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CHEMISTRY DIVISION

QUARTERLY REPORT

FOR THE MONTHS JUNE, JULY, AUGUST, 1948

D.C. BARDWELL and J.A. SWARTOUT

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CHEMISTRY DIVISION

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FOR THE MONTHS JUNE, JULY, AUGUST, 1948

D. C. Bardwell
AND
J. A. SWARTOUT

DATE ISSUED: NOV 9 - 1948

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ABSTRACT OF QUARTERLY REPORT
CHEMISTRY DIVISION

1. REACTOR FUELS

With the completion of developmental work on the processes for recovering uranium from enriched piles and U^{233} from thorium, research on the chemistry of heavy elements in solutions has been emphasized.

On the basis of results obtained for the extraction of protactinium with di-isopropyl carbinol from fluoride solutions under controlled conditions, it is concluded that Pa(V) forms stronger fluoride complexes than Th(IV), that Pa(V) is probably less extensively oxygenated in these complexes than are U(V), Np(V) and Pu(V), and also, that the chloride complex of protactinium should contain less than one oxide ion per complex.

Optimum conditions are being established for an ion-exchange separation of plutonium and lanthanum from the americium sample which is being recovered.

The study of complexes of thorium in aqueous solutions was extended to fluoride systems employing extraction into a TTA-benzene phase for determination of stability constants of the complexes.

Research was completed on the distribution of organic amines and the effect of these amines as complexing agents for uranium in solvent extraction. Upon completion of theoretical treatment of the data a report will be issued.

2. RADIOISOTOPES

Work on the xenon cross-section problem has progressed satisfactorily. The assembly of glass equipment for the large scale preparation of I^{135} is essentially completed. Cold, test preparations will be made in the near future. The mechanical loss of PdI_2 by hold-up on the plastic funnel has been virtually eliminated by application of a SiO_2 coating to the plastic surface. The gas counting apparatus has been calibrated by coincidence counting of Xe^{133} and Xe^{135}. Using this result, the calibration of the ion chamber for assay of I^{135} was checked with satisfactory agreement.

In conjunction with this work the decay scheme of I^{135} has been studied. Although several new facts have been added, it is still not possible to fit these into a satisfactory decay scheme.

Exploratory experiments on the separation of fission zirconium and columbium from separations process wastes by adsorption and ion-exchange showed charcoal to be promising for isolation of these from the Redox, IAW, raffinate. Considerable research and development will be necessary to establish the optimum method.

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Abstract of Quarterly Report (Continued)

Research continues on chemical and physical modifications of ion-exchange procedures for the separation of rare earths, including studies of eluting agents, properties of cation-exchangers, and application of "disjointed" columns.

The development of the chemical process for extracting C^{14} from irradiated beryllium nitride was completed satisfactorily. A process recommendation is being prepared for submission to the Operations Department.

Work on the experimental use of C^{14} has concentrated on three phases, (1) the synthesis of low molecular weight intermediates containing C^{14}, (2) the study of reaction mechanisms, and (3) the development of analytical procedures. Experiments on the first phase include the synthesis of ring-labelled benzoic acid, the reduction of carbon dioxide-C^{14} to methanol C^{14} in high yield by lithium aluminum hydride, the reduction of carboxyl-labelled acetic acid by lithium aluminum hydride to methylene-labelled ethanol, and studies of methods for synthesizing methyl triphenylmethyl ether as well as of the decomposition of this ether. Reaction mechanisms being investigated include the rearrangement of carbonyl-labelled benzalacetophenone epoxide in alkaline solution and the rearrangement of unsymmetrical benzils. In connection with the latter, p-methoxy benzoin has been prepared by addition of p-anisyl Grignard reagent to N, N-diethyl-mandelamide. Since this reaction offers a method for preparing a series of C^{14} substituted unsymmetrical benzoins which may be oxidized to benzils, work is being continued. Analysis of acetic acid and ethanol by oxidation to carbon dioxide with copper oxide followed by manometric determination of the carbon dioxide has been carried out.

3. SUPPORTING CHEMICAL RESEARCH

Inorganic, Physical and Radiochemistry

The preparation of one gram quantities of spectrochemically pure rare earths continued with the separation of pure ytterbium, dysprosium, gadolinium and lutecium.

Deuteron bombardment of enriched molybdenum isotopes in the Carnegie Institution and University of California cyclotrons has made possible the identification of new technetium isotopes, the characterization of their nuclear properties and more definite mass assignments in many cases.

Investigation of the extraction of various metals into benzene solutions of TTA was extended to a study of lutecium, praseodymium and element 61. In addition, evidence for the effectiveness of TTA extraction in separating hafnium from zirconium was obtained.

Initial experiments were conducted aimed at the characterization of 18 m Ba^{141}, as part of the problem of studying the short-lived fission isotopes with half-lives from fractions of a minute to several minutes.

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Abstract of Quarterly Report (Continued)

Considerable progress was made in the determination of the crystal structure of $KRuO_4$ by X-ray diffraction. Means toward refinement of parameter values are in progress.

In the field of radiation chemistry, the calorimetric measurements of the energy imparted to various materials by radiations in the pile were completed and work was initiated to determine the rate at which hydrogen and oxygen combine at high temperatures when catalyzed by an aqueous slurry of U_3O_8.

Data for the solubility of uranyl sulfate in water have been extended to the critical temperature of water. The system uranyl sulfate-water displays a two liquid phase region with concentrations up to 82.7% UO_2SO_4. The lower critical solution temperature is 294° and the aqueous phase undergoes critical transformation at the critical temperature of pure water indicating that it is pure water at this temperature.

Methods developed for the preparation of solutions of heavy element and rare earth compounds which are fluid at 77° K for adsorption spectral studies have yielded satisfactory results.

Major problems arising in the fission-cloud chamber work, including effects of the neutron beam on track quality, diffuse tracks after prolonged operation and photographic difficulties are being attacked and overcome individually.

A sample of tritium gas diluted with normal hydrogen was analyzed for tritium with the gas density balance and condensed on palladium for use in the β-calorimeter. After calorimetric measurements of the tritium decay energy, the sample was converted to water and the heat evolution again measured. From these results and the rate of tritium evolution, now being determined, it will be possible to calculate accurate values for the half-life and average energy of decay.

Analytical Chemistry

All phases of the polarographic and electrolytic studies were completed including those of pentavalent manganese, separation of trace silver from macro amounts of palladium, rotating micro electrode, and the electroseparation of technetium from rhenium and molybdenum.

The following analytical procedures were satisfactorily developed or are now under study: spectrophotometric determination of aluminum in the presence of iron, the use of ammonium thioglycotate as a colorimetric reagent for uranium, colorimetric determination of selenium with pyrolle, determination of uranium in the presence of potassium dichromate with thiocyanate, the colorimetric determination of tellurium with thiourea, colorimetric determination of zirconium and a radiochemical method for plutonium.

Diffraction and Microscopy

The fibrous fracture surface in extruded beryllium has been exam-

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Abstract of Quarterly Report (Continued)

ined by electron diffraction revealing the presence of foreign material. Although the identity of this material is still uncertain, it is known to be amorphous, showing no crystal growth at 800° C. Examination of high-fired beryllia samples by X-ray diffraction leads to the conclusion that not a cubic, zincblende, structure is present but a phase of considerably lower symmetry, in addition to the hexagonal phase. Of interest is the occurrence of this new phase only in samples from which graphite or beryllium carbide was not excluded and which were heated at, or above, 2000° C.

Pile irradiation of magnesium, copper and aluminum has been found to produce no effect on the width of the x-ray diffraction lines, whereas rather strong effects were observed in samples of work hardened copper-beryllium alloy (2% Be). From these and other results for this alloy subjected to different heat treatments, it is tentatively concluded that irradiation produces more distortion of the crystal lattice of hard materials than of soft ones.

Instruments and Physical Measurement

Improvements aimed at circuit simplifications and better operation are being incorporated in the sweep type differential alpha energy analyzer. Several coincidence circuits have been investigated in the process of developing circuits with resolution times of 10^{-7} second or less. A simplified circuit has been developed for use with a flow-type proportional chamber permitting counting of weak beta emitters as well as alpha emitters.

4. ANALYTICAL SERVICE

The Technical and Operations Divisions, together, accounted for more than 97% of the total of 33349 analyses performed during the quarter.

The spectrographic determination of the amount of hafnium in zirconium has been refined further, now permitting analysis over the range 0.065 - 8.0% hafnium.

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1. REACTOR FUELS

Inorganic, Physical and Nuclear Chemistry

Solvent Extraction of Protactinium from Fluoride Solutions
(K. A. Kraus, A. Garen) (P.A. CI3-2)

In the previous quarterly report (ORNL-65, p. 18-24) experiments on the solvent extraction (using di-isopropyl carbinol) of Pa^{233} tracer from aqueous fluoride solutions were described. In these experiments the fluoride concentration was controlled (and varied over a considerable range) by the use of fluoride buffer systems (Al(III) - HF, and Th(IV) - HF). Since in these experiments the conditions were not sufficiently controlled (particularly the H_3O^+ concentration at equilibrium) it appeared desirable to repeat the experiments under more rigidly controlled conditions to determine more accurately the fluoride dependence of the extractability and hence perhaps obtain some information on the Pa species existing in the aqueous solution.

The new results which have been obtained with an Al(III) - HF buffer, using the experimental procedure previously discussed, are shown in Figure 1, where the distribution coefficient $D_o = \frac{P_{aq}}{P_s}$* has been plotted as a function

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* For a discussion of the theoretical considerations and explanation of all symbols used see the previous quarterly report, ORNL-65.

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of the concentration ratio $R = \frac{[HF]}{[Al^{+++}] - [HF]}$ which as a first approximation is proportional to the fluoride concentration of the solutions. Aside of the HF added, the composition of the solutions was: 1.8M H_3O^+, 1.75M Cl^-, and 0.086 M Al^{+++}.

In Figure 1, a plot of $D_o - D_o^o$ has also been included since, as has been previously shown, the slope of a plot of log $(D_o - D_o^o)$ vs. log [HF] (or as an approximation vs. log R) should directly yield the number of fluoride ions attached to the protactinium species in the solutions. As can be seen from Figure 1, the curve relating log $(D_o - D_o^o)$ and log R is S-shaped, with a central straight-line section of slope 2 (indicating a di-fluoride complex of Pa), a shallower initial section, suggesting the existence of a mono-fluoride complex of Pa, and a shallower section for large values of R, where the deviations from a slope of two, almost certainly are due to the assumption that R is proportional to [HF].

Assuming that the fluoride ions replace chloride ions, rather than oxide ions in the complex, which appears more probable, the reactions of protactinium with fluoride can be given by the equations

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$$PaO_xCl_m + HF + H_2O \longrightarrow PaO_xCl_{m-1}F + H_3O^+ \qquad \text{(Ia)}$$

$$PaO_xCl_m + 2HF + 2H_2O \longrightarrow PaO_xCl_{m-2}F_2 + 2H_3O^+ \qquad \text{(Ib)}$$

and $$PaO_xCl_{m-1}F + HF + H_2O \longrightarrow PaO_xCl_{m-2}F_2 + H_3O^+ \qquad \text{(Ic)}$$

The constants $$K^{(1)}_{ClF} = \frac{P^{(1)}_{ClF}\, h}{P_{Cl}\, f} \qquad \text{(IIa)}$$

$$K^{(12)}_{ClF} = \frac{P^{(2)}_{ClF}\, h^2}{P_{Cl}\, f^2} \qquad \text{(IIb)}$$

and $$K^{(2)}_{ClF} = \frac{P^{(2)}_{ClF}\, h}{P^{(1)}_{ClF}\, f} \qquad \text{(IIc)}$$

can be calculated from the data in Figure 1, provided a reasonable estimate of D* (the distribution coefficient $\frac{P_S}{P_{Cl}}$ of the extractable species) can be obtained. In the previous report it was shown that $\frac{P_S}{P_{aq}}$ can be at least 100 (i.e., $D_o = 0.01$) and thus $D^* \geqslant 100$. Using this value for D*, and equations 19, 18, and 13 given in the previous report, one obtains from the data $K^{(1)}_{ClF} \geqslant 1.8 \times 10^6$, $K^{(12)}_{ClF} \geqslant 1.4 \times 10^{11}$ and $K^{(2)}_{ClF} = 7.7 \times 10^4$. The corresponding constants for Th(IV) (where, however, apparently no chloride complexes exist under the conditions of the experiments) are $K^{(1)}_F = 4.5 \times 10^4$, $K^{(12)}_F = 2.9 \times 10^7$, and $K^{(2)}_F = 6.5 \times 10^2$. It should be pointed out that the fluoride complex constants for protactinium given are products of similar constant for the aquo-complexes and the stability constants for the chloride complexes. Since the latter almost certainly are larger than unity, the stability constants of the fluoride complexes with reference to the aquo-complexes (which are directly comparable with the constants given for Th(IV)) must be larger even than those given above. Thus there is little doubt that Pa(V) forms stronger fluoride complexes than Th(IV).

On the basis of these results it appears very unlikely that Pa(V) in the complexes at hand, is extensively oxygenated as are the ions of U(V), Np(V) and Pu(V). Since the (practically) covalently held oxygens decrease the effective (or formal) charge on the central ions, the ions XO_2^{++} have properties similar to those of X^{+4}ions (of the same element) or of ions of even slightly lower positive charge (e.g. $X^{+3.5}$), and the ions XO_2^+ correspondingly have properties similar to X^{+3}(or $X^{+2.5}$)ions(*). Ions of the type XO^{+3}, would thus

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*See also K. A. Kraus, J. R. Dam CN-1817, August 1946.

[redacted]

[redacted]

be expected to behave similarly to X^{+4}(or $X^{+3.5}$)ions. Since the stability of the fluoride complexes of Pa, however, is even higher than that of the corresponding complexes of Th^{+4} and their sizes not appreciably different, the chloride complex of Pa should contain less than one oxide ion per complex. This would suggest formulas of the type Pa (OH) $Cl_4(H_2O)_n$, $Pa_2OCl_8(H_2O)_{2n}$, and even $PaCl_5(H_2O)_n$. Depending on the preferred co-ordination number of Pa(V) in these complexes, "n" might be one or three (for co-ordination number 6 or 8).

Isolation of Americium from Plutonium Waste Solutions
(G. W. Smith, K. A. Kraus) (PA CX3-2)

Work has continued on the development of the isolation procedure for americium and has centered primarily around estimation of the size of adsorption column needed for the separation of Am from Pu and La and around the "recovery" of Am from the $CaSO_4$ - H_2SO_4 slurry obtained in the previous step of the procedure.

Using 1M H_2SO_4 solutions and Dowex-50 and permitting break-through of plutonium, it was found that a ca.25 cm^2 column should be sufficient for the isolation of all the Am in the 1M H_2SO_4 fraction available (20 liters, ca. 15g Pu, ca 10 mg Am).

Regarding the recovery of Am from the $CaSO_4$ - H_2SO_4 slurry, a number of methods were tried on a small scale among which were elution with citrate buffer, and metathesis with tartrate, carbonate and hydroxide .

Treatment of the precipitate with citrate buffers (pH 4 to 8) at room and elevated temperature yielded only 30-62% extraction of α -activity without enrichment of americium.

