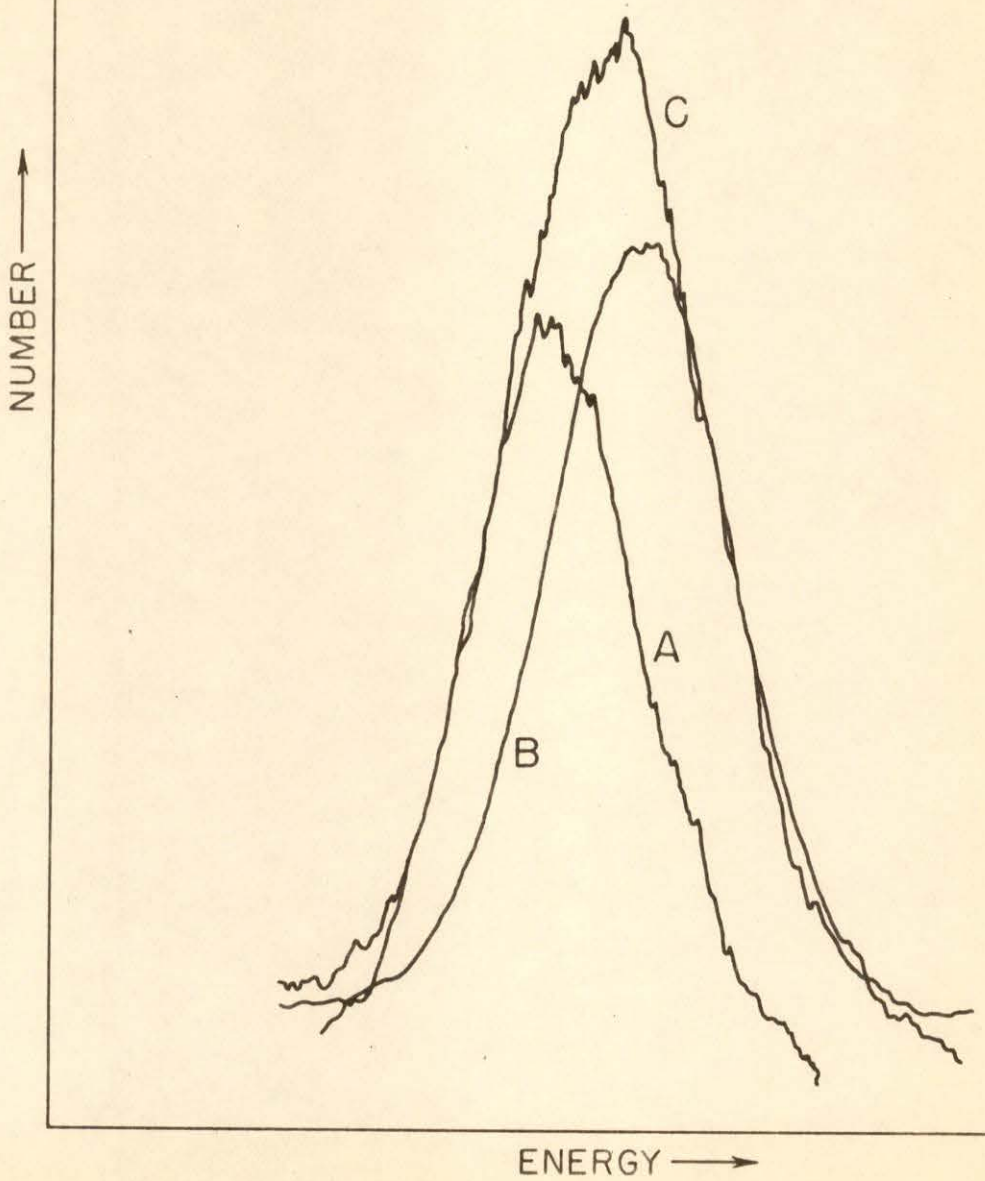


FIG. 28
X-RAY PEAKS

A Co K – X-RAY
B Ni K – X-RAY
C MIXTURE OF Co AND Ni X-RAYS



for energies below 200 Kev. The beta spectra of Tm^{171} has been obtained on a solid sample of this nucleide. Figure 29 shows the Kurie plot for this activity. The end point at 100 Kev as obtained with the proportional counter spectrometer agrees within 2% with the end point obtained on the same activity using the magnetic lens beta ray spectrometer. The Kurie plots also were in close agreement.

In order to evaluate the resolution of the proportional counter spectrometer for solid samples of beta emitters a U^{233} alpha source was run both in the proportional counter at a gas amplification of 10 and in a pulse ion chamber employing a Frisch Grid. Figure 30 shows that the resolution obtained with the proportional counter was as good as that obtained with the Frisch Grid chamber. A half-width of 2.5% was obtained on both instruments. The spreading of the peak was due to the adsorption of the alpha particles in the sample since thin samples give about 1% half-width with the Frisch Grid chamber.

An interesting effect was observed when a differential curve was obtained on the background of the unshielded proportional counter spectrometer. A peak was obtained at about 8 Kev (Fig. 31). This represents a large number of background pulses in a narrow energy interval.

The explanation for this peak is as follows:

Since most of the local radiations are due to scattered gamma radiation they are on the average of relatively low energy. The gamma rays produce photo-electrons in the brass wall of the counter and only a few of these latter reach the sensitive volume of the counter due to their short range. In addition they will have a continuous energy distribution because they originate at various depths of the brass wall so that one should not observe a peak from this source. On the other hand X rays (Cu and Zn) which are produced in each photo-electron process have a greater range in brass than do the photo-electrons but what is more important they are monoenergetic and will be highly absorbed by the filling gas (argon 70 cm CH_4 7 cm) giving a photo-electric peak at about 8 Kev. This peak is absent when the chamber is well shielded with lead. Under these conditions the background is chiefly due to mesons which produce few if any "brass" X rays.

All of the differential curves were obtained with a sweep type differential discriminator designed by Mr. E. Fairstein and described in the following report. The differential curve is automatically plotted on a Brown Recorder and the figures shown are tracings taken from the Brown Chart.