Tartrate metathesis (pH 6-8, elevated temperature) permitted reasonably ready dissolution of almost 80% of the α - activity in acid, but the remaining activity could only be removed with difficulty. In addition separation of americium from calcium in the presence of tartrate is quite difficult.

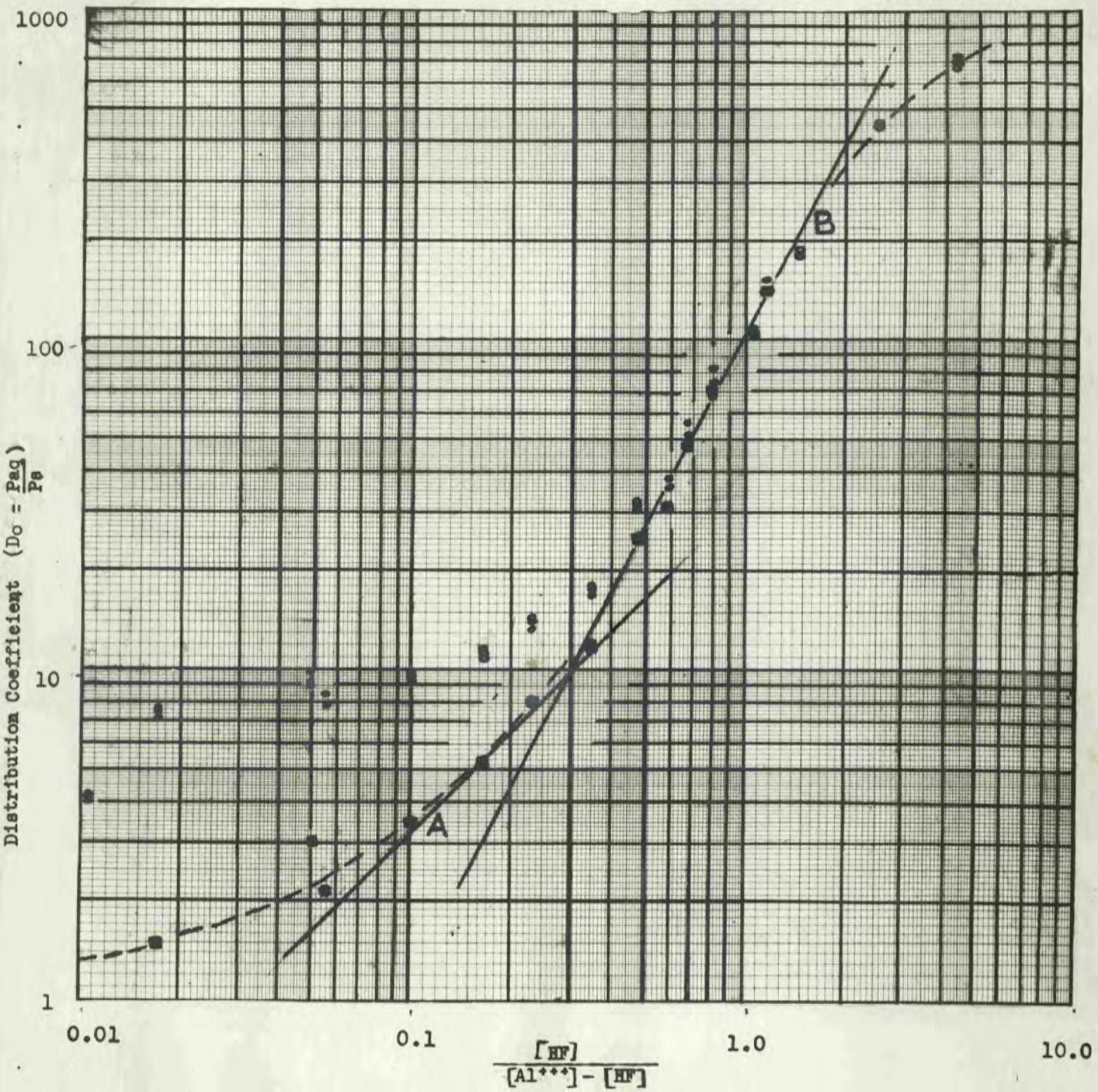
Carbonate metathesis permits ready dissolution of all material in acid, but appears undesirable since the gas evolution from the highly active solution would necessitate special equipment for safe handling.

Fortunately metathesis with ca 0.1M NaOH also is satisfactory for the dissolution of the activity in acid and at the same time permits separation of the activity from the bulk of the calcium, only a small amount of which dissolves in acid after metathesis.

In view of these observations a sodium hydroxide metathesis of the main portion of the $CaSO_4$ - H_2SO_4 slurry was carried out.

[redacted]

Drawing # 6254



Extractability of Pa^{233} from Fluoride Buffers

Legend : open circles - Observed values

—■—■— $D_o - D_o^o$

A Line with slope 1.0

B Line with slope 2.0

[redacted]

Process Chemistry

CX10-22 Chemical, Physical and Nuclear Properties of Heavy Isotopes
(R. A. Day and R. W. Stoughton)

A study of complexes of thorium in aqueous solutions is underway in which the stability constants of the complexes are determined by the observed decrease in extraction of thorium into a TTA-Benzene phase as complexing agent is added to the aqueous phase. The first complexing agent studied was HF in 0.5M HNO_3 medium. The thorium analyses were conducted radiochemically using Th^{234} (i.e. UX_1) tracer and adding macroscopic thorium to 10^{-6} M. Assuming no complexing with nitrate, the constants obtained for the following two equilibria were

$$Th^{+4} + HF = ThF^{+3} + H^+ \quad K_1 = 1.73 \times 10^4$$

$$Th^{+4} + 2HF = ThF_2^{+2} + 2H^+ \quad K_2 = 1.12 \times 10^7$$

The values obtained by H. W. Dodgen* by a different method in perchlorate

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H. W. Dodgen, MDDC-343 (1946)

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media, also at an ionic strength of 0.5, were $K_1 = 4.5 \times 10^4$ and $K_2 = 2.9 \times 10^7$. The two sets of values are consistent if the nitrate complex constant has a value of about 3, that is, if

$$Th^{+4} + NO_3^- = ThNO_3^{+3} \quad K_n \simeq 3.$$

This value is being checked by observing the extraction from HNO_3 - $HClO_4$ mixtures at an ionic strength of 0.5, and preliminary results indicate that K_n is of this order of magnitude.

In the extraction from HNO_3 - HF aqueous solutions, equilibrium seems to be reached in less than ½ hour, and results in pyrex vessels are the same as those obtained with platinum vessels for periods of up to 2 hours.

[redacted]

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CX5-9 The Recovery of Uranium from Enriched Piles
(J. P. McBride, F. T. Miles, J. M. Ruth)

Work has been continued on the distribution of organic amines and the effect of these amines as complexing agents for uranium. The experimental work is now essentially complete, and the data are being fitted to equations. When the quantitative theory has been worked out a report will be issued.

[redacted]

2. RADIOISOTOPES

[redacted]

Xenon Cross Sections as a Function of Energy

(A. R. Brosi, T. W. DeWitt, S. Freed, G. M. Hebert, G. W. Parker, H. Zeldes; and from the Physics Division, S. Bernstein, J. Dial, M. M. Shapiro and C. P. Stanford)

The assembly of glass equipment for the large scale preparation of I^{135} activity is virtually complete. This equipment is described by G. W. Parker in another section of this report. Tests of various components is under way and it is planned to proceed to cold test preparations in the near future.

Decay scheme of I^{135}

Previous spectrometer work on the decay scheme of I^{135} has shown the presence of three β groups of energies 0.47 Mev (35%), 1.0 Mev (40%), and 1.4 Mev (25%) and two γ groups of 1.27 Mev and 1.8 Mev (4%). The Xe^{135} isomer has a partially converted γ ray of 0.52 Mev, and has been estimated to occur in about 10% of the disintegrations. It has not proved possible to find suitable combinations of the several radiations to give a consistent total energy for the decay of I^{135} to the ground state of Xe^{135}. Also the estimated percent of disintegrations involving the Xe^{135} isomer was not consistent with its association with any of the β groups. Part of the difficulty was resolved by the results reported in the last quarterly report wherein a determination by a coincidence method of the fraction of decay by the isomer route gave a figure in the neighborhood of 20%. These experiments have been repeated with results of about 31 and 35% for two determinations. Thus, the earlier result has been confirmed qualitatively but not quantitatively. While the actual percentage of decay by the isomer route is thus still in considerable doubt, it does seem that it is in the neighborhood of 25-30% and that an assignment of the isomer to the 1.4 Mev β group is at least consistent with the percentages. This argument, and indeed, the whole determination of the percentage of decay by the isomer route, may be invalidated if an additional delayed γ ray of any appreciable half-life is found in the isomer mode of decay. Additional information was provided by coincidence counting of a calibrated I^{135} sample. This work definitely showed that the 1.4 Mev β group did not have a coincident γ ray. It was also noted that γ-γ coincidence occurred in about 40% of the disintegrations. Analysis of the coincidence counting data showed that it led to a disintegration rate about 30% higher than that given by the calibrated ion chamber. Using a tentative decay scheme, it can be shown that, if the 1.4 Mev β group had no γ associated with it, coincidence counting should have given the correct disintegration rate. On the other hand, a delayed γ would qualitatively give the results obtained (the Xe^{135} isomer does not interfere with this conclusion since the experiments were done under conditions permitting the escape of Xe from the sample). These data suggest that perhaps the Xe^{135} isomer is associated with the 1.4 Mev β group; but if this is so, one would expect to find another γ ray in this mode, since the 1.4 Mev β and the 0.52 γ of the Xe^{135} isomer do not give a sufficient total energy to match that of the other modes of decay. The missing energy amounts to 0.35 Mev. Coincidence counting on the Xe^{135} isomer showed conclusively that there is no prompt γ ray following the 0.52 Mev γ ray of the isomer. A search for such a γ ray was made on the β ray spectrometer with the cooperation of B. H. Ketelle. A large sample of I^{135}, in the form of NaI was prepared and mounted in such a way that moist air continually passed over the sample and removed Xe as it grew in. No γ ray of 0.35 Mev was found. The sample was then stoppered so the Xe would grow in with still no evidence for a low energy γ ray. A peak was found, however, corresponding to a γ ray of 0.84 Mev, whether the Xe was retained or not. This γ ray energy is about right to give the proper total energy (2.27 Mev) when combined with the 1.4 Mev β ray.

[redacted]

One additional piece of information is available from the spectrometer work. The presence of an 0.52 Mev γ ray, which previously had been masked by the 0.52 Mev γ ray of the Xe^{135} isomer, in the I^{135} disintegration was suspected. Such a γ ray showed up in the spectrometer when there was reason to believe the Xe was being continuously removed. On stoppering the sample, the height of this peak increased. While it is still conceivable that the short-lived isomer was not being removed from the sample sufficiently rapidly to completely remove evidence of its γ ray, this seems somewhat improbable and the presence of an 0.52 γ ray in the iodine decay is considered at least tentatively established.

While several new facts have been added concerning the decay of I^{135}, it is still not possible to fit these into a satisfactory decay scheme.

Calibration of the gas counting apparatus

The gas counting apparatus described in the last quarterly report has been calibrated by coincidence counting of Xe^{133} and Xe^{135}. It has also been used to check the calibration of the ion chamber for I^{135}. A sample of NaI^{135} was measured in the calibrated ion chamber. An aliquot of this was placed in the gas counting apparatus and Xe allowed to grow in for 12 hours. This Xe was transferred to the gas counting bulb, and coincidence counting done on it. Absorption curves with both Al and Pb were obtained. Counting was continued until all the 9.2 hour Xe had decayed. It was then found that an appreciable fraction of the disintegrations (9.7%) consisted of the 5.4 day Xe^{133}. When the original coincidence counting data were corrected for the Xe^{133} and for the conversion electrons from Xe^{135}, and absolute disintegration rate of 4.00×10^6 disintegrations per minute was obtained, as an average of fifteen determinations with an average deviation of 2.8%. The disintegrations per minute expected by calculation from the ion chamber data on I^{135} were 4.01×10^6. The agreement is considered satisfactory.

Disintegration rates from coincidence counting on both Xe^{133} and Xe^{135} as a function of absorber permitted calculation of the counting yield as a function of absorber thickness for each of the two xenons. The two resulting curves were extrapolated back until they intersected. This point of intersection corresponded to a window + air + bulb absorber thickness of 23.7 mg/cm^2 and a counting yield with no absorber of 15.2%. Both these figures are quite reasonable for the apparatus.

Processing Equipment for the Separation of $(I\text{-}Xe)^{135}$* P.A. CX1-9: (G. W. Parker, G. M. Hebert, G. E. Creek, P. M. Lantz)

I. Introduction:

In the following sketches, a fairly detailed representation is made of the exact status of the chemical processing and mechanical remote-control equipment for the high radiation level separation of the 6.7 hr I^{135}-9.2 hr Xe^{135}. Only a few final pieces of small equipment are not shown including those which are already fabricated but are left out to maintain access through the small doorway.

In a previous Quarterly Report, MonN-432, pp. 73-76, a proposed scheme of separations is outlined and related to an earlier sketch of the incomplete processing equipment. In the earlier description, consideration is given for a number of influencing factors including: scale of operation; installation of auxiliary shielding; choice of glass equipment; advantage of the centrifuge technique; need for elaborate off-gas system; etc. At the same time an outline of necessary time lapse is given for 8 major steps in the process from the procurement and loading of slugs to the release of the finished wafer assembly in a carrying shield. The entire chemical operation is designed to require a minimum expenditure of time from the instant of pile shut-down to the "zero" or trapping time when the Xe is approximately quantitatively held in the PdI_2 crystals. This period as estimated would vary from 3½ to 5 hours. For previous history of the Xenon Problem, see papers by S. Freed, A. R. Brosi, S. Bernstein, M. Shapiro and others, e.g., in MonN-311 and subsequent Quarterly Reports.

II. Sectional Views of the Processing and Handling Equipment:

A. View of the Cell Rear Wall Showing Most of the Glass Equipment

A simplified plan of the connection of the three major glass vessels and the two slug coating dissolver vessels is arranged with the deletion of a great many connecting tubes, control shafts and supporting parts. The chemical flow plan would consist of:

(1) dropping of the slugs into the Hastelloy Baskets for removal of aluminum coats;
(2) dissolution of the uranium with HCl in two Dissolvers;
(3) oxidation of the UCl_4 with $Li_2Cr_2O_7$ and of the iodide with $Fe_2(SO_4)_3$;
(4) distillation of I_2 from the Central Reactor;
(5) reduction of I_2 with SO_2 and the precipitation of PdI_2 in the Distillate Receiver;
(6) transfer of a PdI_2 slurry through the Decanting Pipette into the Centrifuge Funnel.

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* This operation is part of the general program, "The Cross-Section of Xe^{135m}.

In this view are also included some details indicated by circled figures:

(1) one of three 650 watt quartz covered resistance winding heaters; these heaters supplement the radiant lamps and are designed for compactness, efficiency and freedom from corrosion;
(2) the 1000 watt radiant drying lamps for additional heating;
(3) a platinum-tungsten electrode pair for the precise control of the $Li_2Cr_2O_7$ and $Fe_2(SO_4)_3$ oxidations;
(4) view of the slug chute brake for loading the slugs into the Hastelloy Baskets.

B. View of the Cell Left Wall with Details of the Centrifuge and Cup

The essentials of the mechanism for operating the centrifuge can be seen here which stepwise approximately constitutes the following operations:

(1) the prepared centrifuge cup and balance cup are pre-arranged in the centrifuge;
(2) the slurry of PdI_2 is charged into the centrifuge cup while it is held in the "stop" position. The decanting pipette is then elevated and the stop withdrawn;
(3) the first centrifugation is made, requiring about 5 minutes. The cup is brought again to the stop position and the supernatant liquid is syphoned off through the decanting pipette. At the same position a new tare weight is placed in the balance cup by means of the wafer tongs;
(4) a small amount of wash solution is added through the receiver vessel and the decanting pipette spray head and a second centrifugation is made;
(5) the centrifuge cup is again brought to the stop position and decanted thoroughly using the platinum tube capillary pipette. Wash solvents of alcohol or ether are added and a third centrifugation is made which also requires a change in tare weights;
(6) again at the stop position the vacuum drier is attached and allowed to draw a small amount of air through the sample to free it of remaining solvent vapors;
(7) the stop is released and the cup is rotated 180° to the stop position where the funnel tong is used to remove the plastic funnel. At the same position the wafer tong picks up the active wafer and deposits it in a vacuum holder on the turntable shown in the view facing the operating wall.

In this view the circled figures indicate:

(5) the assembled metal wafer block with the active and blank capillary in cross-section;
(6) the plastic centrifuge funnel.

C. View of the Cell Facing the Interior Operating Wall

A more realistic view of the size of the centrifuge housing and the nature of the remote handling equipment is available here. The positions of the periscope, the access door and the manipulating boom are indicated. The functional operations which can be related to this view are:

(1) The sealing of the capillary with aluminum tapered plugs is performed by manually inserting and pressing them into the ends of the wafer by means of a rod through an opening not shown just above the turntable.

(2) The final operation consists of loading the wafer into a shield which is stationed before a small opening in the 3" lead inner door to the cell. A track for guiding the drawer into the shield is also omitted from this view.

III. Improvement of the Mechanical Yield of the PdI_2 in the Centrifuge Assembly

A. Choice of the Plastic Centrifuge Funnel

In view No. 2, or the left wall of the separations cell, an additional detail is given of a cut-away view of the centrifuge assembly and wafer carrier. The fluorothene plastic centrifuge funnel illustrated represents the second plastic material tried for this most important feature, the first having been of the more transparent material, lucite or plexiglass. Fluorothene, while not able to offer the useful advantage of water-white transparency, is considerably tougher and less likely to fracture during centrifugation or dismantling of the assembled unit.

A more detailed drawing of the Capillary Tube Assembly has been reproduced in the Quarterly Report, CNL-37, pg. 64, together with an account of the experience with types of filters, coating of the plexiglass funnel and with macrographs of desirable and undesirable PdI_2 centrifuged precipitates.

B. Effect of SiO_2 Coating on the Physical Loss of PdI_2

Until recently, it was feared that the yield of the PdI_2 because of physical losses on the walls of the plastic centrifuge funnel would eventually result in a serious discrepancy in yield from the operation. For this reason, steps have been taken for preparation of a highly polished surface on the fluorothene and also for the production of a third type plastic funnel of molded saran. In the meantime a comparative test was made of the effect of a quartz (SiO_2) coating vaporized in a vacuum and deposited on the plastic surface by L. T. Newman. The effect of the SiO_2 coating toward inhibiting loss of PdI_2 on either of the existing plastic funnels was highly pleasing and has, in fact, afforded almost quantitative centrifugation into the capillary tube. For a rough comparison: in a number of tests the average PdI_2 recovered weight was about 7 mgs out of a theoretical 10.5. In the test with the quartz coated fluorothene funnel the yield was 10.5 out of 10.5. It

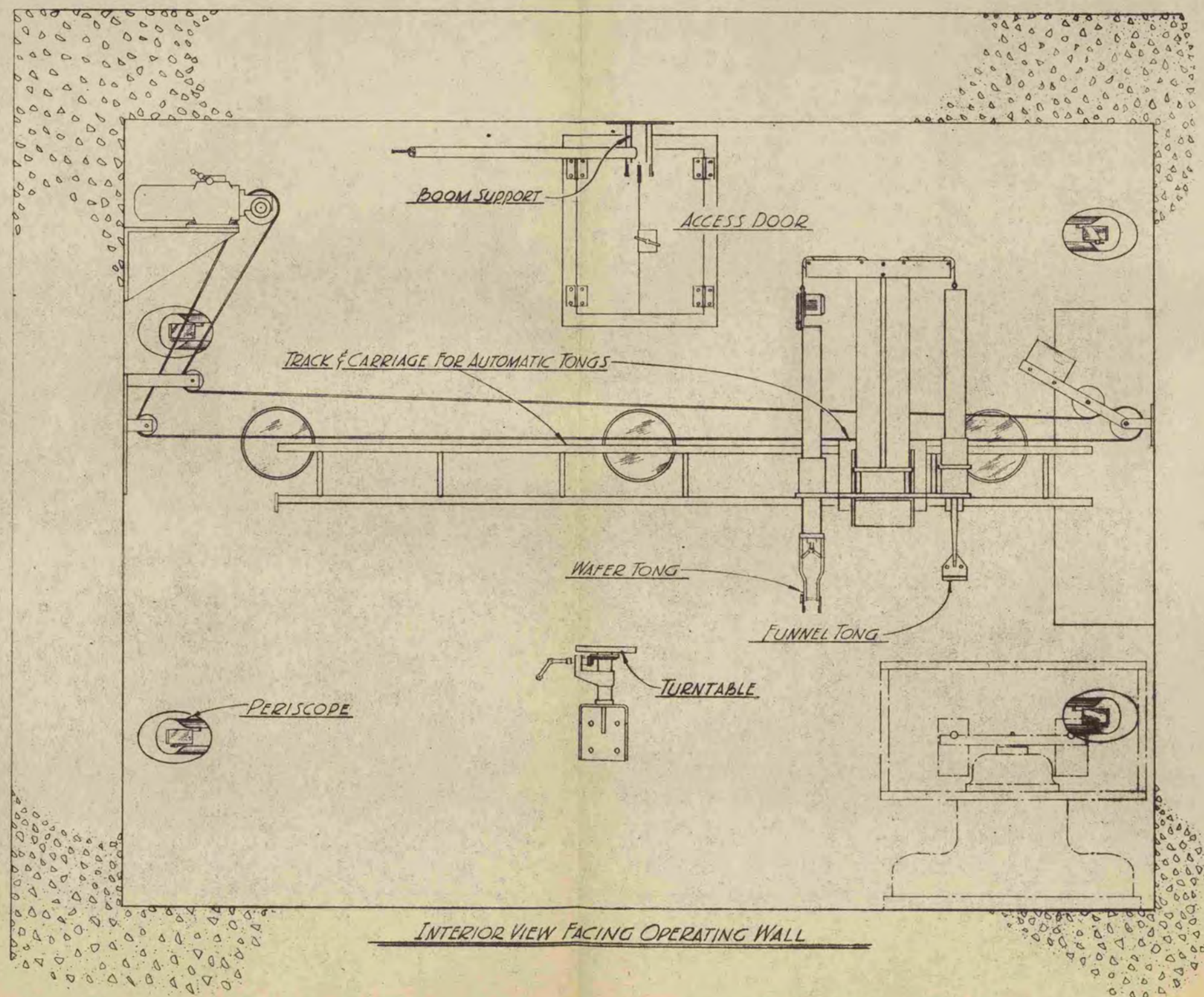
is expected that should any SiO_2 coating be carried with the precipitate into the capillary, it will have an insignificant scattering effect, of the same order as the carrier palladium.

C. Angulation of the surface PdI_2 Sample in the Capillary

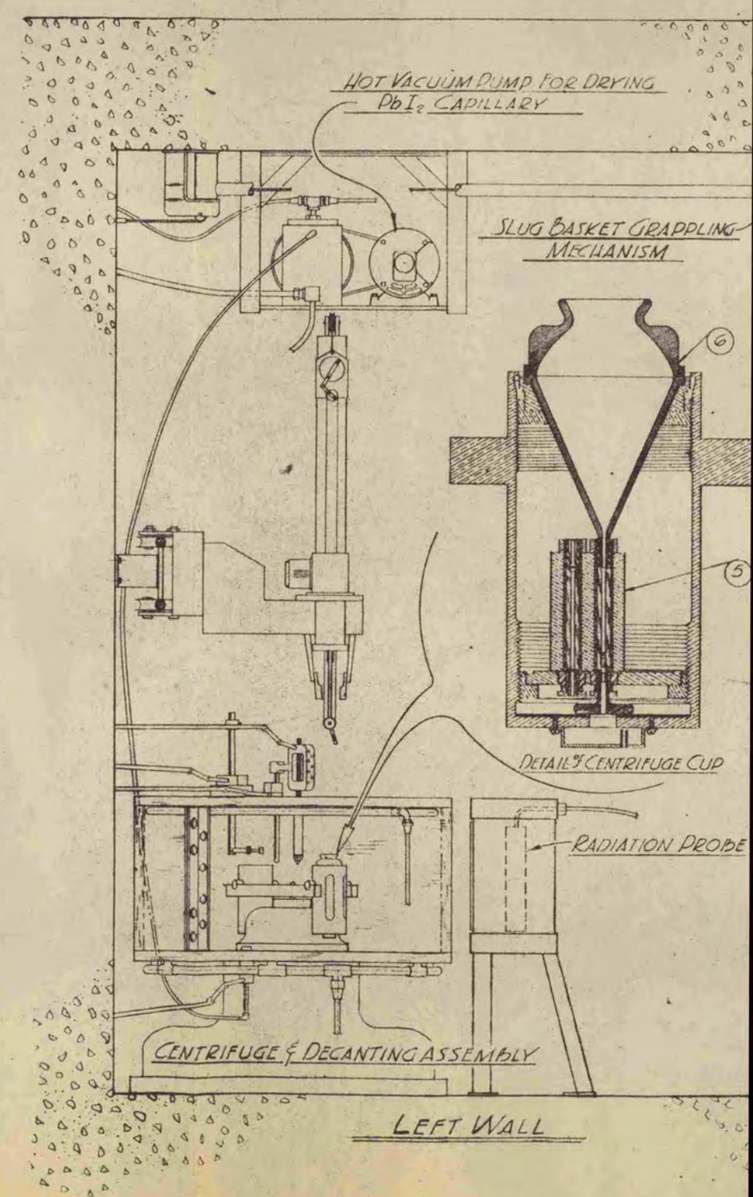
It has been noted consistently that due to the length of the capillary tube and the effect of the rotation, the precipitate tends to pack with a surface angle in excess of 45°. Since the precipitate has a unit length of about 0.7 mm per mg, this means a rather thick sample depth of about 7-8 mm with one side approximately 2 mm longer than the other. If it is shown that the angulation is highly undesirable, it may be possible to correct it by re-suspending the top portion of the precipitate and centrifuging again more slowly.

[redacted]

PROCESS EQUIPMENT FOR SEPAR

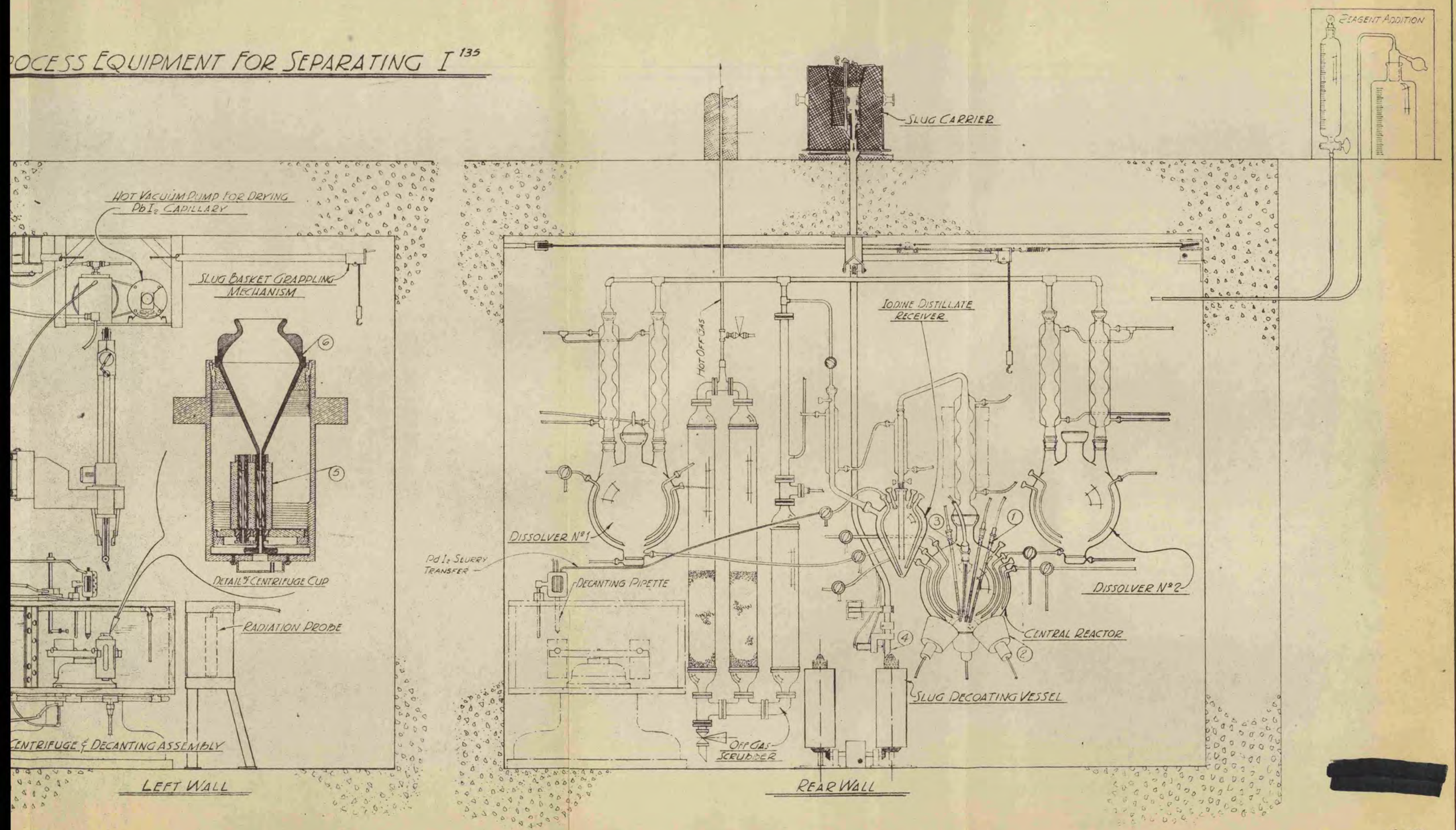


INTERIOR VIEW FACING OPERATING WALL



LEFT WALL

PROCESS EQUIPMENT FOR SEPARATING I^{135}



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F-4582

Research Relating to Radioisotope Production

Ion-Exchange Separations with a "Disjointed" Column: (H.W. Kohn, J.A. Swartout)

During the course of research on the removal of alpha emitters from fission products by ion-exchange techniques, the potential attractiveness of a disjointed, or segmented, column for more rapid separations became apparent.