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FIG. 29

KURIE PLOT FOR Tm^{171} PROPORTIONAL COUNTER SPECTROMETER

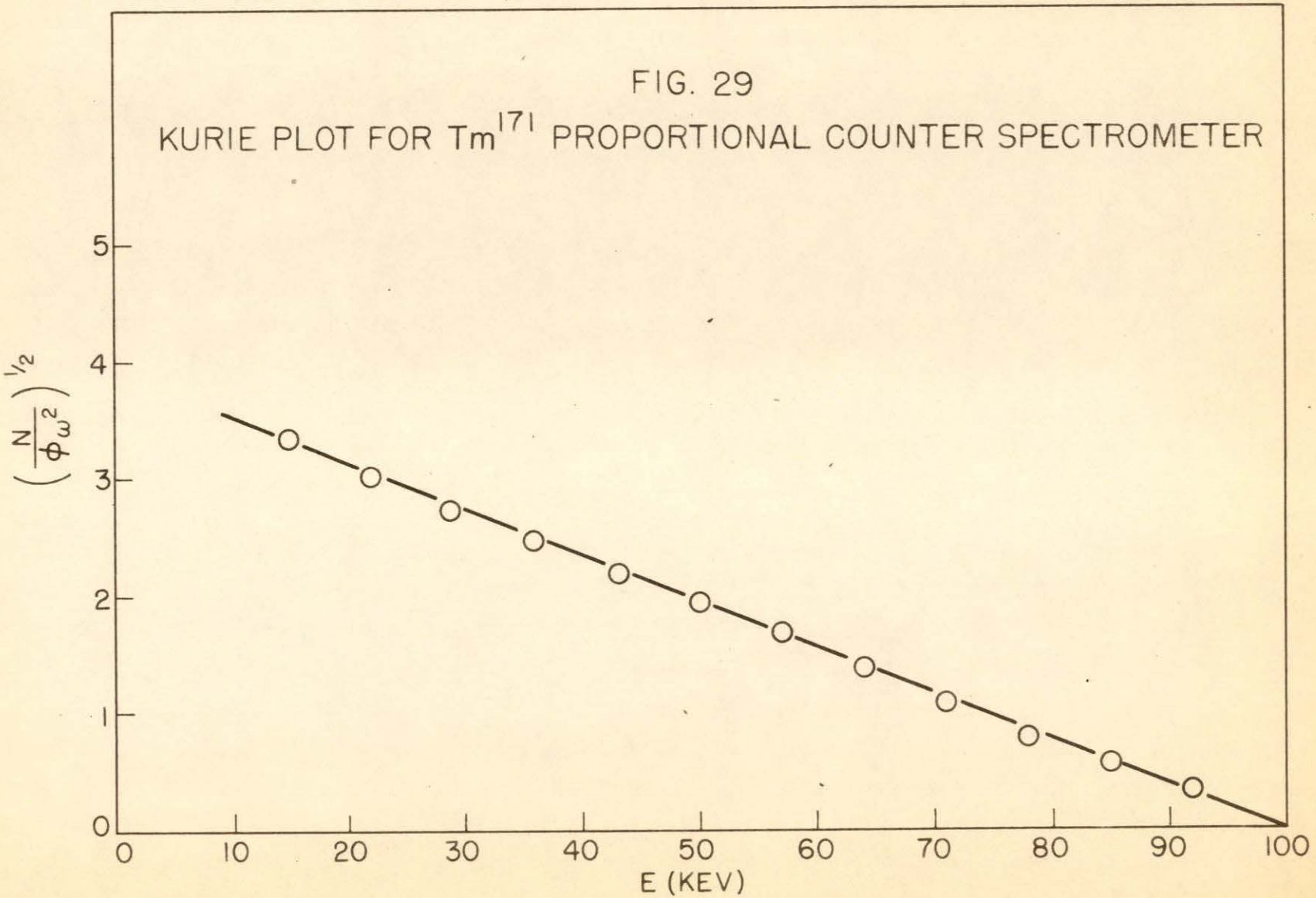

FIG. 30

U^{233} ALPHA SOURCE

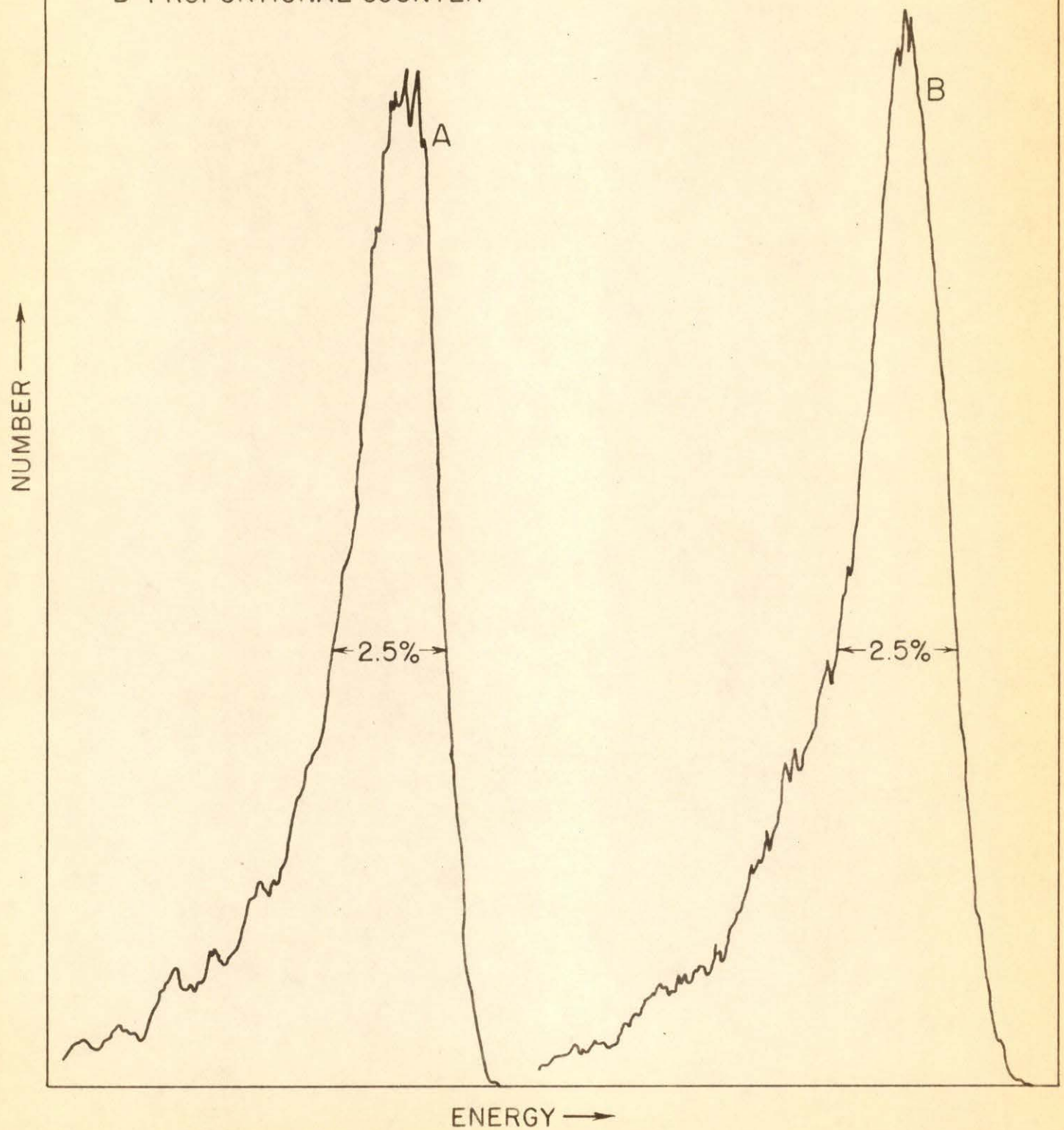

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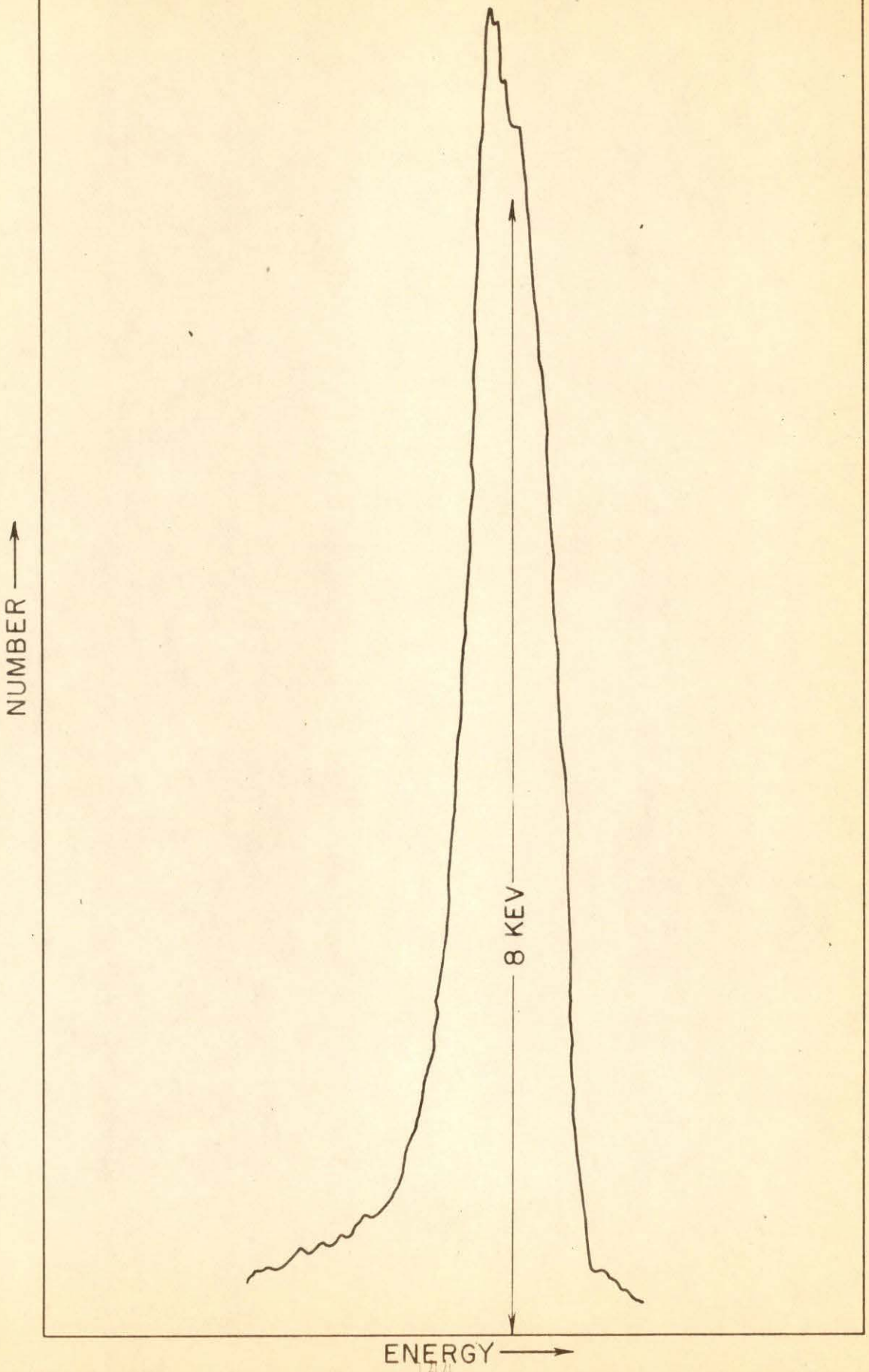
FIG. 31
DIFFERENTIAL CURVE FOR BACKGROUND PULSES
FROM UNSHIELDED PROPORTIONAL COUNTER



A DIFFERENTIAL AND INTEGRAL DISCRIMINATOR CIRCUIT

E. Fairstein

This report describes a differential-integral discriminator which will give the pulse height distribution obtained from the output of a fast, linear amplifier. When the amplifier signal is supplied from an appropriate radiation detector, the instrument combination may be used to obtain energy distribution curves.

Two instruments have been in use for some months with a proportional chamber (used for X-ray and beta energy measurements in the range of 0-200 Kev) and a parallel plate chamber (used for 1-8 Mev alpha measurements). They exhibit excellent stability and dependability of operation.

Since a complete report on the instrument will be available shortly, only the essential parts of the circuit will be discussed.

1. Requirements. The basic requirements for a differential discriminator are:

(a) All the pulses within a small voltage increment (hereafter called the "slit width") must be recorded and all those outside the slit width must be rejected.

(b) The height of the slit above some reference value must be adjustable and accurately known (on a relative basis).

(c) The slit width must be adjustable, and independent of its position above the datum.

The requirements for an integral discriminator are:

(a) All the pulses above a certain value must be recorded.

(b) This value must be adjustable and accurately known (on a relative basis).

2. Results. The requirements set forth above are met quite well in practice. It is possible to set both the recording threshold (pulse-height setting) and the slit-width to a fraction of one percent. The present instrument works properly on rise-times of 0.25 microsecond and greater, and has a fixed dead time of 6.0 microseconds. If necessary, the dead time can be reduced to less than two microseconds, and under these conditions is controlled by the driving amplifier rather than the discriminator. The slit width is constant to one or two percent over the complete range of pulse height adjustment, and is expected to be better than this in the new instruments which are being built.

The six microsecond dead time refers only to those pulses which are being recorded. When the instrument is used as a differential discriminator, the number of pulses within the slit width is rarely more than ten percent of the total number, resulting in an entirely adequate dead time for total counting rates up to 1,000,000 per minute.

The instrument in use now has 5693's (specially built 6SJ7's) and 6SL7's in the critical parts of the circuit. The 5693's were chosen because of their stability rather than speed, a consideration important for parallel plate alpha counting.

For beta counting, the reverse situation is in effect. Two instruments are now under construction which will use 6AK5's and 12AT7's in the critical parts of the circuit. It is expected that these instruments will operate properly on pulse rise times of 0.1 microsecond and total pulse widths of less than one microsecond.

3. *The Circuit.* T_1 through T_4 constitute a pair of Schmitt trigger pairs. T_3 is biased beyond plate current cut off by an amount equal to the pulse height setting. T_1 is biased beyond plate current cutoff by this amount, plus the slit width setting. The circuitry of T_5, T_6, and T_7 is such that only pulses large enough to trigger T_3-T_4 are transmitted to the scalar or ratemeter. Pulses large enough to trigger T_1-T_2 also, are prevented from reaching the ratemeter or scalar when the instrument is operated as a differential device.

T_7 is the anti-coincidence tube. T_{7a} is normally conducting, while T_{7b} is not. If T_{7b} receives a positive pulse, the situation is reversed. If both T_{7a} and T_{7b} receive a positive pulse, both grids move up, but because of the cathode coupling, T_{7b} remains in the non-conducting state.

When both input channels are triggered by a large pulse, for positive anticoincidence to occur, it is necessary that T_{7a} receives a signal before T_{7b}, and that it remains on until the signal at T_{7b} has dropped below the operating threshold. Because the pulse output from an amplifier has a finite rise and fall time, the signal at T_{7b} would normally be applied before that at T_{7a}, and would normally disappear after that at T_{7a}, just the reverse of the requirements. Evidently, it is necessary to delay the pulse to T_{7b} and stretch the pulse at T_{7a}.

The delay is accomplished by a lumped constant .25 microsecond delay line. The stretching is accomplished by T_{5a} and C.

T_{5a} is a cathode follower impedance transformer. T_{5b} is a clamp which is normally conducting, keeping C discharged. T_6 is a phase inverter and mixer.

As soon as the lower channel is triggered, T_{6b} receives a positive signal. Its output is sufficiently negative to bias T_{5b} beyond cutoff, opening the clamp. If the upper channel is now triggered, C can charge up in less than 0.1 microseconds. This voltage is applied to T_{7a} before the signal for T_{7b} can pass through the delay line.

When the signal disappears from the upper channel, C retains its charge because of the high impedance circuit it sees. Because of T_{6a}, the clamp is held open until 0.25 microsecond after the signal has disappeared from the lower channel. The clamp discharges C in less than .5 microsecond after it is applied.

This method for obtaining anti-coincidence operation has one undesirable characteristic; if a signal large enough to trigger both channels disappears from the lower channel in a time shorter than the delay line, it is possible to record this unwanted pulse. The simplest remedy is to make the voltage stored in C large enough and/or the clamp slow enough to keep the grid of T_{7a} above the operating threshold for a time greater than the delay time. This situation can be aided by holding the delay time to a value not greater than the rise time of the initiating pulse. Delay line differentiation rather than R-C differentiation in the main amplifier will make this palliative unnecessary.

In actual practice, application of the remedy suggested solved the problem sufficiently.

This consideration places an upper limit on the rise time and lower limit on the duration of pulses applied to the instrument. The range of the instrument can be extended by changing the delay line.

The instrument group in the Physics Department is now working on a circuit in which no signal is applied to the off-side of the anti-coincidence circuit until after the pulse has disappeared from the lower channel. This instrument will not have the limitations mentioned above, and will operate on any width pulse. However, the relative simplicity of the circuit described in this report will still make it a desirable one for fixed condition applications. The circuit is far simpler than the one described in Chapter 4, Volume 1 of report number LA 1002 by Elmore and Sands.

Integral discriminator operation is obtained by preventing the transmission of the upper channel signal through T_5.

The remainder of the circuit consists of a regulated power supply, an extremely flexible ratemeter circuit (with a 6 microsecond dead time), provisions for using a Brown Elektronik Recorder for obtaining spectra automatically, positive and negative output terminals for scalar operation, and controls which permit the expansion of any portion of the spectrum.