Two experiments (Exps. 2 and 3) were performed to determine more exactly the feasibility of this disjointed column procedure proposed in the last quarterly report (ORNL-65, pg. 70) on the basis of calculations from an initial experiment (Exp. 1). The procedures used in these subsequent experiments are as follows:

A Tygon tube, 3/16" diam., was filled to a height of 86 cm with Dowex 50* and preconditioned to a pH of 3 with 5% citrate solution. Fifty ml of a solution of a 7 day cooled ORNL U-slug was absorbed on a small preabsorption column of Dowex 50 which was 4 mm in diameter x 4 cm long. After the bulk of Cb and Zr had been removed by washing with $(NH_4)_2SiF_6$ at pH 3 to prevent excessive contamination of the monitoring devices, the column was washed with 5% citrate at pH 3 until the yttrium peak of activity had been eluted. The flow was stopped and the "radiograph" so developed was determined by separating the column into 1 cm portions with hemostats and cutting it up. The activity in each portion was determined by equilibrating the portion with 6 N HCl and counting an aliquot. Since Experiment 2 did not agree with Experiment 1, Experiment 3 was run as a check. It agrees essentially with Experiment 2. The results are shown in the table and graphs.

The discrepancies between the results of Experiments 2 and 3 and the calculated values from Experiment 1 lead the experimenter to the conclusion that the activity bands may not move down the column at a linear rate, an assumption which was made in the calculations for the first experiment. The only substantiating datum is the fact that the number of theoretical plates in a column is not directly proportional to its length.(1)

Table I

Position of Rare Earth Activities on Dowex 50 Column

	Position of Peak			Position of Band		
Element	Exp. 1	Exp. 2[2]	Exp. 3[2]	Exp. 1	Exp. 2[2]	Exp. 3[2]
Y	86	86	86	79-86	78-86	64-86
Eu	73.5	71.5	---	67-79.5	61.5-80	-----
61	57.5	46.5	41.5	51.8-62.3	41.0-56.5	34-45[3]
Am	54.5	----	----	49.0-60.0	-----	-----
Nd	40.5	31.0	29.0	35.7-45.3	22.5-35.0	22-34
Pr	24.1	18.0	17.5	20.4-27.8	11.5-25.5	11.5-22
Ce	14.5	8.5	8.0	11.8-17.4	4-12	4-11.5
La	----	3.0	1.5	-----	0-4	0-4

* The Dowex 50 was the same resin which had been used in Experiment 1.

(1) Matheson, L.A., Private communication.
(2) Normalized so that the Y peak is always at 86 cm. from the top of the column.
(3) A young slug was used in Experiment 3 so that low levels of radioactivity make the positions of 61 and Eu open to considerable doubt.

Recovery of Zirconium and Columbium from Separations Process Wastes: (H. W. Kohn, J. A. Swartout)

Introduction:

Because of the current interest in the isolation of fission zirconium and columbium from separations process waste, exploratory research was initiated to determine the feasibility of their extraction from bismuth phosphate and Redox wastes. Emphasis has been placed on ion-exchange and physical adsorption methods because of our extensive background in this field and because reports indicated that other laboratories were investigating solvent-extraction and precipitation procedures.

The chemical compositions of the waste solutions from which extraction of zirconium and columbium is desired are indicated below:

Table I: Composition of Waste Solutions

$BiPO_4$ Extraction Waste Solution	Redox Raffinate (IAW)
20% UNH	0.7 M $Al(NO_3)_3$
0.5 M H_3PO_4	(or 4 M NH_4NO_3)
0.5 M H_2SO_4	0.6 M HNO_3
1 M HNO_3	0.05 M $Na_2Cr_2O_7$

Experimental Work:

Two sets of experiments were conducted to compare the efficiency of various adsorbents and ion-exchangers in removing zirconium and columbium from synthetic wastes solutions spiked with tracer and also of various elutriants in removing the adsorbed Zr and Cb.

(1) A series of equilibrium experiments was performed to determine the distribution coefficients of Zr-Cb tracer between several adsorbents and Redox and precipitation process wastes. The tracer was prepared by absorbing Zr-Cb from an oxalate solution (about 30% absorbs) on a Dowex column, washing with dilute acid and then digesting the column with concentrated HNO_3. The excess HNO_3 was removed by volatilization. Ten ml. of the waste solution, to which 100 λ of the tracer had been added (giving 1870 γ c/m) was shaken with amounts of adsorbent varying between 0.04 - 1 gm. Dowex 50, coconut charcoal, sea sand, and glass wool were used with controls, and the amount of tracer adsorbed was determined by gamma counting the supernatant. The change in γ counts was often too low to give more than an order of magnitude, i.e., Kd varied between 0-4, except in the case of adsorbent charcoal on Redox process wastes. A typical set of data is given in Table II.

Table II: Adsorption of Zr and Cb from Redox Raffinate by Charcoal

Adsorbent	% Adsorbed	Kd
200 mg. C.	72	126.4
1,000 gms. C.	95	207

The 207 figure is open to considerable question because of the low counting rate involved. The Zr-Cb activity was slowly eluted from the charcoal with saturated $H_2C_2O_4$.

(2) The specificity of charcoal for adsorption of Zr and Cb from the Redox raffinate and methods for eluting the adsorbed Zr and Cb were investigated.

A sample of "synthetic" Redox raffinate solution, spiked with 7 day cooled fission product mixture, was equilibrated with coconut charcoal. The separated charcoal was treated with various reagents to determine if the Zr and Cb could be selectively desorbed. Results are indicated briefly below:

Table III: Desorption of Zr and Cb from Charcoal

Reagent	Comments
H_2O	Slow removal, large volume - 240 ml/gm C
0.3N HCl	Slow removal, large volume - 240 ml/gm C
5% oxalic acid	No separation of Zr and Cb from other adsorbed F.P.'s
5% $(NH_4)_2SiF_6$, pH ≐ 3	Preferential elution of Zr and Cb

Measurements of the decay and absorption of radiations from the $(NH_4)_2SiF_6$ elutriant indicated only Cb and Zr with a small amount (1.5%) of a hard beta emitter, possibly 17 h Zr.

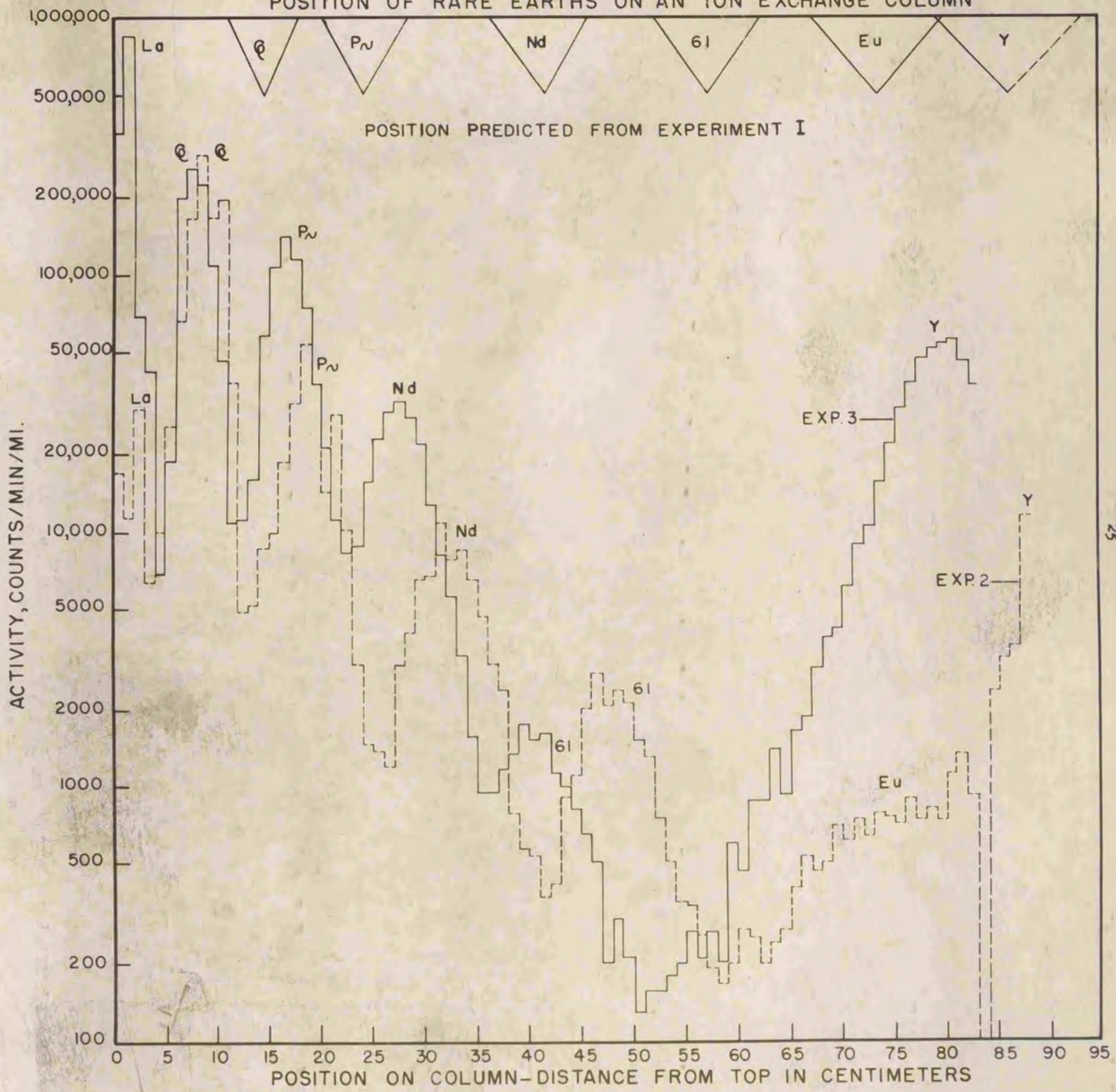
Direct adsorption of Zr-Cb from the Redox raffinate passed through a charcoal column was unsatisfactory; in addition, considerable gas evolution occurred as a result of variations in room temperature.

Conclusions:

From these preliminary results, the use of charcoal to adsorb Zr and Cb from the Redox raffinate appears promising. Considerable more research to establish optimum conditions, the purity of the products, and eventually the feasibility of larger scale application will be required. No promising adsorption method for removing Zr and Cb from the $BiPO_4$ extraction waste was disclosed. Continuation of this research depends upon decisions as to the ultimate feasibility of the use of the products.

UNCLASSIFIED

Drawing # 6299



Separation of Fission Rare Earths: (W. H. Baldwin, A. W. Smith, J. A. Swartout)

I. Introduction:

As reported last quarter (ORNL-65, pg. 76), the primary problem in the separation of Eu and Sm from fission product mixtures which have "cooled" only a short time is the preliminary separation of the two from fission yttrium. Tests with TTA extraction, reported previously and here, indicate that an ion-exchange procedure is to be preferred. Therefore, emphasis will be applied to the establishment of the optimum conditions for ion-exchange separation, compatible with the necessary restrictions imposed by remote control. Of the readily available resins, Dowex 50 appears to have the most desirable properties. Among variables in its use which are being investigated are (1) eluting agents which give more favorable distribution ratios than citrate solutions and (2) temperature. An apparatus to permit the study of equilibrium distributions at temperatures between 25° and 100° C has been installed.

II. Ion-Exchange:

A. Eluting Agents - Other than Citrate:

Tompkins and Mayer[1] reported distribution coefficients for element 61 and Eu between Dowex 50 and several complexing agents in aqueous solution. Two complexing agents, acetylacetone at pH 7.2 and tartaric acid at pH 2.85, seemed to give more favorable separation; these have been examined further for the separation of Y and Eu. Acetylacetone (5%) has proved to be insufficiently stable at pH 7.2 to warrant further investigation. A separation of Y and Eu was made with 5% tartrate at pH 2.85 but the solution was so concentrated as to deposit crystals slowly. This interfered with the flow of solution through the column by plugging the outlet. Further investigation is planned with more dilute tartrate (i.e. 1%). This will involve equilibrium experiments with Dowex 50, 1% tartrate solutions and Y and Eu at room temperature before attempting column runs.

B. Lower Concentrations of Citrate:

Since the Ames group has reported lower concentrations (0.1%) of citrate to be more satisfactory for separating milligram quantities of rare earths than the 5% citrate, these lower concentrations are being examined by equilibration studies to select suitable column conditions. A preliminary test with 0.1% citrate indicated that this suffered from the fact that when column conditions were changed, a relatively long washing was required to attain steady-state conditions. When the pH of the eluting solution was raised from 3.1 to 5.0, the effluent from the column had a pH less than 4.5 after 20 column volumes had been allowed to run through the column at room temperature. Since the conditions often used for column separations require that the rare earth mixture be placed on the column at pH 1, this time lag is considered undesirable.

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(1) E. R. Tompkins and S. W. Mayer, J. Am. Chem. Soc. 69, 2864 (1947).

C. Physical Properties of Dowex 50:

In order to develop reliable methods for the preparation of reproducible lots of resin for use in ion-exchange columns, two lines of attack have been followed. The first is a determination of the effect of chemical pretreatment on the resin and the second, the development of methods for uniform physical classification of resin particles.

(1) Cations, other than H^+, were removed from Dowex 50 by washing with 3 M HCl. The resin was then refluxed with constant boiling HCl (20%) and is now being examined for structural changes.

(2) A resin of uniform particle size is desirable for reproducible experimental results and for minimum flow resistance in column operation. Wet and dry screening did not give predictable or consistent results. A counter-current sedimentation apparatus was devised and revised to produce head control and eliminate bubbles (Figure 1).

III. Solvent Extraction with TTA:

It was reported previously (ORNL-65, pg. 76) that single stage equilibration of Y and Eu between benzene containing 0.2 M TTA and an aqueous solution containing 0.1 M NaCl gave distribution ratios of Y/Eu of about 2.2. It was believed that an advantage would result if the aqueous solution contained a buffer which would form a complex with the rare earths. Accordingly, equilibrations were made with benzene containing 0.2 M TTA and aqueous solutions containing 0.23 M citrate. A somewhat more favorable ratio of distribution coefficients resulted (i.e. 3.2 and 3.5, see Table I) but this has not been tested in the counter-current machine.

Table I

Single Stage Equilibrium Distribution of Y and Eu at R. T.