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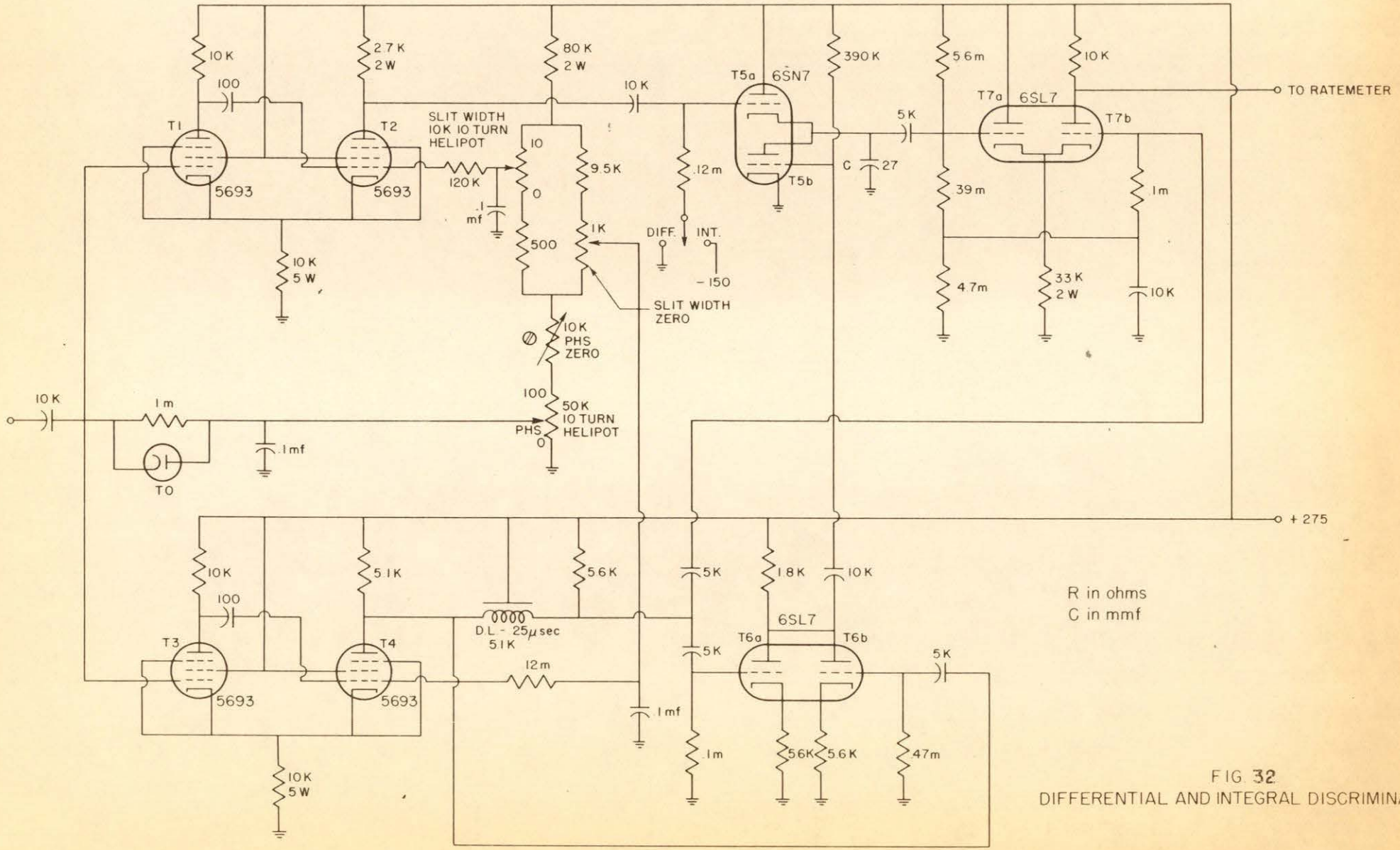

R in ohms
C in mmf

FIG. 32
DIFFERENTIAL AND INTEGRAL DISCRIMINATOR

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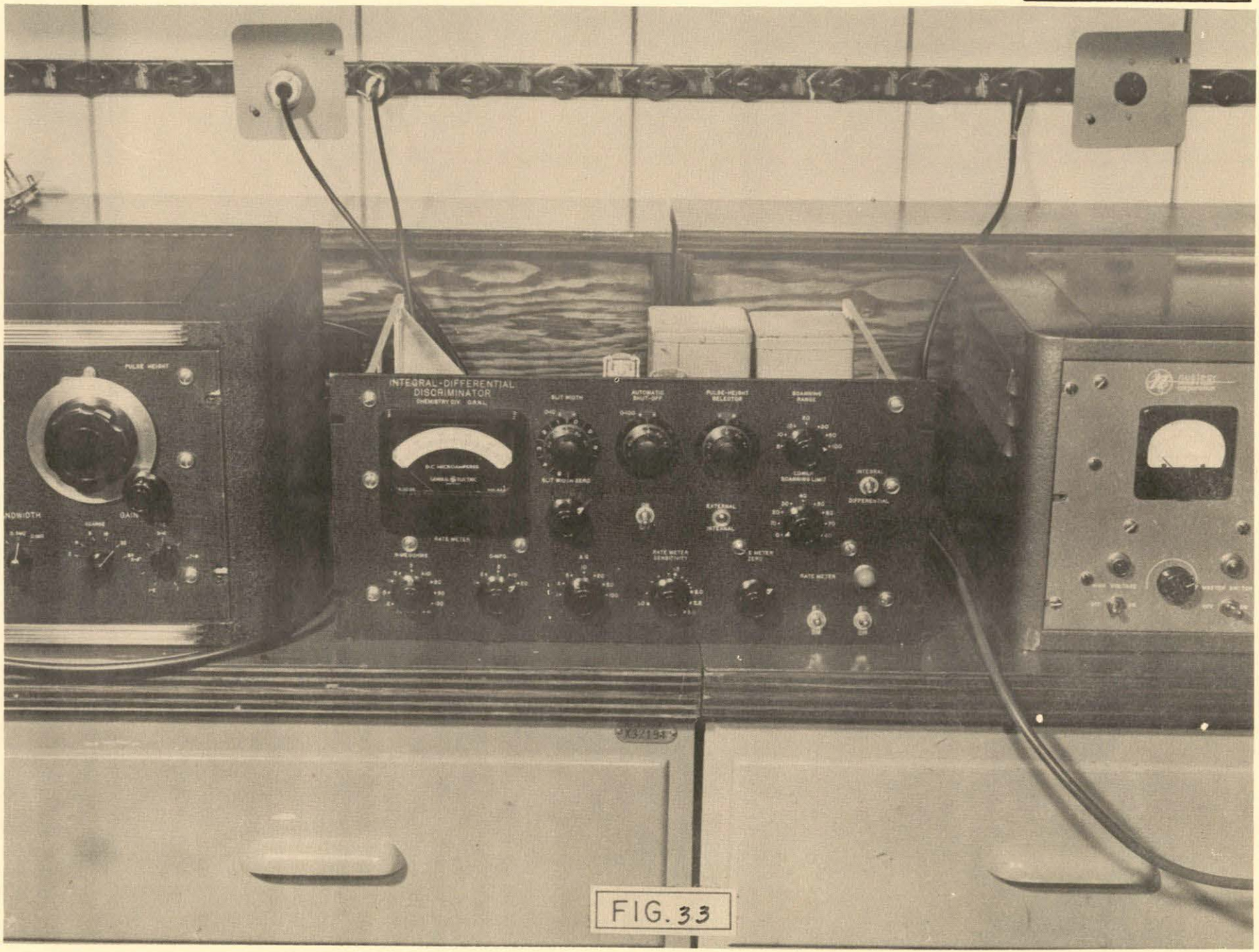


FIG. 33

GROWTH OF ANTHRACENCE CRYSTALS FOR SCINTILLATION COUNTERS

H. Zeldes and A. R. Brosi

The detection of radiation with scintillation counters has for a considerable period of time been known to offer tremendous advantages over other methods. With a suitable type of crystal, it is possible to use very high counting rates (resolution time $\sim 10^{-8}$ sec), much higher γ counting efficiency than is possible with G-M counters and pulses proportional to α or β energies of secondary electron energies in the case of γ radiation. Having been stimulated by P. R. Bell's (Physics Division, ORNL) success in developing an anthracene crystal β spectrometer and encouraged by the interest of a number of people in the Chemistry and Electronics Departments, it was decided to develop an anthracene crystal growing apparatus in order to outfit scintillation γ, coincidence and spectrometer counters for the Chemistry Division.

The most successful method of growing single anthracene crystals previously employed is probably the liquid melt method. In this method, anthracene is slowly lowered through a furnace in which there is a temperature gradient such as to sharply define a surface having the anthracene melting point. The anthracene crystal forms from the melt.

The method reported here might aptly be termed the reflux method. A sketch of the apparatus is shown in Fig. 34. The apparatus is similar to a vacuum sublimer. The anthracene is contained in a brass pot equipped with glass windows, gasketed with teflon. A cover assembly bolts in, also with teflon gasketing. The central region of the cover facing the anthracene is thermostated by a jet of fluid pumped from the upper thermostating bath. The entire pot and cover assembly is submerged in the fluid of the lower thermostating bath. The cover assembly also contains a value and pressure transmitter which is under the bath fluid level, so that the pot can be evacuated and the pressure measured at any time during a run. During the growing period, the bottom bath is kept at a fixed temperature several degrees above the melting point of anthracene. The top bath starts at about the same temperature and is steadily lowered at a linear rate. For the moment, let us assume that the surface of the cover plate is covered with a thin film of mono-crystalline anthracene at a time when the top bath temperature is such as to make the surface temperature of the thin

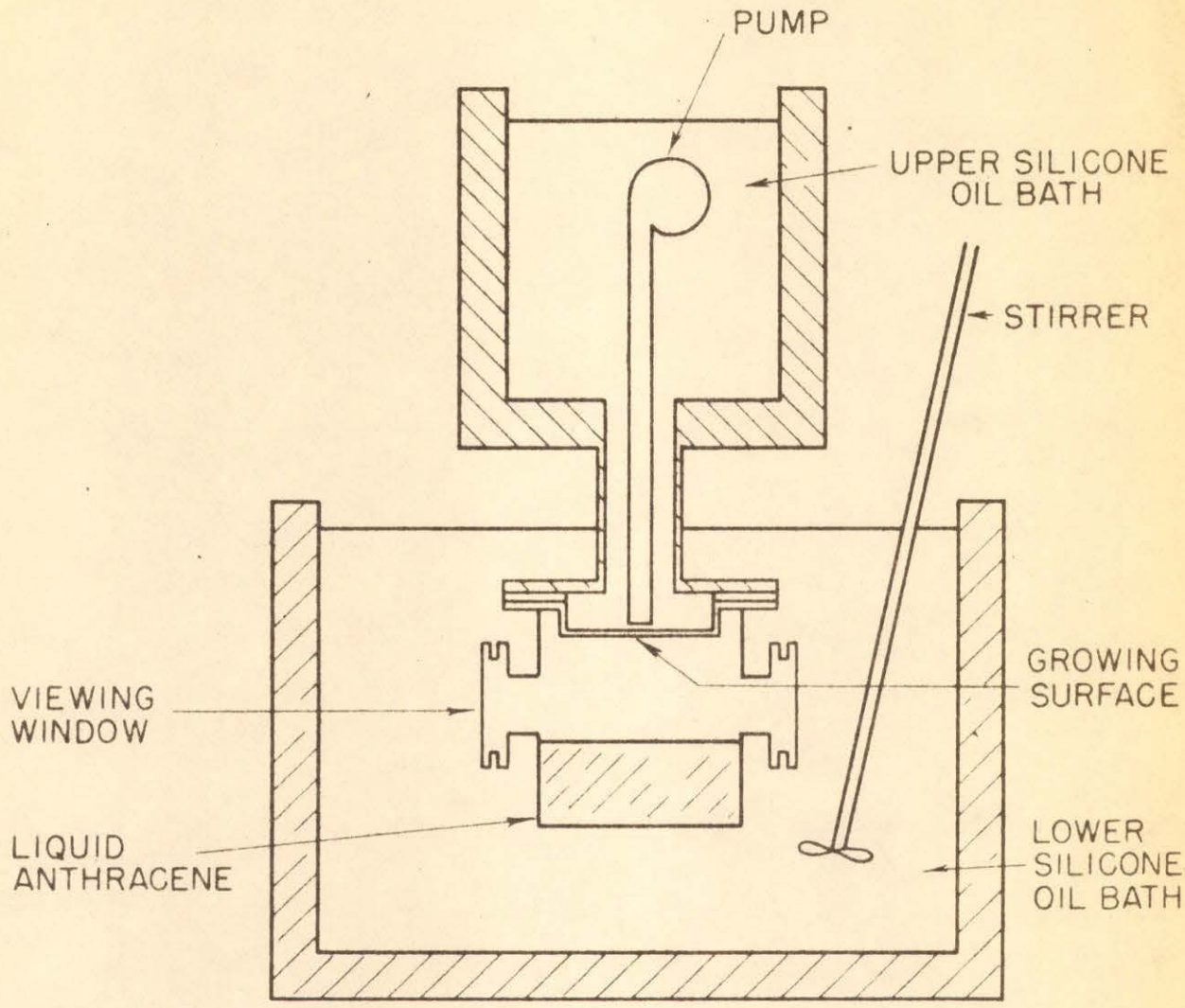


FIG. 34
ANTHRACENE CRYSTAL GROWING EQUIPMENT

film the melting point temperature. The system is now in a steady state. Heat flows from the bottom bath to top bath through the anthracene. Therefore anthracene continually condenses from vapor to liquid on the thin anthracene film and drops down. Although the thin film is being bathed in liquid, no anthracene leaves or adds to the film as the melting point region is sharply defined at the original surface of the film. If the top bath temperature is lowered, the film thickens to the point where the added layer of heat insulation is just enough to leave the surface at the melting point. Provided the top bath is not lowered at an exceedingly high rate (never attained) the anthracene condenses out first as liquid rather than solid. These growing conditions, we think, are conducive to yielding a good crystal. The growing surface is always very sharply fixed at the melting point where the crystal is most fluid. The reflux method allows for slow linear rate of growth with large temperature differences, so that the growing, if necessary, can be done at an exceedingly slow rate with modest control equipment. Also, the continual refluxing helps to keep the surface clean. The vaporization step leaves behind non-volatile impurities and decomposition products which is of considerable advantage in that less pure starting anthracene may be used.

Preliminary work was carried out in an all-glass apparatus similar to the apparatus sketched in Fig. 35. With the all-glass apparatus it was found that the liquid anthracene condensed out on the top surface would repeatedly supercool about 30° before solidifying. This led to the feeling that seeding was likely to prove very successful as the large range of supercooling would prevent random nucleation. With this in mind and also the desire for a large grower which might be operated without danger of implosion, the metal apparatus in Fig. 35 was constructed. With this apparatus it is possible to cement a seed crystal on the top surface.

Three types of runs have been made to date with the metal apparatus. The first type of run was performed with a thin aluminum foil covering the cooled region. An anthracene seed (obtained from the all-glass apparatus runs) was cemented to the foil with sauereisen. A second type of run was performed with seed material on a solid aluminum plate. The third type of run was an attempt to obtain seeding from a small region of early polycrystalline growth with the continuing growth on a glass surface. The cooled surface was covered first with an aluminum plate with a raised well shape in the center. A glass filler plate with a hole in the center was then placed around the well shape. A thin glass with a 1/16 in. D hole centered over the well was then placed over the

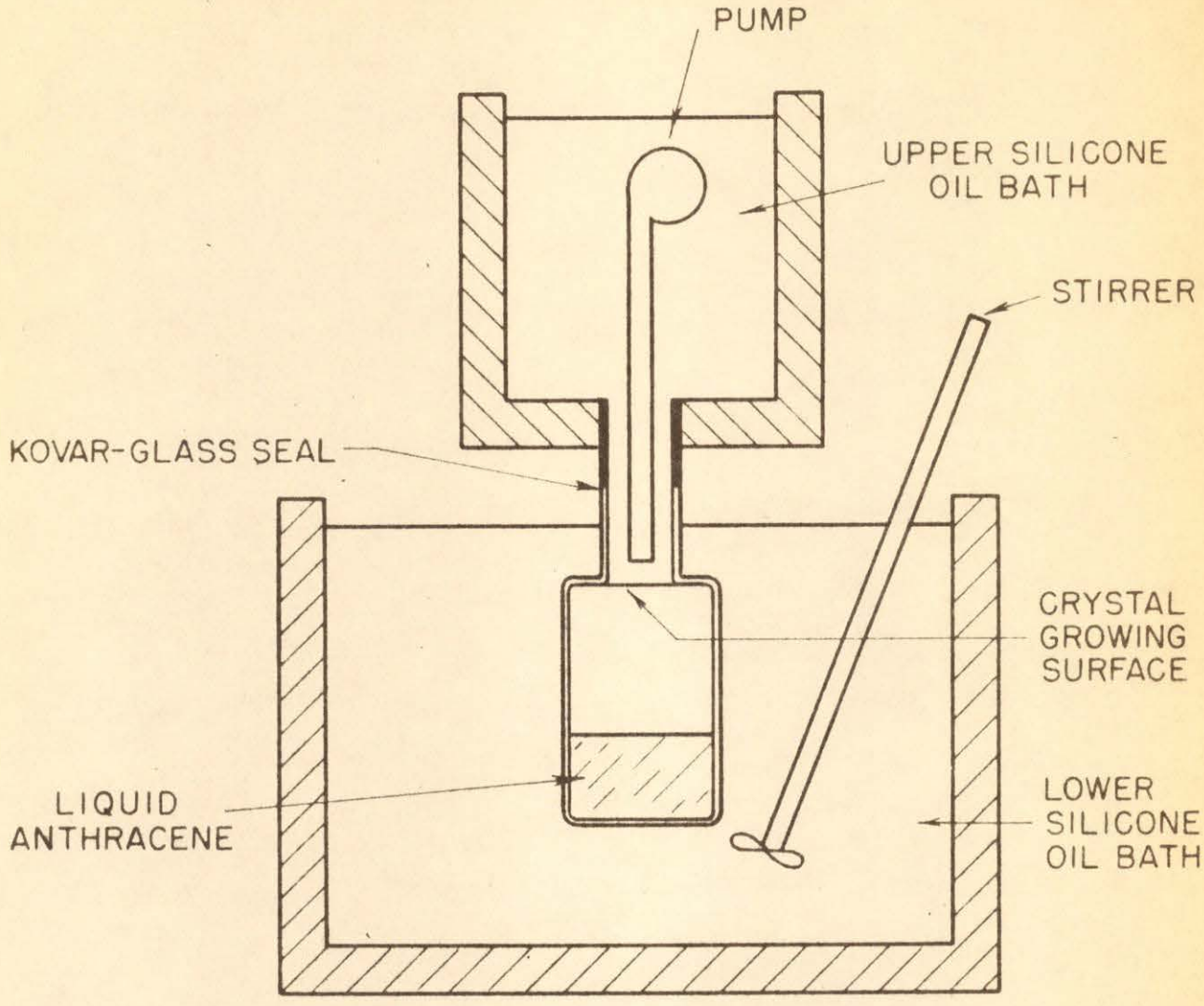


FIG. 35
GLASS EQUIPMENT FOR CRYSTAL GROWING

other plates. The three plates were held in place with two metal clips. From these runs, it was learned that while anthracene supercools on glass, it does not on aluminum. It was also learned that it is not necessary to use foils (which is very inconvenient) to obtain reasonably strain-free material, provided one anneals the crystal at a high temperature. Another ovservation is that even where the first deposit is polycrystalline, succeeding growth becomes rapidly less so. Seeding is probably not possible from a metal surface. Even from a glass surface, it is likely to be very difficult, as the crystal seed must be held in contact with the coldest region of the plate. This is easily done only with a cement. This, however, introduces the possibility of nonsupercooling on the cement surface. Also, the cement being an insulator, the surface is likely to become a hot region instead of a cold one. Rather than attempt to work out a crystal seeding procedure, we plan to start the growth from a very small area of aluminum on which there is no supercooling.. The continued growth will be on glass on which there is supercooling, so that the only crystal orientations in the large mass of crystal grown will be those which are formed on the small aluminum area. These, we feel, will be very few in number. The third type of run could also, we feel, be made to operate very satisfactorily without much refinement. The run of this type which was made was not successful in the sense that the seeding was not from the 1/16 in. hole over the well, but from the fairly large area presented by the metal clips holding the plates to the cover plate. This failure was due to the fact that the thermal conductivity of anthracene was lower than was anticipated with the result that the well geometry was arranged incorrectly. Nevertheless, the resulting crystal (1 in. thick, 5-5/8 in. diameter) was very satisfactory in that there were large clear areas with only a few crystal orientations. Also the entire mass was satisfactorily strain-free. The temperature time program was as follows: The bottom bath was held constant at 222° C while the top bath was cooled at the rate of 3°/hr (starting at 212° C) for 31 hrs. At the end of this time, the entire crystal was formed. The bottom bath was then lowered at the rate of 3°/hr to 190° C. This was to prevent losing crystalline material during the ensuing annealing period. The top bath was then raised (3°/hr) to 190° C. Then the two baths were brought down to room temperature (3°/hr rate). The overall time starting with the beginning of the growth period was somewhat less than 5 days.

The earlier runs were made with anthracene purified by B. H. Ketelle (Chemistry Division, ORNL). Miscroscopic and X-ray studies were made by T. E.

Willmarth to determine the purity of the anthracene. His studies identified on impurity (endo-anthracene maleic anhydride) which had come through the early purification procedure and was subliming with the anthracene. This impurity was actually the starting compound for the synthesis of the anthracene. The runs in the metal apparatus were carried out with commercially available anthracene (scintillation grade, Reilley Tar and Chemical Company) without further purification.

An anthracene crystal made in this apparatus has been used for several months as a gamma ray detector in a coincidence counter. Gamma ray counting efficiencies of from 5 to 10 times the G-M counter efficiencies have been observed. Another crystal has been used in a scintillation spectrometer. On the basis of preliminary results, it appears possible to detect several hard gamma rays in the presence of each other and measure their energies to within about 10%.

The anthracene crystal growing program in the Chemistry Division is deeply indebted to S. A. Hluchan (Instrument Development Department) who designed and constructed the control equipment. He has also followed each run very closely, which has made it possible to alter operating conditions rapidly so that the art of growing these crystals might be developed in a reasonable period of time.

ANALYTICAL CHEMISTRY

IONIC ANALYSES—RESEARCH AND DEVELOPMENT

Summary. Several radioisotope products were investigated with the polarograph. Micro volumetric acid determinations were developed for the radioisotope product solutions of mercury and iron. The personnel of the Pilot Plant Control Group have been trained in the use of the polarograph and the Recordomatic titrator. As mentioned in the last quarterly report[1] these instruments will be used routinely by this group.

A method for the determination of tributyl phosphate in Varsol has been developed. A volumetric method using Karl Fischer Reagent has been used to determine the water content of several synthetic organic ion-exchangers.

Routine Analysis of Uranium by the Polarographic Method (H. H. Miller). The calibration of the polarograph designed by M. T. Kelley for routine analysis of uranium was completed and two different procedures were outlined for the control groups.