Benzene, 0.2 M TTA
Aqueous, 0.23 M citric acid pH adjusted with NH_4OH contained Eu and Y tracer

pH	Observed D.C. Y	Observed D.C. Eu	Ratio D.C. Y/Eu
5.7	0.017	0.0049	3.5
6.4	5.5	1.7	3.2

COUNTERCURRENT SEDIMENTATION APPARATUS

1. Heat exchanger - warms distilled water entering lower end of jacket and cools hot water descending bore.

2. Heater - heats warmed water from 1. almost to boiling expelling dissolved gases.

3. Variac - controls current to 2.

4. Fluid head regulator - regulates head to vest of apparatus and allows escape of gases.

5. Cooler - cooled water from 1. is cooled to room temperature.

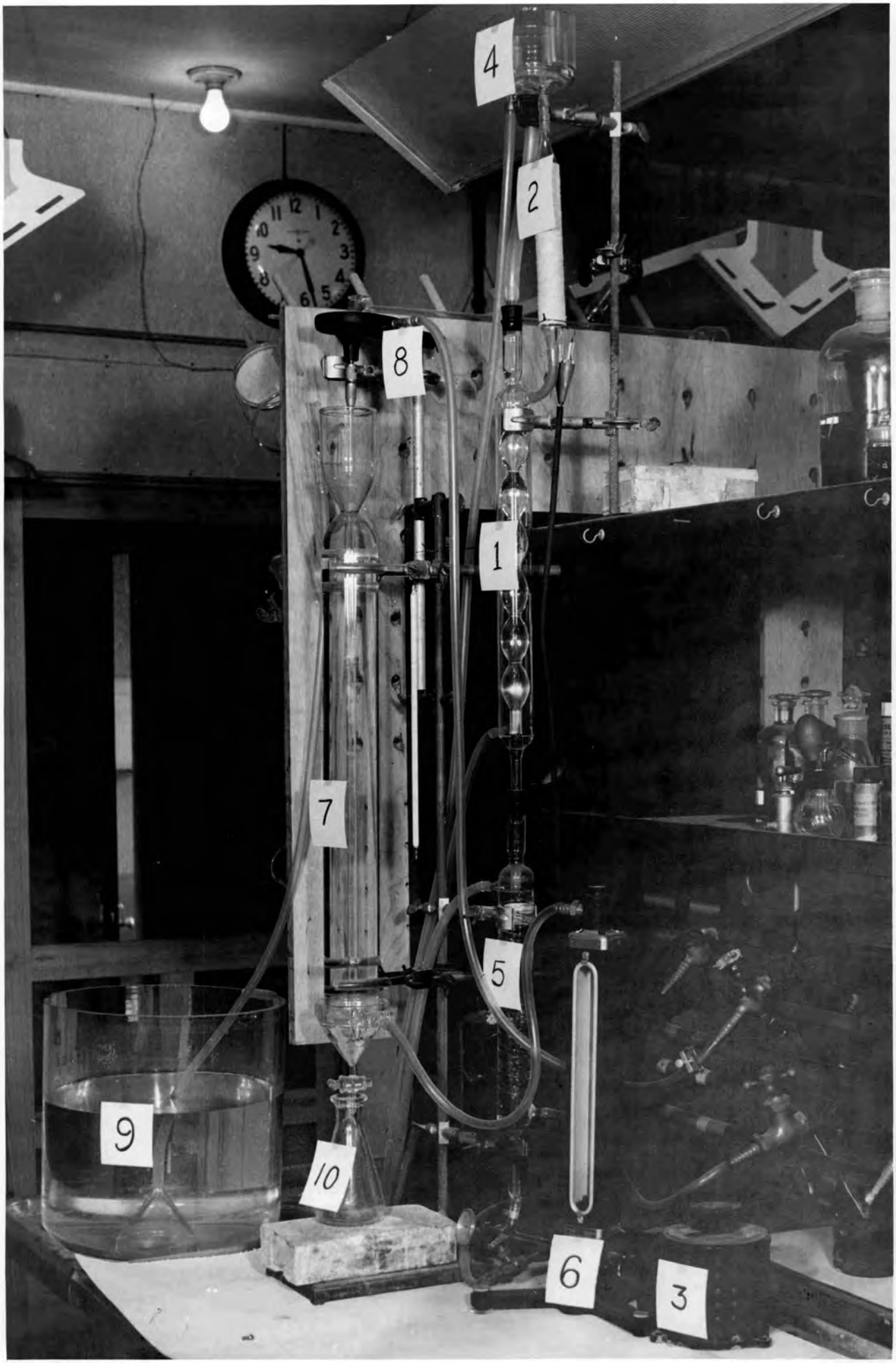
6. Flowrator - indicates flow through 7.

7. Sedimentor - resin slurry fed from top is dispensed across the rising column of water separating the coarse from fine particles.

8. Stirrer - agitates slurry.

9. Fine particle collector.

10. Coarse particle collector.


4
2
8
1
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3

<u>C^{14} from Beryllium Nitride</u>: (A. J. Weinberger, J. A. Swartout)

The work on this problem has been essentially completed. Details of the approved chemical process for extracting C^{14} from Be_3N_2 and results of the extensive testing will be reported in ORNL-141, "Extraction of C^{14} from Beryllium Nitride", which will also serve as a process recommendation to the Isotope Development Branch of the ORNL Operations Department.

 [redacted]

Experimental Use of C^{14} (C. J. Collins, D. N. Hess, O. K. Neville, R. F. Nystrom, W. J. Skraba, A. R. Van Dyken) - P.A. CX4-4

Summary

The rearrangement of carbonyl-labelled benzalacetophenone epoxide in alkaline solution has been studied further.

Fair yields of p-methoxy benzoin have been obtained by the addition of the p-anisyl Grignard reagent to N, N--diethyl-mandelamide. Further work is in progress on this reaction, since by the use of other Grignard reagents a series of C^{14} substituted unsymmetrical benzoins may be prepared. Oxidation of these benzoins will yield the corresponding benzils.

Model experiments have been carried out on the synthesis of ring-labelled benzoic acid. A material balance on the decomposition of methyl triphenylmethyl ether was carried out and methods of synthesizing the ether devised. Carbon dioxide-C^{14} has been reduced to methanol-C^{14} in high yield by lithium aluminum hydride. The reduction of carboxyl-labelled acetic acid by lithium aluminum hydride to methylene-labelled ethanol has been accomplished on a tracer scale.

The oxidation of acetic acid and ethanol to carbon dioxide by copper oxide and determination of the carbon dioxide manometrically was carried out.

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

Formaldehyde (A. R. Van Dyken)

The decomposition of ϕ_3COCH_3 was carried out especially to obtain a material balance. More than 95% of the material present as the $-OCH_3$ group can be recovered or determined as CH_2O, CO, and CH_3OH. Complete decomposition takes place in less than two hours at 375°C.

Methods of preparing ϕ_3COCH_3 avoiding an excess of methanol have been devised. It was found that metharol and a slight excess of ϕ_3CCl react in the presence of pyridine at room temperature using either benzene or diethyl ether as solvent. From such preparations pure ϕ_3COCH_3 can be recovered in 85% yield by recrystallizing from methanol.

If the crude product from the above preparation can be decomposed in a satisfactory manner (i.e. good yields of CH_2O) maximum recovery of C^{14} from labelled $\phi_3COC^{14}H_3$ can be obtained. Therefore, ϕ_3COCH_3 was decomposed in the presence of ϕ_3COH and ϕ_3CCl. In the presence of ϕ_3COH decomposition took place satisfactorily yielding 65% CH_2O, however, in the presence of ϕ_3CCl the yield of CH_2O was decreased to less than 30%, and CO and CH_3OH were found in correspondingly larger amounts. Therefore, in any preparation of ϕ_3COCH_3 it is necessary to hydrolyze carefully the excess ϕ_3CCl to ϕ_3COH before decomposition is carried out. Preparation of "dead" ϕ_3COCH_3 using quantities similar to those to be used in tracer experiments have been carried out and decomposition of this ether to check the methods of chemical and radio-chemical assays is underway.

[redacted]

The CO formed during decomposition may arise directly from CH_2O in which case an equivalent amount of H_2 would be formed. This was checked and within the limits of error no hydrogen was found, which agrees with that of Norris[1] who reports only CO as a gaseous product of his decomposition. This work is near completion and a final report will be issued in the succeeding period.

Methanol, Ethanol and Acetic Acid (D. N. Hess, R. F. Nystrom, W. J. Skraba)

It was previously reported that a 16% dilution had occurred in the synthesis of methanol from carbon dioxide and lithium aluminum hydride. As a consequence of this all the reagents used in the process were carefully analyzed and blank experiments performed. Ethyl ether present to the extent of 2 to 3% in the lithium aluminum hydride was found to be the diluent. The amount of methanol in the hydride was redetermined and found in smaller quantities than previously reported. Methanol-C^{14} has now been prepared in yields ranging from 77 to 92% by the hydride process without any appreciable dilution.

Carboxyl-labelled acetic acid has been reduced to ethanol by lithium aluminum hydride on a tracer scale in 90% yield. It should be noted that if the Grignard reaction could be conducted in such a way that only acetoxy magnesium iodide would form, then the latter could be reduced to ethanol without isolating the acetic acid.

At present, the best method for preparing acetic acid is the addition of carbon dioxide to the Grignard reagent at -30°C. In this procedure the carbon dioxide is added to an excess of the Grignard reagent and this may explain the presence of by-products, namely, acetone and tertiary butyl alcohol. Therefore, it is hoped that the "reverse" addition described below will eliminate or reduce these side reactions.

An apparatus for the carbonation of Grignard reagents at low temperature (i.e. from 0°C to -80°C) has been constructed. The general technique involves the addition of an equivalent quantity of Grignard reagent to carbon dioxide at lowered temperatures. A material balance for the reaction can be obtained from the initial and final concentration of the Grignard reagent and the amount of carbon dioxide taken up during the reaction which is determined manometrically in a system of known volume.

Experimental

Reduction of Carbon Dioxide-C^{14} to Methanol-C^{14}. The apparatus and equations for the preparation of methanol from carbon dioxide and lithium aluminum hydride have been described previously. Barium carbonate-C^{14} was calibrated by converting it to carbon dioxide and transferring the latter to an ionization chamber. Nitrogen gas was used as a diluent. The specific activity of the barium carbonate-C^{14} was found to be 5.75 uc./mmol. Dry carbon dioxide, diluted with helium, generated by adding 30% perchloric acid to 2.014 grams (10.2 mmols.) of barium carbonate (containing 58.76 uc. of C^{14}) was passed through a solution of 0.9 gram

(1) Norris, J. F. and Cresswell, J. Am. Chem. Soc. 55, 4946-51 (1933)

[redacted]

of lithium aluminum hydride in 100 cc. of diethyl carbitol (b.p. 84°C./16 mm.). The time required for the addition of carbon dioxide was 75 minutes. Fifteen minutes after the last addition of carbon dioxide, 60 cc. of n-butyl carbitol (b.p. 126°C./26 mm.) was added dropwise. Then the ethyl ether was removed by passing helium through the solution for 45 minutes at 40°C. A small amount of methanol was lost at this point. The receiver was then cooled by liquid nitrogen and the still-pot temperature held at 140°C. for two hours. Next the traps containing the distillate were sealed off and attached to the vacuum-line. The methanol was vacuum distilled from the distillate at -45°C. and 10^{-4} mm. into a trap cooled by liquid nitrogen. After four distillations the methanol was freed of the diethyl carbitol. The vapor pressure of the product was 29.0 mm. at 0°C. A yield of 252 mg or 77% of methanol-C^{14} was secured. The specific activity of the methanol was 5.71 uc./mmol as compared with 5.75 uc./mmol for the barium carbonate. Eleven microcuries of C^{14} were found in the still-pot which suggested that a higher yield of methanol may be realized if the still-pot is heated for a longer period of time. Hence, in another experiment the still-pot contents were heated for four hours at 140°C. and a 92% yield of methanol was obtained.

Reduction of Carboxyl-labelled Acetic Acid to Methylene-labelled Ethanol. A 250 cc. flask containing a magnetic stirring bar and provided with a dropping funnel and suitably arranged gas inlet and outlet connections was employed. The latter was attached to a trap cooled to -195°C. and thence to a bubbler flow indicator. In the flask was placed 0.9 gram of lithium aluminum hydride in 100 cc. of diethyl carbitol (b.p. 95°C./34 mm.). Then 0.6647 gram (11.07 mmols) of acetic acid-C^{14} (m.p. 14.5°C.) in 15 cc. of diethyl carbitol was added slowly to the hydride solution. Thirty minutes after the last addition 70 cc. of n-butyl carbitol (b.p. 126°C./26 mm.) were added dropwise. Next the still-pot temperature was raised to 140°C. and held there for 3½ hours. The traps containing the distillate were sealed off and attached to the vacuum-line. Ethanol and ethyl ether were separated from the diethyl carbitol by four distillations from the mixture at -40°C. and 10^{-4} mm. to a trap cooled by liquid nitrogen. The ethyl ether was removed by distillation from the ethanol at -80°C. and 10^{-4} mm. to a trap cooled by liquid nitrogen. A yield of 0.56 cc. or 90% of ethanol-C^{14} was obtained. The vapor pressure of the product was 12.5 mm at 0°C. The specific activity of the acetic acid was 1.17 uc./mmol. as compared with 1.16 uc./mmol. for the ethanol.