A standard curve was established for uranyl solutions in 0.1 *M* HNO_3 and 0.002 *M* $N_2H_4 \cdot H_2O$ supporting electrolytes. The curve was determined using solutions with concentrations of 10-50 γ U/ml which is the optimum range for the pilot plant samples. The hydrazine hydrate was added to the sample to reduce the interfering ferric ion to ferrous ion which does not interfere with the polarographic wave for U(VI)→ U(V). This standard curve was measured at 35.0° C because of the average high temperature in the instrument room. The resulting curve is shown in Fig. 36.

The standard addition method of analysis was also adapted to this instrument to be used on samples with lower levels of radiation. With either method of analysis the accuracy of the analysis was about ± 3%.

The modified polarograph[2] mentioned in the last quarterly report has been received and preliminary studies have been started.

Recordomatic Titrator (F. J. Miller). Several *p*H titration curves of ion-exchange resins were measured for G. E. Boyd using the automatic titrator. However, this work was interrupted since the titrator had to be installed for use by the control group for the 25 Process solutions.

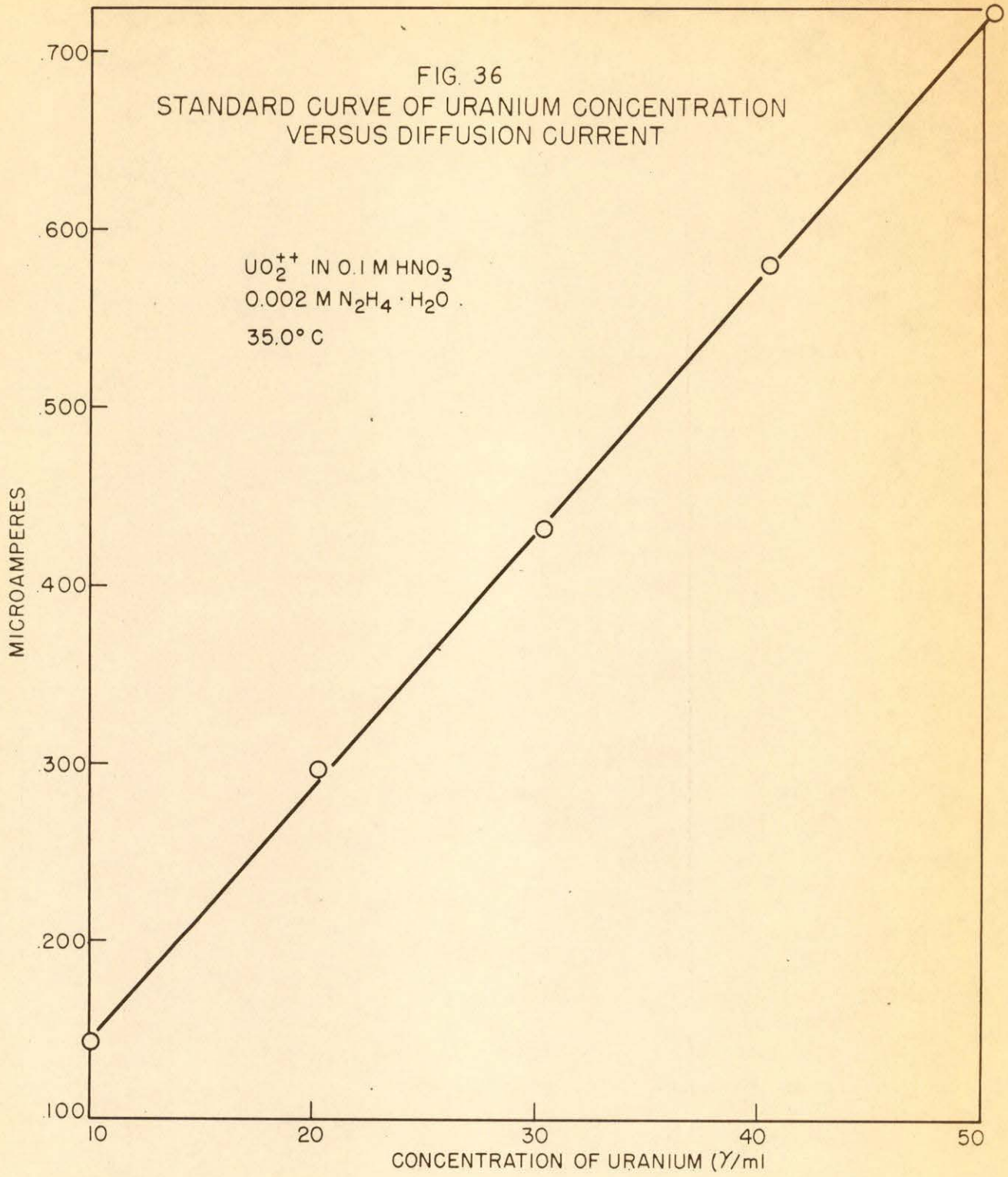
Polarography (W. H. Davenport, Jr.). During the past quarter polarographic data were obtained for the elements iodine, cobalt, mercury, antimony, lead and selenium.

(1) ORNL 286, p. 210.

(2) ORNL 286, p. 215.

NOT CLASSIFIED
DWG. 7791

FIG. 36
STANDARD CURVE OF URANIUM CONCENTRATION
VERSUS DIFFUSION CURRENT



Cobalt and iodine service analyses were performed by methods described in previous quarterly reports.[3][4]

Procedures were developed for mercury, antimony, and selenium based mainly on work which had been reported in the literature. An investigation was made of a possible method for lead in a field of polarography in which very little work has been reported.

(a) Mercury. Kolthoff and Miller[5] reported a wave for mercuric ion in a 0.1 *N* nitric acid, supporting electrolyte. This wave had a pronounced maximum which could be suppressed by certain dyes or gelatin.

A 0.1 *N* nitric acid solution has been found to be a satifactory supporting electrolyte for the determination of mercury in pilot plant feed solutions. The wave starts at a zero applied voltage and is sufficiently more positive than the uranium wave to permit simultaneous determinations of both cations when they are present in the polarographic concentration range. No maxima were encountered in our waves. It was also found that the addition of methyl red as maximum suppressor or failure to remove oxygen from the solution resulted in high diffusion current values.

Mercury cannot be determined in uranium solutions to which hydrazine hydrate has been added to reduce ferric iron. Low results were obtained for known mercury solutions containing 0.02% hydrazine hydrate which were permitted to stand overnight. This was probably due to complex formation.

(b) Antimony. Well defined waves have been reported for antimony in acid, neutral, and alkaline media[6]. The choice of supporting electrolyte is limited, however, by difficulty in keeping the antimony in solution while adjusting the concentration of the electrolyte.

A sample of antimony in 20 *N* H_2SO_4 submitted by the Radioisotope Production Group started to hydrolyze as soon as the normality of the acid was decreased by dilution. Therefore, a small aliquot of the sample was added directly to a large volume of 5 *N* NaOH. The resultant solution was diluted to give a final supporting electrolyte 1 *N* in NaOH. A well defined reduction wave was obtained at -1.17 V *vs* the SCE and the antimony stayed in solution for a relatively long period of time.

(3) ORNL 336, Progress Report, December 1948 - Jan. - Feb. 1949, p. 109.

(4) ORNL 286, Quarterly Progress Report for period ending June 30, 1949, p. 214.

(5) I. M. Kolthoff and C. S. Miller, J. Am. Chem. Soc. *63* 2732 (1941).

(6) K. Kacirkova, Collection Czechoslov. Chem. Commun., *1*, 477 (1929).

(c) Selenium. This element may be determined polarographically in a 0.1 *N* NH_4Cl solution made slightly alkaline with ammonium hydroxide. The procedure based on the work of Schwaer and Suchy[7] is to adjust the hydrochloric acid concentration of the selenium sample to give a final chloride concentration of 0.1 *N* and then neutralized with ammonium hydroxide to a faint pink phenolphthalein end point. The half wave potential appears at -1.5 V *vs* SCE.

(d) Lead. An investigation has been made of the feasibility of using the deposition of PbO_2 at a micro platinum anode as a polarographic method. Possible advantages of such a technique might be found in the direct determination of lead in the presence of large concentrations of reducible cations or organic matter. Results indicated that a lead oxidation wave with a large maximum could be obtained at + 1.15 V *vs* SCE by depositing lead from a nearly neutral nitrate solution.

Micro Determination of the Acidity of Radioisotope Product Solutions (P. F. Thomason). Some of the radioisotope product solutions must be analyzed for free acid in order to determine whether they are within specifications. Since it is desirable to conserve these solutions, a micro acid titration is necessary. The use of microliter volumes of the solutions also reduces the hazardous radioactivity.

The mercury isotope product solution could not be titrated directly with standard NaOH because of the hydrolysis of the mercury. Attempts to remove the mercury by precipitation as the oxalate or iodate before the acid titration resulted in inaccurate results on synthetic samples. This was probably due to the precipitation of the basic salt of mercury.

It was found that sodium thiocyanate complexed mercury sufficiently to allow the titration of the free acid without the hydrolysis of the mercury. The micro volumetric apparatus consists of a Kirk type burette, porcelain titration dish, and a micro vibrating-type electric stirrer.

A synthetic sample was made by dissolving mercuric nitrate in 0.1016 *N* nitric acid to give a solution with 90 mg Hg per ml of 0.1016 *N* HNO_3. 50 λ and 100 λ aliquots of the synthetic samples were treated with 500 λ of a 10% NaSCN solution and titrated with 0.0502 *N* NaOH to a phenolphthalein end point. The end point was very sharp and reproducible, and there was no indication of mercury hydrolysis. A solution of mercuric nitrate in distilled water gave a very low blank when titrated in the same manner. The results are given in

(7) L. Schwaer and K. Suchy, Collection Czechoslov. Chem. Commun., 7 25 (1935).

Table I.

TABLE I

Acid Titration of Mercury Samples

SAMPLE	λ OF 0.0502 *N* NaOH	ACIDITY FOUND (Normality)	ACIDITY PRESENT (Normality)
100 λ-Synthetic No. 1*	204 λ	0.1024	0.1016
50 λ-Synthetic No. 1	101 λ	0.1014	0.1016
100 λ-Synthetic No. 2**	4 λ	0.002	--
100 λ-of Product Hg^s	239 λ	0.1199	--

* Synthetic sample No. 1 contained 90 mg of Hg/ml in 0.1016 *N* HNO_3.

** Synthetic sample No. 2 contained 90 mg of Hg/ml in distilled water.

The free acid in an iron product solution was determined by a micro adaption of the procedure given by J. Rosin[8]. 250 λ aliquots of the iron product solution were added to 1 ml of a neutralized 25% sodium fluoride solution and made up to 3 ml with distilled water. The mixture was thoroughly shaken and allowed to stand one hour. 100 λ and 300 λ aliquots of the clear supernatant were titrated to a phenolphthalein end point. A synthetic sample was made by dissolving 90 mg of $FeCl_3$ in ml of 0.1016 *N* HNO_3 and adding this to 5 ml of 25% NaF. 100 λ aliquots of the supernatant were titrated. The results are shown in Table II.

TABLE II

Acid Titration of Iron Samples

SAMPLE	λ OF 0.1012 *N* NaOH	ACIDITY FOUND (Normality)	ORIGINAL ACIDITY (Normality)
Synthetic	50 λ	0.1012	0.1016
Synthetic	51 λ	0.1032	0.1016
300 λ $FeCl_3$ #13 product	74 λ	0.2995	--
100 λ $FeCl_3$ #13 product	25 λ	0.3037	--

(8) J. Rosin, Reagent Chemicals and Standards, D. VanNostrand C., Inc. N. Y., 1946; p. 178.

Determination of Phosphorus in Tributyl Phosphate-Varsol Solution (A. D. Horton). Tributyl phosphate-varsol solution containing 15% by volume of tributyl phosphate is being tested as an extracting agent in the metal recovery program. Samples were received from the Technical Division for determination of total phosphorus as the phosphate ion.