Ring-labelled Benzoic Acid

The synthesis of ring-labelled benzoic acid by the following series of reactions has been undertaken:

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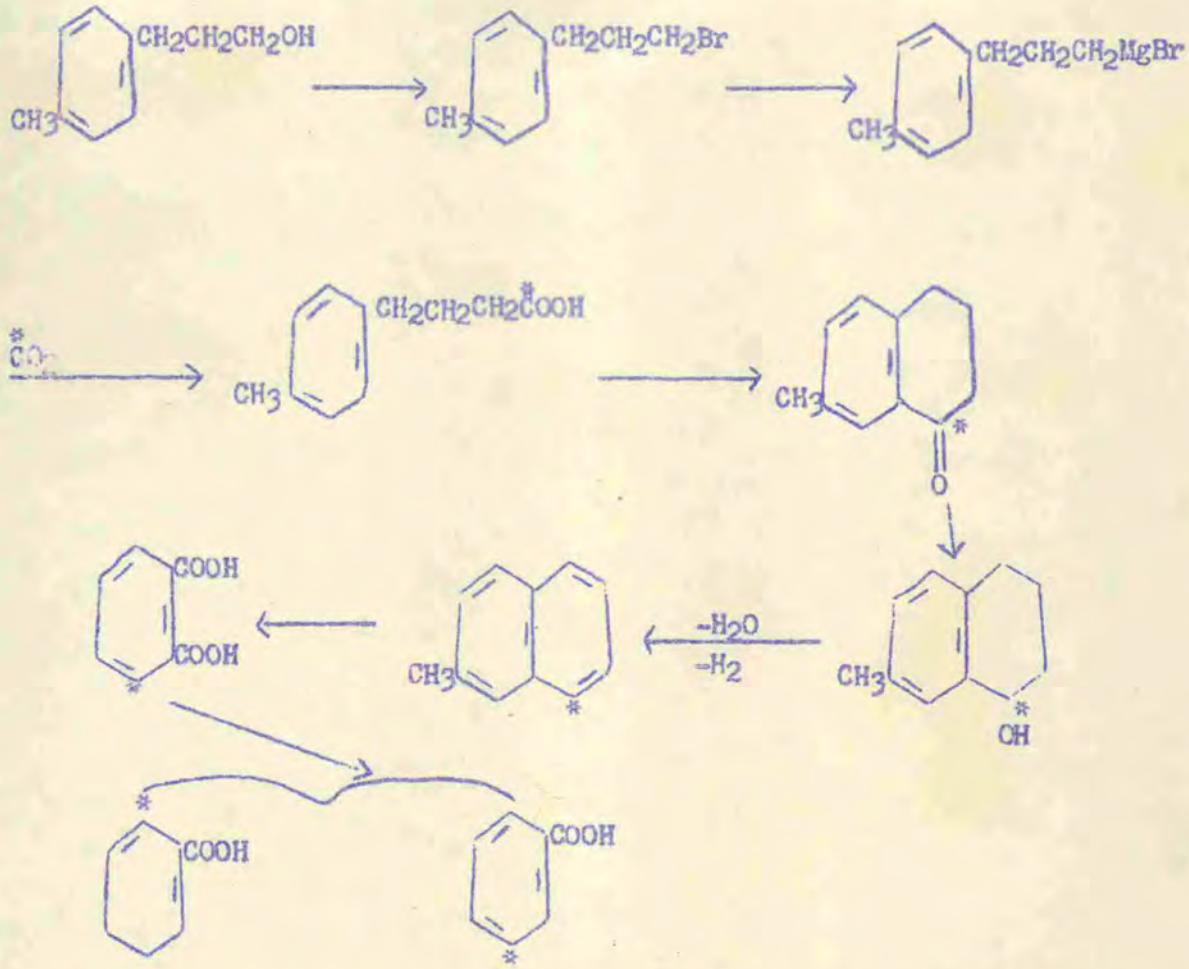


Model experiments have been undertaken upon the synthesis of napthalene through the carbonation of γ-phenylpropylmagnesium bromide to produce δ-phenylbutyric acid. It has been found that carbonation of this Grignard reagent proceeds in 45% yield by freezing the carbon dioxide into the ether solution of phenylpropylmagnesium bromide on a vacuum line. A new vacuum line has been constructed by which it will be possible to add an ether solution of the Grignard reagent to carbon dioxide dissolved in ethyl ether at -80°C. It is anticipated that the yields obtained by this reverse addition will be satisfactory. Approximately 5 grams of δ--phenyl butyric acid have been prepared and the cyclization of this material has been studied in a preliminary fashion. Thus 500 milligrams of this acid were cyclized by the anhydrous zinc chloride method to yield 144 milligrams of a crystalline product believed to be the acetate of the enol form of alpha tetralone. Two such attempts failed to produce satisfactory yields so this method of cyclization has been abandoned.

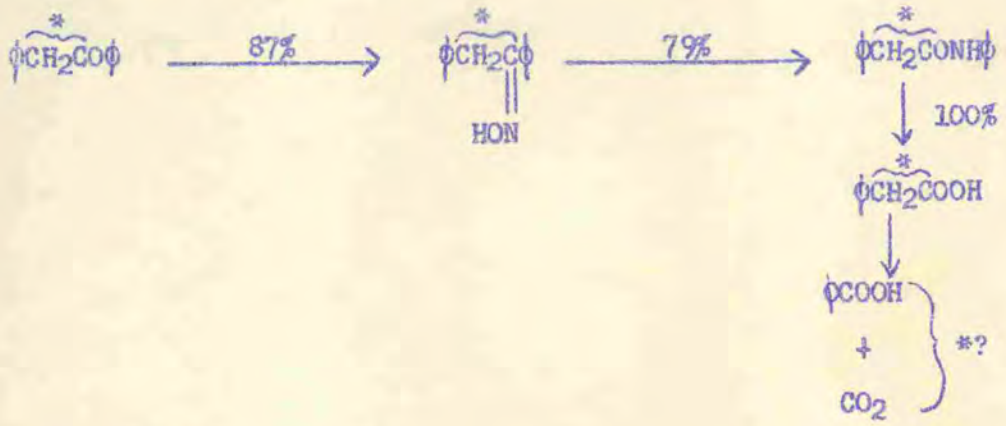
p-Methylcinnamic acid has been reduced to p-methylhydrocinnamyl alcohol by the lithium aluminum hydride method in excellent yields.

[redacted]

The Study of Reaction Mechanisms with C^{14}

Rearrangement of Chalcone Epoxide (C. J. Collins)

Desoxybenzoin containing carbon-14, which had previously been obtained by the alkaline rearrangement of chalcone epoxide, has been converted to radioactive phenylacetic acid by the Beckmann rearrangement of its oxime followed by acid hydrolysis. Oxidation of this acid to benzoic acid and carbon dioxide and analyses of the latter two fractions should indicate the position of the carbon-14 in the desoxybenzoin. The following chart shows the reactions involved:



Experimental

Desoxybenzoinoxime-C^{14}. Five hundred milligrams of desoxybenzoin, 500 milligrams of hydroxylamine hydrochloride, 4 ml. of absolute ethanol and 4 ml. of pyridine were heated under reflux for 90 minutes. The solution was evaporated to dryness in an air stream and desiccated by evaporation with a high vac pump in series with a dry ice trap. After the flask had reached constant weight, 10 ml. of ether and 10 ml. of 6 N hydrochloric acid were added. This mixture was agitated until the gray crystals had completely dissolved. The layers were separated and the ether layer was washed with 10 ml. of 6 N hydrochloric acid and then with 5 ml. of water. The aqueous layer was washed with 5 ml. of ether, and the ether was washed with several 2 ml. portions of water. The combined ether layers were evaporated to dryness in an air stream and desiccated over phosphorous pentoxide. The yield of solid crystals was 527.5 mg.

Phenylacetanilide-C^{14}. The desoxybenzoin (527.5 mg.) was dissolved in 5.0 ml. of pure benzene. Three hundred mg. of PCl_5 was weighed into the flask in a dry box. After the solution was heated under reflux for fifteen minutes, 20 ml. of water was cautiously added. The benzene layer was evaporated in an air stream and the yellow solid was dissolved in 20 ml. of ether. The aqueous layer was washed with two 5-ml. portions of ether, the ether layers were combined and washed with saturated $NaHCO_3$ solution (two 5-ml portions). After washing with two 5-ml. portions of water, the ether was evaporated. The solid residue was placed in a desiccator over-night. The yield of solid materials was 490.8 mg. This crude product melted 76-102°C.

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The crude phenylacetanilide was dissolved in 4 ml. of benzene and placed on an alumina chromatograph (80-200 mesh) 11 millimeters in diameter and 140 millimeters in length. The flask was washed with 1 ml. of benzene and this was added to the column. The column was then developed with 30 ml. of benzene. A yellow fraction came through the column with the first portions of benzene. Five ml fractions were evaporated; the fourth fraction produced pure white crystals. At this point the benzene development was stopped and the phenylacetanilide was washed off the alumina with alcohol. In this way a 378.4 mg. yield of phenylacetanilide was obtained (72.9% of theoretical).

Phenylacetic acid-C^{14}. Two hundred milligrams of phenylacetanilide were placed in a thick wall pyrex tube with 5 ml. of glacial acetic acid and 1 ml. of concentrated HCl. The tube was immersed in a Dry Ice-carbon tetrachloride-chloroform bath, evacuated, and sealed. The tube was placed in a micro carius furnace and heated at 190° for 8 hr. The tube was then opened and the contents were evaporated to dryness. Five milliliters of ether and 5 ml. of 6 N HCl were added, the layers were separated, and the aqueous layer was washed with six 5-ml portions of ether. The ether layers were combined and washed once with 3 ml. of 6 N HCl and then with 2 ml. of water. The water and hydrochloric acid fractions were washed once with ether. The combined ether layers were evaporated to dryness. The yield of phenylacetic acid was 129 mg. or 100% of theoretical.

Rearrangement of Unsymmetrical Benzils (O. K. Neville)

Further investigation of general methods for the preparation of C^{14}-carbonyl-labelled unsymmetrical benzils has been in progress. The Friedel-Crafts condensation of phenyl-acetyl chloride with anisole has not given consistently good yields of benzyl p-anisyl ketone. Considerable yields of an unidentified product other than the desired one have been obtained in every case. This is in agreement with the work of Jenkins[2] who has previously carried out this condensation in a slightly different manner. The condensation of p-nitrophenylacetyl chloride with benzene has given good yields, indicating that the difficulty with the previous reaction may be due to the unreliability of orientation in the Friedel-Craft reaction.

The reaction of a Grignard reagent with mandelamide has been reported[2][3] to give poor yields of the corresponding benzoin. It was felt that better yields might be obtained by using an N,N-disubstituted amide, to prevent Grignard replacement of the amide hydrogens. The diethylamide is formed quite readily from the mandelic acid acetone derivative. When this amide was heated under reflux for four hours with the p-anisyl Grignard reagent in diethyl ether, hydrolysis of the reaction product gave a 30% yield of the desired p-methoxy benzoin. Work is in progress to improve the yield of this reaction, since by use of other Grignard reagents, a series of C^{14}-labelled unsymmetrical benzoins could be made from the previously prepared carbinol-labelled mandelic acid.

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(2) Jenkins, J. Am. Chem. Soc., 54, 1159 (1932)
(3) McKensie and Wren, J. Chem. Soc., 93, 311 (1908)

[redacted]

Experimental

Mandelic Acid Acetone Derivative

a. Sulfuric acid method[3]. One gram of mandelic acid was dissolved in 5 ml. of acetone, and the solution was cooled in an ice-HCl bath to -15°C. While the cold solution was stirred magnetically, 0.652 g. of cold sulfuric acid was added dropwise. After standing with stirring for 15 minutes, the solution was poured into 10 ml. of water containing 1.37 g. of Na_2CO_3. The white acetone derivative which precipitated was filtered and dried. The yield was 0.59 g. or 45% of theoretical.

b. Zinc chloride method. One gram of mandelic acid was dissolved in 30 ml. of dry acetone. To this was added 3 g. of anhydrous zinc chloride. After standing overnight, the solution was distilled at room temperature under vacuum to remove the excess acetone. The resultant syrup was dissolved in water and extracted several times with ether. The ether was evaporated and the resultant white crystalline acetone derivative was dried in a desiccator. The yield was 0.984 grams or 74.5% of theoretical.

N,N-dimethylmandelamide. To 0.66 g. of the mandelic acid acetone derivative was added 10 ml. of dry diethyl amine. The white crystals went into solution immediately with a small evolution of heat. Almost immediately a white crystalline precipitate formed around the edge of the flask. The mixture was heated under reflux for one hour and the crystals were filtered. The yield was 0.65 g. or 91% of theoretical of N,N-diethylmandelamide.

p-Methoxybenzoin. The p-anisyl Grignard reagent was prepared from .224 g. of magnesium 1.76 g. of p-bromoanisole in 20 ml. of dry ethyl ether. The 0.65 g. of amide was added in one portion, the mixture was heated for four hours, and was then decomposed with water and sulfuric acid. The ether layer was evaporated, and the solution was steam distilled until the distillate was clear. The crystalline solid in the flask was extracted into ether, the ether was evaporated, and the material was recrystallized from ethanol. The yield of the p-methoxybenzoin was .232 g. or 30.5% of theoretical.

A repetition of this experiment under practically the same conditions, except that the reflux period was 20 hours, gave a 55% yield of the substituted benzoin.

Development of Analytical Procedures

Oxidation and Assay of Low Molecular Weight Compounds Containing C^{14}. (R. F. Nystrom and W. J. Skraba)

Isotopic acetic acid and ethanol have been oxidized quantitatively to carbon dioxide by passing the organic compound over copper oxide at 800°C. in a sweep of purified helium. After two and one-half hours the amount of carbon dioxide was determined manometrically and the water gravimetrically. Next the carbon dioxide-C^{14} was transferred to an ionization chamber which was attached to a vibrating reed electrometer and the activity of the carbon dioxide was determined.

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3 - SUPPORTING CHEMICAL RESEARCH

Inorganic, Physical and Radiochemistry

The Fundamental Chemistry of Ruthenium (M. D. Silverman, J. A. Swartout)

Research on the solution chemistry of the upper valence states of ruthenium was temporarily suspended this quarter in order to place full time on crystal structure studies. It is expected that work on solution chemistry will be resumed next quarter.

Ion-exchange Separations: Rare Earth Purification (D. H. Harris, G. E. Boyd)

The program directed towards the separation of one gram quantities of all of the rare earths in a spectrochemically pure condition has continued. (See ORNL-65, p. 94)) During the quarter now elapsed the following additional quantities of pure earths have been prepared:

Yb_2O_3	0.519 g.
Dy_2O_3	0.671
Gd_2O_3	4.511

Also, moderate quantities of pure Lu have been produced in a separation just completed, although the complete data have not been obtained as yet. Additional quantities of spectrographically pure Tm will become available in the near future from a new separation presently in progress.

A considerable interest has developed during the course of this work in the position of yttrium in the rare earth "exchange potential" sequence. In the initial work [cf. B. H. Ketelle and G. E. Boyd, J. Am. Chem. Soc., 69, 2800 (1947)] in which either micro or else fractional milligram quantities of the heavy rare earths were separated, yttrium was observed to follow Ho and either to precede slightly or to eclipse Dy which in turn preceded Tb. Subsequent studies (cf. ORNL-65, p. 95) at tracer concentrations using the cyclotron produced 105d Y^{88} confirmed the position of yttrium as intermediate between Ho and Tb. The Dy peak was found to be almost superimposed upon the Y peak. In these macro-separations at one gram level, however, yttrium has been observed repeatedly to fall between Dy and Gd and almost coincident with Tb. It is possible that displacement effects may be important in producing this shift, for in the separations just cited the Dy and Gd were present in a much larger percentage than either Y or Tb.

Another problem of incidental interest in these separations is the possibility of the occurrence of element 61 in nature. Recently some observations of possible relevance were made in connection with the working up of an Eu fraction which had been concentrated from a one hundred pound batch of cerium earth oxalate. In the final crystallization for the concentration of the Eu a curious discontinuity seemed to appear: in several Sm fractions an apparent Nd impurity persisted at an unexpected point.

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[redacted]

This Nd was later isolated from the associated Sm by extracting the latter (plus Eu) with sodium amalgam. The absorption spectrum of this "stray Nd" appeared somewhat abnormal, and since it is now known that 61 resembles Nd in certain of its salts it was thought that the abnormalities might be related to the missing element. Examination of the emission spectrum (copper spark) showed Gd principally. The color of the oxalate precipitate formed from the material suggested an appreciable fraction of Nd, but the initial spectrochemical results gave no Nd. This was re-checked and some Nd was found, but not a great amount. When searched for, one line characteristic of element 61 was indicated faintly but another could not be found. This fraction and similar additional material will be separated on an ion-exchange column to check for 61.

Survey of Element 43 Activities Produced by Deuteron Bombardment of the Separated Molybdenum Isotopes (E. E. Motta, G. E. Boyd)

The separation of weighable quantities of each of the seven stable isotopes of Mo at the electromagnetic separation plant in Oak Ridge, made possible an advantageous way of producing and studying the various radioisotopes of element 43. It represented a unique method by which one could compare the yield of any given Tc activity produced from one of the separated Mo isotopes, with its yield from any of the other separated isotopes - thus making a mass assignment possible. This distinction was not completely clear cut, since each of the separated Mo isotopes always has a few percent, at least a fraction of a percent, of all the other Mo isotopes. However, the yield of a given Tc activity produced from one of these isotopes, say by a (d,2n) reaction, should be favored by a factor of 30 to 100 over its yield from any other Mo isotope. This is indicated by Table I, which gives the isotopic analysis of each of the enriched Mo isotopes. For example, if a d,2n reaction is carried out on Mo enriched in Mo^{96}, more Tc^{96} should be produced than from the bombardment of any of the other isotopically enriched Mo mixtures. Deuteron bombardments appeared to be the most convenient method available for using these Mo isotopes.

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Table I

Isotopic Composition of Separated Mo Isotopes

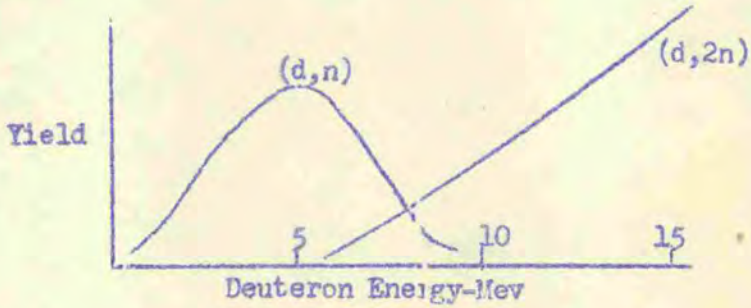
Mo^{92}			Mo^{94}		
Mo^{92}	92.07%	± 1.0%	Mo^{92}	1.96%	± .3
Mo^{94}	1.67	.1	Mo^{94}	74.68	" .7
Mo^{95}	2.39	.3	Mo^{95}	10.09	" .2
Mo^{96}	1.15	.3	Mo^{96}	4.44	" .2
Mo^{97}	.54	.2	Mo^{97}	2.46	" .2
Mo^{98}	1.65	.3	Mo^{98}	4.46	" .2
Mo^{100}	.53	.2	Mo^{100}	1.91	" .3
Natural Mo			**Mo^{95}**		
Mo^{92}	14.9%		Mo^{92}	.67%	± .3
Mo^{94}	9.4		Mo^{94}	2.93	.5
Mo^{95}	16.1		Mo^{95}	80.75	1.0
Mo^{96}	16.6		Mo^{96}	5.01	.5
Mo^{97}	9.65		Mo^{97}	1.51	.3
Mo^{98}	24.1		Mo^{98}	3.24	.5
Mo^{100}	9.25		Mo^{100}	5.89	.5
Mo^{96}			**Mo^{97}**		
Mo^{92}	2.18	± .3	Mo^{92}	.78	± .1
Mo^{94}	0.7	.2	Mo^{94}	.64	.1
Mo^{95}			Mo^{95}	1.28	.1
Mo^{96}	88.2	.3	Mo^{96}	3.78	.2
Mo^{97}	3.82	.3	Mo^{97}	77.97	1.0
Mo^{98}	3.41	.1	Mo^{98}	12.96	.5
Mo^{100}	1.03	.05	Mo^{100}	2.94	.5
Mo^{98}			**Mo^{100}**		
Mo^{92}	0.55%	± .1	Mo^{92}	.85%	± .3
Mo^{94}	0.33	.1	Mo^{94}	1.82	.5
Mo^{95}	0.51	.05	Mo^{95}	1.29	.4
Mo^{96}	0.68	.05	Mo^{96}	1.33	.3
Mo^{97}	0.84	.1	Mo^{97}	.89	.3
Mo^{98}	95.0	1.0	Mo^{98}	2.85	.5
Mo^{100}	2.01	.2	Mo^{100}	90.2	1.0

[redacted]

Discussion of Predominant Reaction

In this study, deuteron bombardments were obtained at the cyclotron at the Carnegie Institution in Washington, D. C. and at the 60 inch cyclotron at Berkeley, California. The nominal deuteron energies in the Berkeley bombardments were 20 Mev and at the Carnegie cyclotron 15 Mev. In order to help establish mass assignments, it was necessary to know the predominant reaction which was occurring in these bombardments with deuterons of this energy. It was found, as expected, that the (d,2n) was the dominant reaction. However, a discussion of this factor is warranted.

To begin with, the deuteron energies were in the range where the d,2n reaction generally predominates. The well known simple plot below illustrates



how, in general, as deuteron energy increases the (d,n) yield rises and then falls off. At approximately 5 to 10 Mev, the (d,2n) reaction begins to occur and at about 16 Mev, it is the principal process. It is possible to give many examples of where this occurs. Thus, general considerations indicated that the d,2n would predominate.

However, in order to confirm the fact that this was also occurring in the Mo region, it was decided to determine the yields of some of the already well assigned Tc activities and to show that the (d,2n) was indeed dominant.

The mass number of the 4.2 day Tc^{96} had been very well established by previous work[1,2]. If the d,2n was the principal reaction, then the greatest cross section or greatest relative yield for the production of the Tc^{96} activity should have been found in Mo^{96}. This was actually observed to be the case and confirmed the expected (d,2n) predominance in the Berkeley bombardments.

The (d,2n) dominance in the Carnegie Institution cyclotron bombardments was confirmed by the following results:

As described previously, the assignment of the 13-15 minute Tc^{101} had been well established. In these bombardments, this isotope could be produced only by a (d,n) reaction on stable Mo^{100}, since Mo^{101} is un-

(1) Ewing, Perry and McCreary, Phys. Rev., 55, 1136 (1939)
(2) Edwards and Pool, Phys. Rev., 72, 384 (1947)

[redacted]

stable and does not occur in nature. If the (d,2n) was the principal reaction, then the cross section of Mo^{100} in the (d,n) reaction to produce Tc^{101}, should be of a smaller order of magnitude than all the other cross sections. On the other hand, if the various Tc activities were being produced by (d,n) reactions rather than (d,2n), the yield of the Tc^{101} should have been of the same order of magnitude as the yield of the other Tc activities. However, it was found to be much smaller. This served as an acceptable confirmation of what was expected on the basis of deuteron energy - namely that the (d,2n) reaction was prevalent.

In the Berkeley bombardments with 22 Mev deuterons, some (d,3n) reactions may have occurred - but not in sufficient quantity to affect the mass assignments.

Preparation and Analysis of Cyclotron Targets

Since the cyclotron targets became very hot during bombardment, it was necessary to have the Mo isotope in a non volatile form. These isotopes were obtained originally in the form of MoO_3, which is volatile at the temperature to be encountered during bombardment. A method was finally devised in which the MoO_3 powder was reduced to a thin layer of sintered Mo metal (20 mg) centrally located on a Cu backing. This was done by heating the MoO_3 on the Cu backing at high temperatures in a stream of H_2. The reduction was carried out in a large quartz tube heated by blast lamp. After bombardment, the Mo was carefully removed with a sharp edge from the target. It was dissolved in concentrated H_2SO_4 and the Tc distilled away. Tc samples of varying intensities were prepared using platinum sulfide carrier, and very thin deposits of Tc were electroplated out, so that the very soft radiations might be studied.

Study of Tc Activities Produced by Bombardment of the Various Mo Isotopes

Starting with the heaviest Mo isotope, Mo^{100}, bombardments of varying length were carried out on the various isotopes and the following information was obtained from the Carnegie work.

80 second Tc. Short deuteron bombardments on Mo^{100} produced a new short lived Tc activity which decayed with a half life of 80 ± 10 seconds and which emitted charged particles having an energy of 2.3 ± 0.5 Mev. A gamma ray of 0.6 ± 0.1 Mev energy was also found associated with this period. The decay curve also shows the previously known[3] 13-15 minute Tc^{101} period as a longer lived component. The new activity is best assigned to Tc^{100} on the basis of the much greater cross section for its production from Mo^{100} than for the production of the 15 ± 2 minute Tc^{101} - which can be produced here only by a (d,n) on Mo^{100}.

40 minute Tc. Bombardment of Mo^{97} and Mo^{98} gave rise to a 40 ± 5 minute Tc radioactivity emitting charged particles having an energy of 2.0 ± 0.5 Mev. The decay curves show the presence of the previously known 2.7 hour and ~2 day Tc activities. No mass assignment is as yet proposed for this activity. Its identity should be studied further.

(3) Sagane, K. M. and Ikawa, Phys. Rev., 57, 750 (1940)

[redacted]

2.8 day Tc. Deuteron irradiation on Mo^{98} varying between forty minutes and one hour were found to yield another Tc activity of 2.8 ± 0.1 day half life in good abundance. Beta rays of 1.3 ± 0.2 Mev maximum energy and gamma rays of 0.9 ± 0.1 Mev were found to be associated with this period. Previously half lives of ca 2 d and 2.7 d in element 43 have been reported but the radiation characteristics[4,5,6] were different from the above. The yield in the production of the 2.8 day Tc activity makes it best assigned to mass 98.

20 hour Tc. One hour deuteron bombardments on Mo^{95} were observed to give rise to a Tc activity of 20 ± 2 hour half life which decayed with the emission of 16.5 ± 1.5 Kev X-rays. ($\mu_{\frac{1}{2}}$ = 110 ± 15 mg Al/cm^2) and a gamma ray of 0.8 ± 0.1 Mev energy. Yield considerations have led to the assignment of this period to mass 95. Quite recently the formation of what appears to have been the same radioactive species of Tc by decay from Ru^{95} has been reported[7]. It appears to be an independent isomer of Tc^{95} along with the 50-60 day activity.

50 minute Tc. Deuteron bombardments on Mo^{94} of about one hour duration led to the formation of a Tc activity in good yield, which decayed with a half-life of 50 ± 2 minutes and emitted positrons of 2.5 ± 0.3 Mev energy. A gamma ray of 0.9 ± 0.1 Mev energy was found to be associated with this period also. These characteristics appear to be in good agreement with previous observations on a 53 minute activity produced in natural molybdenum by proton bombardment[8,9]. On the basis of the yield of the activity from the molybdenum enhanced in Mo^{94}, the 50 minute Tc period is best assigned to mass 94.

2.7 hour Tc. Although a 2.7 hour activity had been previously observed in a Mo target[10], no work had been done on the character and energies of its radiations or on its unambiguous chemical identification. Bombardment of Mo^{92} gave good yields of a 2.7 ± 0.1 hour Tc which was shown to be a positron emitter by magnetic deflection. A positron energy of 1.2 ± 0.2 Mev, and a hard gamma ray of 2.4 ± 0.5 Mev were determined by absorption measurements. This activity is best assigned Tc^{93} on the basis of the low cross section (by d,n) for its production from Mo^{92}. The more energetic 4.5 minute Tc was produced from Mo^{92} with a cross section which indicates a d,2n reaction and a mass number of 92.

4.5 minute Tc. Five minute deuteron bombardments of Mo^{92} gave rise to a new positron emitter with a half life of 4.5 ± 0.5 minutes and a positron energy of 4.3 ± 0.5 Mev. A gamma ray of 1.3 ± 0.3 Mev energy was also present. The decay curve showed a longer lived period with a 2.7

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(4) Seaborg and Segre, Phys. Rev., 55, 808 (1939)
(5) Glendenin, Plutonium Project Record Vol. IXB (12,9)
(6) Abelson, P., Phys. Rev., 56, 753 (1939)
(7) Eggen and Pool, Bull. Am. Phys. Soc. 23 (3) 56 (1948)
(8) Ewing, Perry and McCreary, Phys. Rev. 55, 1136 (1939)
(9) Gugelot, Huber, Medicus, Preiswerk and Steffen, Helv. Phys. Acta., 19, 418 (1946); ibid., 20, 240 (1947)
(10) Delsasso, Ridenour, Sherr and White, Phys. Rev. 55, 113 (1939)

[redacted]

[redacted]

hour half life, the existence of which has already been indicated. As a result of its mode of production and yield, this 4.5 minute Tc activity is best assigned to Tc^{92} as discussed in connection with the 2.7 hour Tc.

Longer bombardments were carried out on Mo^{96}, Mo^{95} and Mo^{97} ($\sim$100 u.a.h.), in order to obtain substantial yields of the longer lived Tc activities. The following Tc activities were found in this series of bombardments with the 60" Berkeley cyclotron.

4.2 day Tc. This well established Tc^{96} activity[11,12] was produced in greatest yield from the deuteron bombardment of Mo enriched in Mo^{96} and decayed with a half life of 4.2 $\pm$ 0.1 days. This result serves to confirm the predominance of the (d,2n) reaction. Gamma rays of 0.8 $\pm$ 0.1 Mev energy as well as 17-18 Kev X-rays were observed. Charged particles of 0.64 Mev energy were not found however.

50-60 day Tc. The previously studied 50-60 day Tc[12,13,14] was produced in greatest yield from the deuteron bombardment of Mo enriched in Mo^{95}. The decay curve gave an apparent half life of 59 days. This value will be reduced somewhat by the subtraction of a 90 day component which is almost certainly present. The radiations found associated with this period were a 0.8 $\pm$ 0.1 Mev γ-ray, a 0.24 $\pm$ 0.05 Mev γ-ray, and X-rays characteristic of the Mo-Tc region. The γ-ray of lower energy was twice as abundant as that of higher energy in agreement with Huber et al[14], after correcting for counting efficiency. In addition, conversion electrons of $\sim$180 Kev energy were observed (Visual range 40 mg Al/cm^2). The predominantly greater yield of this 50-60 day Tc activity from Mo enriched in Mo^{95} supports its assignment to Tc^{95}.

90 day Tc. Our earlier work[15] on the approximately 90 day Tc had indicated its assignment to mass 97. It was to be expected then that a d,2n reaction would give the greatest yield of Tc^{97}, when carried out on Mo enriched in Mo^{97}. This result was actually found and confirms the assignment of the 90 day Tc. Soft electrons of $\sim$85 Kev energy ($\gamma\frac{1}{2}$ = 1.5 mg Al/cm^2), and 17-18 Kev X-rays were again found associated with this period. The yield of any unconverted soft gamma radiation ($\sim$97 Kev) was so small that its presence was doubtful. The decay curve gave a 90 $\pm$ 2 day half life.