Complete decomposition of tributyl phosphate-varsol mixture was accomplished as recommended by Snell and Biffen[9] by boiling a volume of the 15% solution containing approximately 50 mg of tributyl phosphate, in a 150 ml beaker, with 5 ml of concentrated HNO_3 and 5 ml of concentrated H_2SO_4, adding one gram of Na_2SO_4 as a catalyst. The mixture was boiled on a hot plate until the volume was reduced to approximately 2 ml. The solution was then diluted with 5 ml of concentrated HNO_3 and 25 ml of water, and boiled 5 minutes on the hot plate. The solution was cooled and made up to a given volume. Aliquots of the sample were analyzed for phosphate by the molybdate colorimetric method[10]. The results of several synthetic samples are shown in Table III.

TABLE III

Phosphate Analyses of 15% Tributyl Phosphate-Varsol Solutions

SAMPLE No.	WEIGHT OF TBP (Grams)	CALCULATED $PO_4^{\equiv}$ (mg)	$PO_4^{\equiv}$ FOUND (mg)	PERCENT ERROR
1	.0456	16.28	16.50	+1.35
2	.0484	17.28	16.80	-2.78
3	.0482	17.21	16.80	-2.38
4	.0476	16.99	16.80	-1.11
5	.0460	16.40	16.50	+0.61

(9) Snell, F. D., and Biffen, Frank M., Commercial Methods of Analysis, McGraw Hill Book Co., Inc., New York, 1944, p. 482.

(10) Fisk, P. B., et al - CN 1791.

Determination of Water in Ion-Exchange Resins (A. D. Horton). The water in several ion-exchange resins was determined by titration with Karl Fischer reagent. These determinations were requested by G. E. Boyd as a check on the oven drying method.

(a) Experimental. The Karl Fischer reagent, obtained from the Fischer Scientific Company was standardized twice daily with a known water-methanol solution. Absolute methanol, CP quality, was used to extract the water from the resins.

The titration apparatus consisted of a 25 ml automatic buret which was protected from air moisture with drierite drying tubes and arranged to deliver the reagent into a tall form 250 ml beaker, fitted with a snug bakelite top. The bakelite top contained two platinum electrodes which were connected to a titrimeter that was designed by M. T. Kelley. This titrimeter is similar to the Serfass[11] titrimeter although it employs a 100 microampere ammeter rather than a cathode ray tube indicator. Stirring was accomplished by a magnetic stirrer with a fluorothene covered nickel stirring bar.

The resin samples had been equilibrated with acid vapors of various molar concentrations. The molarity of the acid in the equilibration bottle was taken as the sample number. To determine the water in the resins, approximately 100 mg of resin was weighed into the tall beaker, 25 ml of absolute methanol added, and the extracted water titrated to the "dead stop" end point. An excess of Karl Fischer reagent was then added, and the solution was back-titrated with the standard water methanol solution.

Typical results for the resins are shown in Tables IV and V.

(11) Serfass, E. J., Ind. Eng. Chem., Anal. Ed., 12, 536-9 (1940).

TABLE IV

Water in Dowex-50-8% Divinyl Benzene Equilibrated with HCl (24 Hours)

SAMPLE No.	WEIGHT OF SAMPLE (gms)	KFR* (ml)	H_2O-METH. SOLUTION (ml)	PERCENT H_2O-(KFR)	AVERAGE PERCENT H_2O (KFR)	PERCENT H_2O** OVEN DRYING METHOD
0-a	0.0983	16.52	0.36	43.54	43.82	41.74
0-b	0.0793	14.43	0.44	44.10		
0-7-a	0.0909	17.00	0.27	43.60	43.81	40.50
0-7-b	0.1183	20.97	0.34	44.01		
7-0-a	0.1028	16.35	0.30	35.98	3709	36.92
7-0-b	0.0796	14.40	0.36	38.19		

TABLE V

Water in Dowex-50-80% Divinyl Benzene Equilibrated with HBr (24 Hours)

SAMPLE No.	WEIGHT OF SAMPLE (gms)	KFR* (ml)	H_2O-METH. SOLUTION (ml)	PERCENT H_2O-(KFR)	AVERAGE PERCENT H_2O (KFR)	PERCENT H_2O** OVEN DRYING METHOD
0.3-a	0.0901	16.77	0.34	42.47	42.03	41.87
0.3-b	0.0787	14.70	0.42	41.58		
0.7-a	0.0912	12.73	0.32	43.38	44.52	43.10
0.7-b	0.1080	14.92	0.29	45.65		

* KFR - abbreviation of Karl Fischer Reagent.

** Determined by Q. V. Larson.

RADIOCHEMICAL ANALYSES—RESEARCH AND DEVELOPMENT

Summary. U^{233} alpha standards have been prepared and distributed to all analytical groups requiring them. The thermal-neutron cross section for Zr^{96} has been determined. Methods for assaying Be^{7}, Se^{75}, and $Hg^{203,205}$ were developed, and investigations of methods for Zr^{95} and Pu has continued.

Alpha Stands (W. A. Brooksbank). Alpha standards have been prepared by electroplating U^{233} on stainless steel discs. The disc served as cathode in the cell, and a rotating Pt anode was used. The electrolyte contained ammonium oxalate, ammonium nitrate, and a small amount of HNO_3. The applied voltage was 8.2-9.8. A very adherent film of U^{233} was obtained. Standardization was effected by counting on several proportional counters. The standards were distributed to analytical groups who require alpha counting.

Activation Cross Sections (G. W. Leddicotte). The thermal-neutron cross section of Zr^{96} for production of 17-hour Zr^{97} has been found to be 0.045±0.01 b. The method used has been discussed previously(12). Resonance capture is very important, because the cross section for ordinary pile neutrons is ~ 0.2 b. Three samples have been measured, two exposed in the pneumatic tube and one in the boat provided in H. S. Pomerance's oscillator, wherein the neutrons are almost all thermal.

Analysis of Various Radioisotopes (W. A. Brooksbank, D. J. Coobe, T. H. Handley, S. A. Reynolds). Be^{7} decays by K-capture, with 0.48 Mev gamma following 10-13% of the capture processes(13). After establishing the material as Be^{7} by radiochemical separations and absorption curves, the assay was made by means of the 100% geometry gamma chamber.

Na^{22} emits 0.4 Mev positrons, followed by 1.3 Mev gamma rays(14). After identification of Na^{22} by chemical means and checking by aluminum absorption curves the material was assayed by coincidence counting. The 100% geometry gamma chamber was calibrated for Na^{22} measurements and will be used in future assay.

Se^{75} decays by K-capture, followed by several gammas(14). The As K X rays were counted on a proportional counter filled with a 90% argon 10% methane mixture, then with pure methane. A ~ 50 mg Be absorber was used to absorb Auger

(12) Chemistry Division Quarterly Progress Report, ORNL 286 (June 30, 1949).

(13) C. M. Turner, Phys. Rev. *76*, 148 (1949).

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

electrons. The count in methane was subtracted from that in argon-methane (Methane count is due primarily to conversion electrons and secondaries). Efficiency of counting As X rays was estimated by determining the efficiency for Cu and Co X rays from sources of known strength. These standards agreed when compared by the formula

$$\log(1-f_1)/\log(1-f_2) = [(M/d)_1]/[(M/d)_2]$$

where f is the fraction counted under definite conditions, and M/d is the mass absorption coefficient for the X ray in the filling gas. The same relation was used to calculate the efficiency for As X rays. After correction of the observed counting rate for fluorescent yield, the K-capture rate was calculated By coincidence counting the disintegration rate was checked. The result was ~40% lower. The discrepancy was probably due to X rays accompanying the internal conversion of some of the gamma rays. This would raise the proportional counter result more than the coincidence figure. It is believed that the coincidence figure is accurate within 50%. Much valuable aid in this problem was given by C. J. Borkowski and A. R. Brosi.

In analyzing for Nb^{95} by the customary method[15] serious contamination of the "purified" Nb_2O_5 is found in UAP waste-recovery samples and certain others. Identification and elimination of this contamination is now in progress.

Previous work with $Hg^{203,205}$ tracer has shown volatilization of the activity when solutions were evaporated to dryness for counting. This has been eliminated by addition of a small amount of ammonium sulfide before evaporation. Samples were measured in the 100% geometry gamma chamber before and after drying. The loss was 1% or less.

Radiozirconium Analyses (F. L. Moore, R. H. Powell, S. A. Reynolds). Effort during the past quarter has been in an attempt to eliminate the interference of phosphate ion. Solvent extraction by various means has been investigated, but distribution coefficients of only ~ 0.4 have been obtained in the best circumstances.

The conventional precipitation method for Zr[15] has been shown to yield high results due to contamination in the same type of materials as for Cb (above). Investigation is proceeding.

(15) D. N. Hume, et al, CN 2815 (1945).

Plutonium Analysis (F. L. Moore). A procedure has been devised for determining valence states of Pu even in the presence of Pu (IV) polymer. The polymer is destroyed by making the solution ~1.3 *M* in HF (HF previously treated with slight excess of $Na_2Cr_2O_7$). Ten minutes treatment is sufficient. The HF is destroyed by H_3BO_3. A holding oxidant, 0.02 *N* $NaBrO_3$ or $Na_2Cr_2O_7$, is added, Pu(III) is oxidized to the tetravalent state by $NaNO_2$. Pu(IV) is then extracted into TTA-xylene in the usual manner[16]. This result represents the Pu(III) and Pu(IV) originally present in the sample. By reducing with hydroxylamine at 80°, then treating with $NaNO_2$, the Pu(VI) may also be determined. It has been demonstrated that HF does not cause reduction of Pu(VI) under the above conditions, that Al does not interfere, and that good reproducibility and accuracy are obtained.

(16) F. L. Moore and J. E. Hudgens, ORNL 153 (1948).

SPECTROCHEMICAL ANALYSES—RESEARCH AND DEVELOPMENT

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

Aqueous Solutions. Curves and procedures were developed for spectrochemical analysis of the following sample solutions by the porous cup method, accuracy and precision estimated as ± 2-3%:

(a) 50-500 ppm Li in 0.5% Mg solutions (1-10% Li in Li-Mg alloys),

(b) 5-100 ppm Cb in 0.5% stainless steel solution (0.1-2% Cb in stainless steel),

(c) 0.5-5 ppm Mn and 1-10 ppm Co in 0.25% Al solution (0.2-2% Mn and 0.4-4% Co in Al alloy).

Non-Aqueous Solutions. 1:4 Bu_3PO_4-varsol mixtures were found to show almost no tendency to ignite during PCE exposures. Zr-Hf mixtures in this solvent are therefore analyzed as such, with no chemical treatment.

Analysis of Uranium Compounds for Impurities. Work has continued on investigation of the extraction of impurity elements from aqueous solution. The following results were obtained using the technique described in ORNL 286. It should be emphasized that the present and previous "Upper Limit for Distribution Coefficient" figures represent a one-minute shaking period. Equilibrium values may be higher than those given. (See remarks below on material balance.)

TABLE I

Extraction of Trace Constituents into 1:4 Tributyl Phosphate—Hexane Mixtures

TRACE ELEMENT	CON. IN AQ. LAYER IN ppm.	APPROX. AQ. DETECTION LIMIT BY PCE IN ppm.	UPPER LIMIT FOR (NON-EQUIL.) DISTRI. COEFF. (Org/Aq)
Be	25	0.03	2.3×10^{-4}
Ce^{+++}	500	25	1×10^{-2}
Cu	50	0.6	2.4×10^{-3}
La	250	5	4×10^{-3}
Sr	50	0.5	2×10^{-3}
VO^{++}	500	5	5×10^{-3}

Tin, zirconium, and hafnium were extracted into the organic layer, but determination of their concentration in this layer was delayed pending development of a suitable internal standard procedure.

In order to check on the effect of UO_2^{++} ion on the extraction of trace elements from the aqueous layer, the analysis had to be performed on the aqueous layer, since an organic layer charged with U salts cannot be analyzed spectrographically for trace constituents with the accuracy necessary for the present purposes.

Two sets of test solutions were prepared and run in a manner identical with the above. One set was spiked with trace solution only; the other was treated with trace solution and made 1 *M* in UNH. Immediately before analysis, these solutions, along with a control (unextracted) solution, were made 75 ppm in Co, and analyzed by PCE. The apparent relative concentration of six elements in the test and control solutions was measured in terms of element/Co intensity ratio of the test solution divided by the same ratio for the control solution. Results were as follows:

TABLE II

Recovery of Trace Elements from Aqueous Residue

	FRACTION OF TRACE ELEMENT RECOVERED IN AQUEOUS LAYER					
	V	Sn	Sr	La	Ce	Hf
Solution 2 (U absent)	1.05	0.91	0.56	0.52	0.55	0.35
Solution 3 (U present; extracted before exposure)	1.01	0.98	0.73	0.79	0.72	0.48

Visual estimates indicate that the amount of Sn appearing in the organic layer may account for the losses of Sn in the aqueous layer. The amount of Hf detected in the organic layer was not sufficient to account for the amount missing from the aqueous layer. Since Sr, La and Ce were not detected in the organic layer, it appears that factors other than extraction into that layer are causing the disappearance of some elements from the aqueous layer. Until these causes are ascertained, it is premature to interpret the above results in terms of any salting effect on the part of uranium salts.

ANALYTICAL SERVICE

There have not been any great changes in analytical load in the past quarter. The significant developments in each service group are the following:

Spectrochemical Analyses. There are increasing numbers of requests for quantitative analyses particularly from the Metallurgy Division. Over half of the time of this group is spent in qualitative and quantitative analyses of "hot" samples of radioisotope preparations.

General Ionic Analyses. This group is assembling a vacuum fusion apparatus for determination of oxygen in metals at the request of the Metallurgy Division. The apparatus will be located in the Metallurgy building but will be operated by Chemistry Division personnel.

This group (D. E. LaValle) is also continuing the preparation of compounds for neutron diffraction work by C. G. Shull. Titanium dioxide and manganese selenide have been prepared. Work is continuing on the hydrides and deuterides of the alkali metals.

General Radiochemical Analyses. This group continues to be primarily occupied with analyses from the decontamination studies in the various solvent extraction processes under development in the Technical Division. The introduction of butyl phosphate as a solvent has introduced several problems in the present radiochemical methods which must be solved before semi-works operation is started.

Water Analyses. This group is primarily concerned with analyses of water samples from corrosion studies in the Technical Division. However, they are at present also analyzing samples from the RaLa program for Pb, Fe, Cr and Ni.

Lab and Semi-Works Control Group. The increased diversity of the Technical Division program in these groups has increased the load of this group, but they have been primarily engaged in uranium analyses and other controls on the various solvent extraction processes, as well as on the UAP process, which was completed this quarter.

Pilot Plant Control. Since the shut-down of the Redox columns this group has spent considerable time in analyzing synthetic samples in preparation for the enriched "25" run. Dummy runs on this process have been completed and the processing of the enriched material will start very soon.

Production Control. In addition to the analysis of radioisotope preparations this group has also been analyzing the Zr-Nb preparations made by Baldwin in the Chemistry Division and they have done much of the radiochemical analysis for the RaLa development work by Blanco in the Technical Division.

This group will move into its new laboratory in the Radioisotope Area in the very near future.

Summary of Service Analytical Work for Period

(July 1 - September 30, 1949, Number of Analyses Reported)

PERSONNEL	RADIOCHEM. DEV.	IONIC DEV.	SPECTRO. CHEM. GROUP	GENERAL RADIOCHEM. GROUP	GENERAL IONIC GROUP	WATER ANALYSES	LAB AND SEMI-WORKS CONTROL	PILOT PLANT	PRODUCTION CONTROL	TOTALS
Tech.	8	4	4	4	4	1	2	5	7	39
Non-Tech.	4	2	-	6	1	4	10	21	18	66
Biology	Less than 1% of time devoted to analyses.									
Physics			29		6*					35
Chemistry		41	31	235	33				1710	2050
Technical		302	60	3536	30	1035	8165	4304	1626	19058
Metallury			152		65					217
Operating Div.		36	183		2	89			8878	9188
Health Physics		2		138						140
Misc.		40	44							84
		421	499	3909	136	1124	8165	4304	12214	30772

* Time of 1-1/3 men spent on inorganic preparations for Physics Division.

Form AEC 426
(5-74)
AECM 3201

U.S. ATOMIC ENERGY COMMISSION

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N. T. Bray, Classification Officer

14. Organization

Oak Ridge National Laboratory

15. Signature Original Signed by: N. T. Bray

16. Date October 23, 1975

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RADIATIONS AND HALF-LIFE OF LONG-LIVED FISSION ~~IN~~ SELENIUM

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RADIATIONS AND HALF-LIFE OF LONG-LIVED FISSION SELENIUM

G. W. Parker, G. E. Creek, G. M. Hebert, P. M. Lantz

and W. J. Martin

Introduction. L. E. Glendenin[1] and L. Winsberg[2] have described the unsuccessful search for a long-lived fission selenium activity at mass 79. Winsberg established a very low half-life limit of about 30 years and treated his data in terms of different assumed fission yields. On the basis of the smooth-curve yield (~0.035%) Glendenin concluded that a minimum half-life value was $> 7 \times 10^8$ y. Since no other fission isotope has been assigned to this mass, there is no evidence which definitely establishes the chain.

Summary. In the present investigation, having significant advantages over earlier work in quantity of source materials and improvements in fission-product chemistry, the isolation and characterization of a long-lived fission-product selenium activity at mass 79 has been accomplished. Preliminary mass-spectrographic evidence for the assignment has been obtained from R. F. Hibbs at the Electromagnetic Plant Mass-Spectrographic Laboratory. The single electron radiation observed appears to have a maximum energy of about 160 Kev. The half-life, calculated from the observed disintegration rate and the smooth-curve fission yield is 6.5×10^4 years. During the investigation, some difficulty was encountered in obtaining interchange of fission-selenium with chemical carrier.

Experimental. Run No. 1. The highest level, long-cooled Hanford uranium was used in this separation which was adapted from the established fission-product sulfide process[3].

The selenium was first isolated with milligram quantities of selenium carrier from a uranyl chloride-ferric sulfate solution from which the long-lived I^{129} had just been distilled. Details of the chemical procedure are given under Run No. 2 which was more satisfactory. In the very first attempt, it was found that little or no selenium could be recovered from the fission product sulfides after dissolution in a mixture of H_2O_2 and NH_4OH. Assuming that this was due to a difficultly soluble sulfide, CS_2 extraction of the metal and/or sulfide was attempted and also abandoned as unsatisfactory. Finally the metal

(1) L. E. Glendenin; MDDC-1694-C, February, 1948; PPR Vol. 9B 7.3.5.

(2) L. Winsberg; PPR Vol. 9B 7.3.4.

(3) Parker. G. W., J. W. Ruch, and J. Reed, AECD-2043 (Jan. 1948).

solution was freed of sulfide ion by boiling, the acid strength was increased to 6 *N*, and selenium was reduced with SO_2. After washing, the selenium fraction was dissolved in aqua-regia and removed from the shielded cell for purification. The final activity was extremely low but was sufficient to provide conclusive evidence of the radiations and identity of the activity.

Run No. 2. Since the first run had resulted in such an extremely weak sample as well as a very poor chemical yield, a second run was made, using a new uranium slug identical with the first.

In this run, immediately after the metal was dissolved in conc. HCl, 20 milligrams of inactive selenium as selenous acid was added to the UCl_4 slurry. The UCl_4 was then oxidized by the careful addition of 30% H_2O_2. After the oxidation was complete, the mixture was boiled to recover iodine and to effect a volume reduction. After cooling, cold conc. HCl was added to increase the acidity to above 6 *N*. SO_2 was then passed through the solution for several hours during which time a red color was formed and changed to a darker one. The entire solution was then filtered and the selenium washed and dissolved in aqua-regia as before.

Nitric acid was removed by evaporation with HCl, and the selenium was then distilled in silica with two 50 ml portions of 48% HBr into 50 ml of conc. HCl. The selenium was re-precipitated with SO_2 from the 8-10 *N* HCl-HBr mixture, filtered and weighed in a sintered glass filter crucible. After one distillation the activity in the entire sample was only a few microcuries and was found to be essentially free of all activities except that of selenium and lesser amounts of those of antimony and tellurium.

The yield was 14 milligrams of the 20 milligrams added and the 2-3 milligrams expected from fission, or about 60%. The total activity at 2% geometry was about 230 counts per second. The aluminum absorption curve showed essentially a 2.5 milligram half-thickness with a small portion having a 20 milligram half-thickness and a low gamma count.

Final Purification of Selenium. It was expected and was found that the contaminating activity in the selenium was the 2.7 y Sb^{125} and mixtures of the 90 d Te^{129} and the metastable Te^{125}. Accordingly, holdback carriers of antimony and tellurium were added before the second HBr distillation. As an indication of the progress of the purification, Sb and Te were also added to the HBr distillate before the recovery of the Se by SO_2 precipitation. The selenium was again precipitated and weighed. The activity was found to have been reduced from 230 to about 170 counts per second for 13 milligrams. The difference in counts was found to be equally divided between the antimony fraction in the HBr distillate and the Te fraction in the HBr still residue.

By weighing Sb_2S_3 and Te metal precipitated in 1-3 *N* HCl-HBr, it was also found that about 1/3 of the total antimony consistently distilled with the selenium, while the active antimony was almost completely distilled with this portion. The antimony remaining in the still residue was essentially inactive.

The selenium was again distilled with HBr in the presence of Sb and Te holdback carriers and both carriers were also added to the HBr distillate. The Te fractions were inactive but again the Sb fraction in the distillate was active, counting about 20% as much as the first one. Absorption curves indicated that the Sb carried activity was normal for Sb^{125} and could not be confused with the bulk Se activity.

Finally the Se activity was redistilled with holdback carriers of Sb^{+3}, Sn^{+4} and As^{+3}. Again each of these was added to the distillate before the Se was precipitated. Each was isolated and counted by means of fractional precipitation of the sulfides starting in 10 *N* HCl, although the arsenic was found only in the distillate.

None of the above fractions was found to be active except for a trace of Sb in the distillate. The Se did not precipitate cleanly in the presence of all of the holdback carriers and was reduced to about 10 milligrams. It was redissolved and reprecipitated from 8 *N* HCl in the absence of holdback carriers. The activity was about 130 counts per second. The rough absorption curve indicated less than one part per thousand of any radiation harder than the previously observed 2.5 milligram half-thickness (Fig. 5).

Electrodeposition of Selenium. A method described by Jílek and Lukáš[4] has been adapted for the codeposition of copper and selenium on platinum disks for weighing and counting. The plates are dull-black and adhere well particularly if plated slowly on a thin film of copper over the platinum. The voltage was started at 1.9 and the current at 1 ma. The plating solution was a mixture about 6% in sodium tartrate and 0.5 *N* in HNO_3. The sample was washed free of the plating solution before disconnecting the current.

In Table I, the near quantitative plating of selenium and the relative activity of the sample are compared with the previously weighed amount of the metals added to the plating solution. In the above reference, at least equivalent amounts of Cu are suggested for codeposition. However, the yields are believed to have been improved by doubling the amount of copper added.

Energy Approximation of Se^{79} by Comparison with S^{35} and C^{14}. In order to estimate the energy of the beta in Se^{79}, it was found relatively simple to compare its half-thickness value with those of two other well-established nuclides, namely S^{35} (168 Kev) and C^{14} (154 Kev). In Fig. 6, the three absorption

(4) Ant. Jílek and Jam Lúkáš, Chem. Listy 21, 576-583 (1927) Chem. Abst. 1734, 22.

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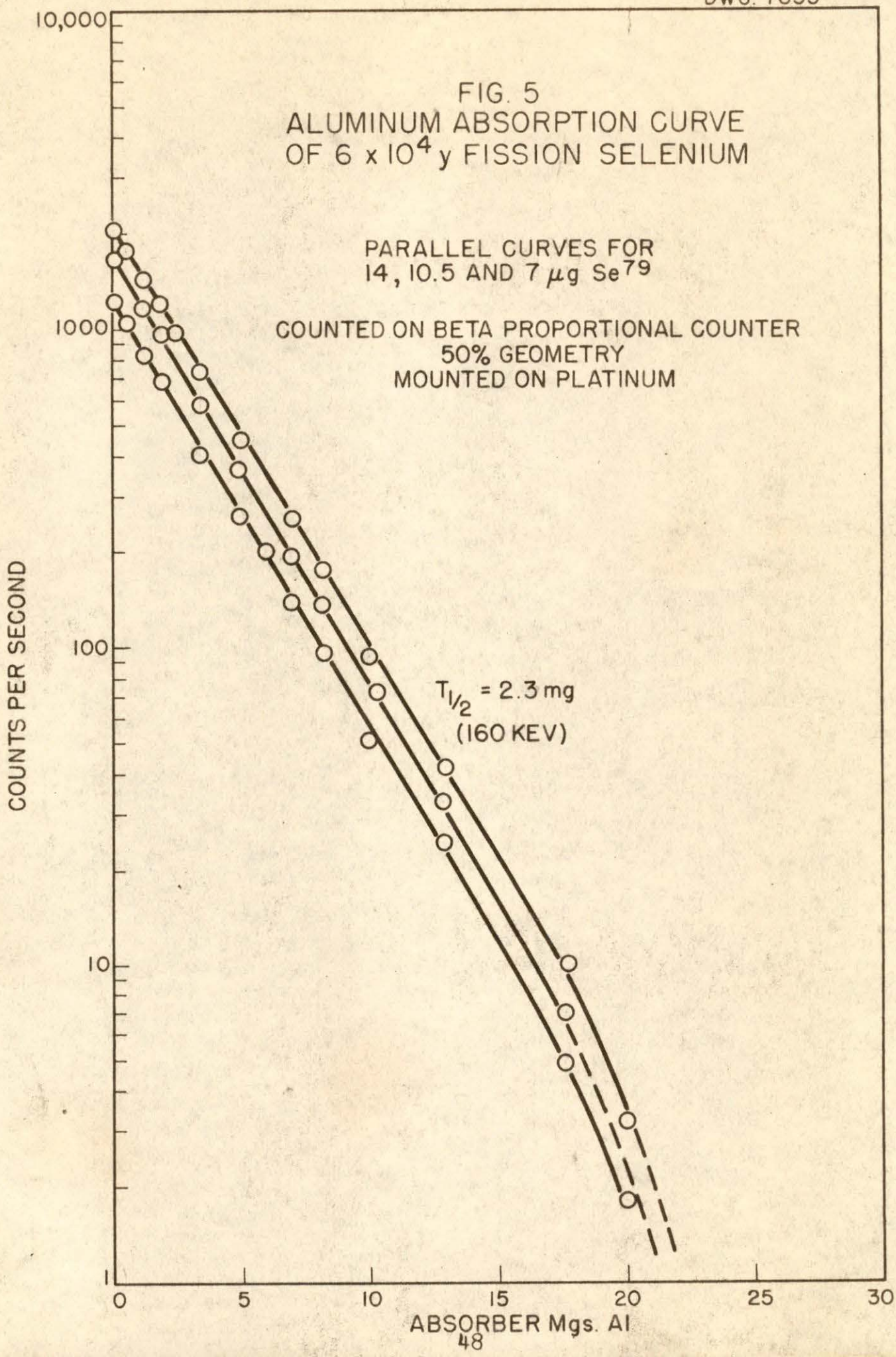

FIG. 5
ALUMINUM ABSORPTION CURVE
OF 6×10^4 y FISSION SELENIUM

PARALLEL CURVES FOR
14, 10.5 AND 7 μg Se^{79}

COUNTED ON BETA PROPORTIONAL COUNTER
50% GEOMETRY
MOUNTED ON PLATINUM

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FIG. 6
ENERGY OF LONG-LIVED FISSION SELENIUM FROM RELATIVE ABSORBER HALF-THICKNESS VALUE COMPARED WITH C^{14} AND S^{35}

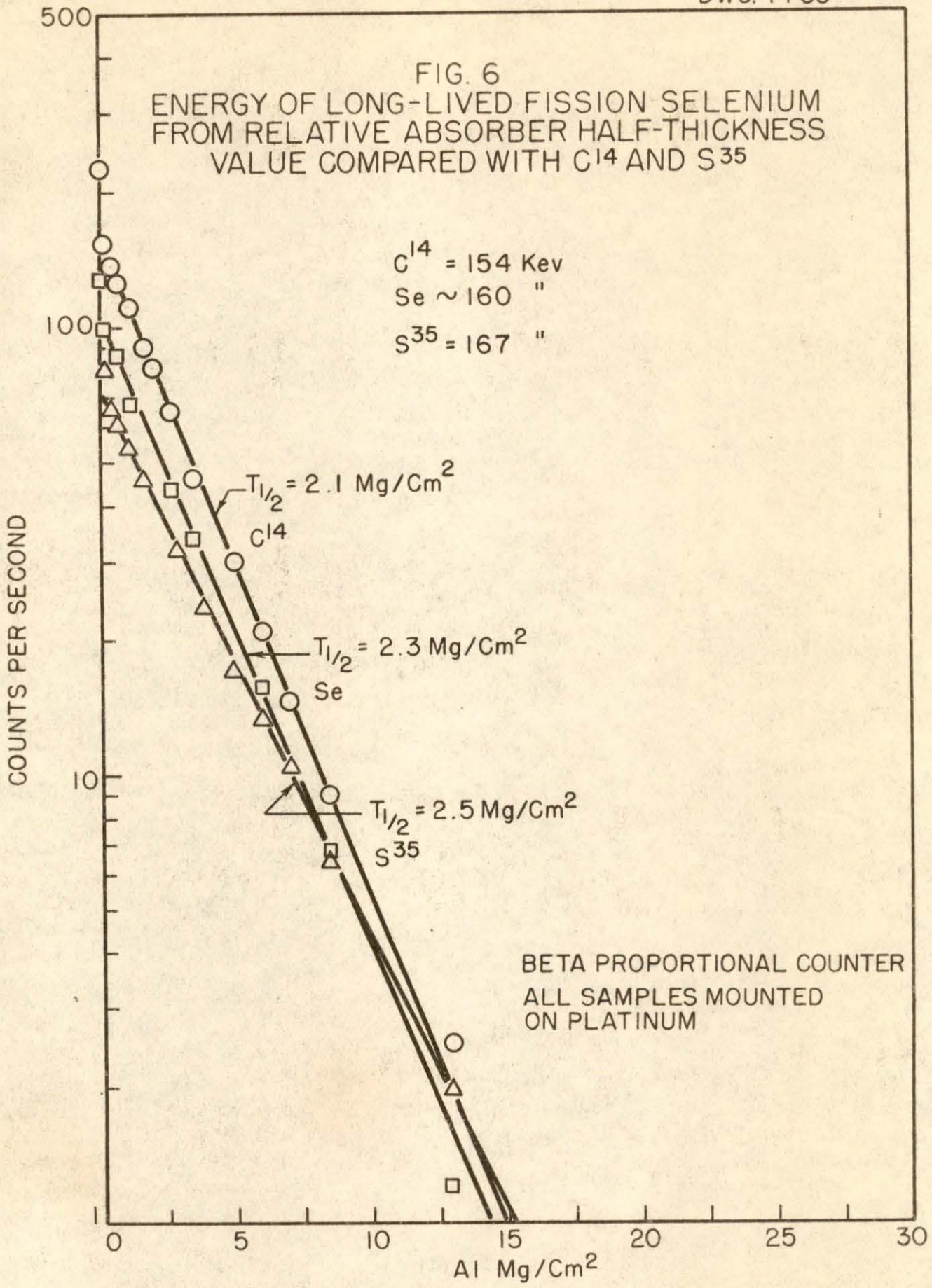

TABLE I

Electrodeposition of Selenium with Copper

SAMPLE No.	PLATING TIME (Hrs)	Se ADDED (mgs)	Cu ADDED (mgs)	Cu-Se YIELD (mgs)	PERCENT YIELD	RATIO OF ACTIVITY FOUND (Corr. for Self absorption)
I	16	0.5	1.0	1.53	102	1.0
II	10	0.75	1.5	2.17	96	1.47
III	10	1.0	2.0	2.84	95	1.94

TABLE II

Disintegration Rate and Half-Life of Long-Lived Selenium

	COUNTING RATE					
SAMPLE No.	OBSERVED 50% geom.	CORR. FOR SELF ABSORPTION Area = 1.75 cm^2	CORR. FOR BACK SCATTER (50%)	MASS Se^{79} (Calc. 1.4% See Table I)	d/s/μg	
					Se^{79}	T½
I	919 c/s	1380 c/s	1220 c/s	7.0 μg	263	6.4×10^4 y
II	1352	2030	1700	10.5	258	6.5×10^4
III	1778	2670	2100	14.0	254	6.6×10^4

TABLE III

Energy Approximation for Se^{79} by Relative Half Thickness Values

ISOTOPE	ENERGY (Kev)	OBSERVED ABSORBER HALF-THICKNESS in Mgs. Al	ESTIMATED VALUE FOR Se (Kev)
C^{14}	154	2.1	
Se^{79}	--	2.3	160 ± 5
S^{35}	168	2.5	

curves are given as observed under the same counting conditions. It is apparent that the initial half-thickness value for Se is approximately at the mid-point between the other two. While this method of energy determination is probably valid only when the spectra are similar, it is of considerable value for approximation.

Specific Activity and Half-Life of Se^{79}. It was noted that Run No. 2, in which the Se^{+3} carrier was added before the UCl_4 oxidation was performed, gave a selenium product with a specific activity approximately 100 times as high as in Run No. 1. Since the samples should have been identical, it has been presumed that the fact that the selenium activity could have been in the selenic state while the carrier was added in the selenous form would account for the very incomplete equilibration between the two. It is also possible that this effect accounts for the considerable difference between the observed half-life and the much greater lower limit proposed by Glendenin. The additional unusual behavior of the antimony here is also indicative of the reason for the early controversy over the existence of the 2.7 y antimony(5).

In Table II, the data used in the calculation of the half-life are summarized. The very high counting rates and the incidental agreement in value between samples are indicated.

Because abundance data on the mixed isotopes are just being obtained, it was necessary to base initial calculations on the theoretical values. In preliminary work in preparing for the spectrographic analysis, plates were made by Hibbs and Fultz of purified chemical selenium in which the positions at 79 and 81 are entirely clear and mass 74 (< 1%) is quite clearly indicated. A 4 milligram selenium sample in a 1/16 in. tantalum tube was given to this group at the Electromagnetic Plant for preliminary study.

They have reported additional lines at 79, 81, 83 and 84 in order of decreasing intensity with the 79 line somewhat heavier than the Se^{74}. The presence of all these lines is not quite understandable. However, the 79 and 81 could possibly indicate a trace by bromine. Even so, the intensity of the 79 indicates it would have had to be enhanced by another particle (assumed to be Se^{79}). Transfer radioautographs and a higher degree of purification of the selenium should help assign the extraneous lines.

In evaluating the half-life data, it is believed that the value 6.5×10^4 y should be considered as a maximum. Further work to improve the specific activity to a point where the radiation may be studied on the beta-ray spectrometer will be continued. A procedure in which tellurium may be employed as an isomorphous carrier would be decidedly useful.

(5) G. Leader and W. H. Sullivan, (H)-CN-3465, Jan. 1946.