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(11) Ewing, Perry and McCreary, Phys. Rev., 55, 1136 (1939)
(12) Edwards and Pool, Phys. Rev., 72, 384 (1947)
(13) Cacciapuoti and Segre, Phys. Rev. 55, 110 (1939)
(14) Huber, Medicus, Preiswerk and Steffen, Phys. Rev. 73, 1211 (1948)
(15) Motta, Boyd and Brosi, Phys. Rev. 71, 210 (1947)

[redacted]

[redacted]

Table II

Summary of Radioactivities of Element 43

Mass No.	Half-life	Radiations
Tc^{92}	4.5 m	β^+ 4.3 Mev γ 1.3 Mev
Tc^{93}	2.7 h	β^+ 1.2 Mev γ 2.4 Mev
Tc^{94}	50 m	β^+ 2.5 Mev γ 2.8, 0.9 Mev
Tc^{95}	20 h	I.T. X-rays γ .76 Mev
	52 d	K capture e's γ .25, .84 Mev
Tc^{96}	4.2 d	K capture γ 0.9 Mev
Tc^{97}	88 d	I.T. X-rays e's γ .097 Mev
	$>$15 y	K capture?
Tc^{98}	2.8 d	β^- 1.3 Mev γ 0.9 Mev
Tc^{99}	6 h	I.T. e's γ .136 Mev
	9×10^5 y	No γ β^- .32 Mev
Tc^{100}	80 sec	β^- 2.3 Mev γ 0.6 Mev
Tc^{101}	14 m	β^- 1.3 Mev γ 0.3 Mev

[redacted]

[redacted]

General Radiochemistry (B. H. Ketelle, G. E. Boyd)

Several isotopes have been studied on the beta ray spectrometer:

In the May, 1948 quarterly report G. W. Parker and members of his group reported on the radiation properties of Sm^{151}, the fission product of about 20 years half-life. Because of the difficulty of interpretation of absorption curves, it was considered worthwhile to attempt a study of this isotope on the spectrometer. It is recognized that there are problems due to scattering and absorption of such soft radiation in the spectrometer but these are less detrimental and more easily studied than the scattering problems arising when one takes absorption curves on the beta proportional counter. The source material consisted of several milligrams of carrier free fission product samarium obtained from Parker and mounted on a thin film. The source thickness was about 5 mg/cm^2. The beta spectrum showed no conversion lines. A Kurie plot was linear from the endpoint, 81 kev, down to 55 kev. Below this energy the ordinate $(N/fI^3)^{\frac{1}{2}}$, decreased due to absorption by the counter window. Several experimental runs were made using counter tubes with windows of differing thicknesses. The end points agree to within 3 kev.

The 51.5 day Hg^{203} or Hg^{205} isotope has been studied previously by L. C. Miller and L. F. Curtiss (CP-3102). The "beta" spectrum given consisted of the K and L conversion lines of a gamma ray of energy .28 Mev., the average value obtained from the two lines which gave values of .276 and .285. A source of this activity produced by neutron bombardment of mercury was obtained from I. R. Whitney. A normal beta spectrum with the two conversion lines was obtained. The gamma energy corresponding to the lines was .265 and .266 Mev. for the K and L lines respectively. Because of the width of the conversion lines and the fact that the L line comes almost at the end point of the beta spectrum, it has not been possible to prepare a Kurie plot. However, it appears that the upper limit must be less than .31 Mev. An attempt to obtain data with the instrument set at higher resolution may make it possible to obtain the Kurie plot. The photo-electron spectrum from a uranium radiator was obtained with two different sources. The K and L lines correspond to .271 and .273 Mev. for one source and .276 and .273 Mev. for the second source. Thus, it appears that the gamma ray energy is about .273 $\pm$ .003 Mev. and the beta ray maximum less than .31.

In addition to these two isotopes the decay scheme of I^{135} has been studied further and the results reported elsewhere in this report.

[redacted]

[redacted]

Studies of Extractions with β-diketones: (H. A. Levy, A. Broido)

Introduction

Research was continued on the extraction of various metals into benzene solutions of TTA (symbol, HT) according to the reaction,

$$M^{+n}\ (\text{aqueous}) + HT\ (\text{benzene}) \rightleftharpoons MT_n\ (\text{benzene}) + nH^+\ (\text{aqueous}).$$

As described in previous quarterly reports[1], the extractabilities have been calculated in terms of the equilibrium constant,

$$K_M = \frac{\left[MT_n\right]_B \left[H^+\right]_A^n}{\left[Me^{+n}\right]_A \left[HT\right]_B^n}$$

in which the brackets signify thermodynamic activities and the subscripts, A and B, refer to aqueous and benzene phases, respectively.

Lutecium and Praseodymium

The elements for which K_M has been determined this quarter are lutecium, $K_{Lu} = 2.0 \times 10^{-7}$, praseodymium, $K_{Pr} = 3.5 \times 10^{-8}$, and prometheum (element 61), $K_{Pm} = 6.2 \times 10^{-8}$. The data for these experiments are included in a report[2], being issued and will not be presented here.

Zirconium-Hafnium Separation

In addition to work on the determination of equilibrium constants, further work has been done on the separation of zirconium and hafnium with TTA. Ordinary zirconium containing 3% hafnium impurity was brought to a concentration of 3 mg/ml in 6 N HCl and mixed with 0.25 M TTA benzene. Although an attempt was made to determine separation under non-equilibrium conditions, the early aliquots of the benzene phase contained concentrations of hafnium too low to measure by the spectrographic techniques used. At equilibrium, with 75% of the zirconium extracted into the benzene phase, an average of four values indicates a 1% Hf impurity in that phase, while the zirconium residue in the aqueous phase contained ~12% Hf impurity. (See Table I)

The value of K_{Zr} calculated from these data is 1.5×10^7 in good agreement with previous results with tracer Zr^{95}[3], but the value for K_{Hf}, 1.3×10^6, is lower than that previously reported[4] by a factor of 5. The reason for this discrepancy is not known.

(1) CNL-37
(2) ORNL-139 - To be issued soon
(3) MonN-311
(4) ORNL-65

[redacted]

Table I: Extraction of Zr and Hf by TTA-Benzene

Aqueous: 6 N HCl, Zr or Hf as shown
Organic: 0.25 M TTA in benzene

Elapsed Time hrs.	Aqueous Phase		Benzene Phase	
	mg. Zr/ml.	Hf/Zr x 100	mg. Zr/ml.	Hf/Zr x 100
Original Aqueous	3.3	2.9	None	None
0.5	3.2	2.6	0.28	-
1	3.0	2.7	0.58	-
2	2.2	3.6	1.2	-
6	0.74	7	2.4	0.86
23	0.42	14	2.1	0.78
30	0.49	10	2.4	1.05
48	0.45	11	2.6	0.91
96	0.45	13	2.3	0.96

High Radioactive Level Chemical Equipment -(H. A. Levy, M. H. Feldman)

Testing of the high level chemical equipment disclosed the need for redesign of several of the mechanical units. This redesign and construction is now complete, and further testing is in progress, with preliminary indications of satisfactory operation.

[redacted]

Radiations from Ba^{141} (H. A. Levy, B. Zemel)

Introduction: The purpose of this investigation is to characterize the 18 min. isotope of Ba, Ba^{141}, as part of the larger problem of determining radiation characteristics and other properties of the fission isotope whose half-lives range from fractions of a minute through several minutes.

To summarize briefly the problem as presented in a prior report(1), the determination of the radiation characteristics of 18 min. Ba^{141} is complicated by the presence of the following known isotopes:

2 min. Cs^{142} ⟶ 6 min. Ba^{142} ⟶ 78 min. La^{142}

"Short" Cs^{141} ⟶ 18 min. Ba^{141} ⟶ 3.5 hr. La^{141} ⟶ 28d Ce^{141}

7 min. Cs^{139} ⟶ 85 min. Ba^{139} ⟶ stable La^{139}

"Short" Cs^{140} ⟶ 12.8 d. Ba^{140} ⟶ 40 hr. La^{140}

Experimental Principles: In order to treat the 18 min. Ba^{141} with any degree of satisfactoon, it was necessary to reduce the amount of 6 min. Ba^{142} and 85 min. Ba^{139} as much as possible and to eliminate the La and Ce daughters of Ba^{142} and Ba^{141}.

The reduction of the Ba^{139} and Ba^{142} isotopes was handled in much the same way as proposed in a previous report(1) - namely by short bombardments of UNH and rapid Ba separations, so that advantage could be taken of the "short" Cs^{141} parent of 18 min. Ba^{141}. Ba^{142} was largely eliminated by permitting a decay of about one hour before final separation.

The problem of eliminating the La daughters was one of continuous separation during counting. This was done by circulating the Ba in solution through a suspension of $Fe(OH)_3$, and counting through a thin windowed pipette.

Experimental Details: The separation of Ba from irradiated UNH is handled in a portable hot cell described in earlier reports(1). This consists of a "Stang precipitator" and auxiliary equipment for emptying the rabbit, collecting the sample, and disposing of "hot" waste.

The rabbit used, as previously described, has a rubber gate whereby the irradiated UNH solution can be rapidly syringed out without having to open the rabbit.

To facilitate the rapid separation of Ba from Cs and other fission isotopes, the portable "hot cell" was moved to the pile floor so that the rabbit could be rapidly emptied into the reaction vessel. Exposures on the average were of 20 seconds duration, and the time between the end of bombardment and beginning of precipitation was of the order of 35 seconds, the first filtration and its subsequent washing being completed in about five minutes. A total of four HCl-ether precipitations were made to insure reasonable separation from contaminations such as Sr.

(1) CNL-37

[redacted]

The separation of the La (and Ce) daughter from the separated Ba was done during counting.

An excess of Fe^{+++} was added to the Ba solution and this made alkaline with NaOH. The alkaline solution containing the $Fe(OH)_3$ suspension was then placed in a vessel having a coarse sintered glass disk at the bottom, and the solution passed through the counting pipette. It was then pumped back into the $Fe(OH)_3$ suspension by means of an air pump which also served to keep part of the $Fe(OH)_3$ stirred up. The rate of flow of the solution was maintained at 3-5 ml/min, the volume of the counting cell being 1/2 ml.

In order to test the efficiency of separation, tests were made using both freshly precipitated and aged $Fe(OH)_3$ in alkaline solutions. In all cases, the retention of lanthanum was greater than 99.9%.

In the actual counting cycle, a series of decay absorption curves was made, absorbers being changed as repidly as possible to delineate the steep portion of the curves as well as possible. The duration of an average decay absorption curve was of the order of twelve hours. A curve of 20-24 hours duration would have been desirable, but for obvious reasons the runs were not carried out that far. It had been hoped originally that the automatic ab-absorption counter described in earlier reports would be available. However, mechanical and electrical imperfections have kept it from being of any use.

Treatment of Data

The data obtained consist of several sets of decay curves through various absorber thicknesses. In a single run it was possible to obtain only three or four complete curves together with the beginning and end portions of a few others. Thus far, we have interpreted only the complete curves, that is, those in which the data extend from one hour after irradiation to about 12 hours. Since the ratio of 18 min. to 85 min. Ba activities depends critically on the timing of the initial chemical steps, and therefore varies from run to run, it did not seem proper to piece together partial curves from different runs.

Each decay curve was analyzed graphically into three components, 12.8 d Ba^{140}, 85 min. Ba^{139}, and the remaining shorter lived activity believed to arise from 18 min. Ba^{141}. In favorable cases this analysis was reasonably straightforward and satisfactory; in others because of dearth of data it was less so. The greatest uncertainty lies in the evaluation of the long lived component. This had, however, little effect in the final estimation of the short lived component.

The resultant short lived component showed half-lives ranging from 17 to 21 minutes; this variation seemed greater than that due to random error, and its significance is not clear.

The absorption behavior of the 18 min. Ba was obtained by plotting the value of the short lived component against absorber thickness. Since data from two runs are represented, a normalization was made by means of two absorber thicknesses common to both (544 and 615 mg), the two normalization factors being in reasonable agreement with each other.

[redacted]

Figure 1 shows a typical decay curve and its analysis into components. Figure 2 shows the resulting absorption curve for the 18 min. component. It is evident that the data does not define the absorption function with precision and the results herein quoted must be considered preliminary.

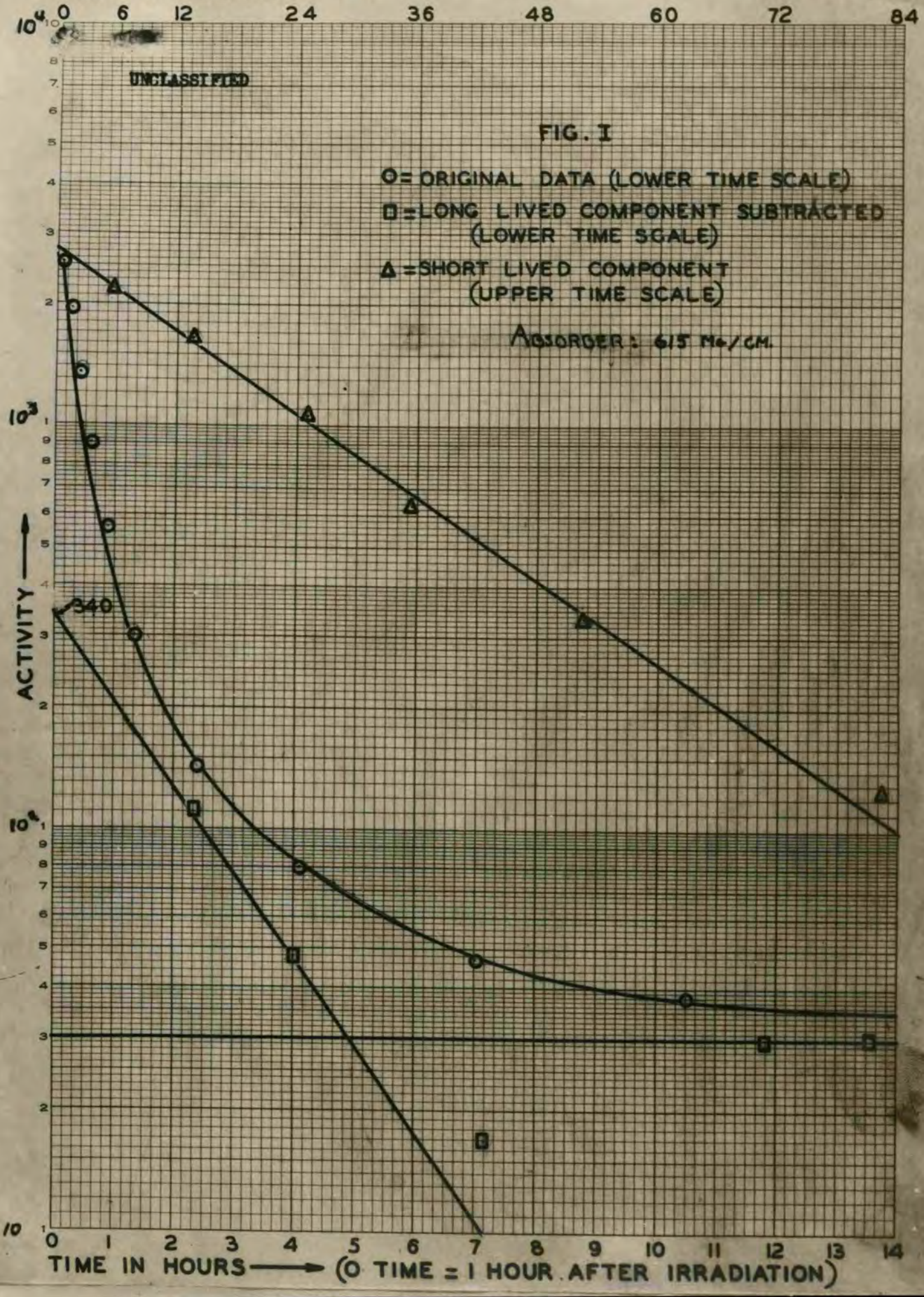
For evaluation of the range of the Ba^{141} β ray, a modified Feather analysis of the absorption curve was carried out, based on an absorption curve of the Ba^{139} β ray as comparison standard, rather than the usual RaE. This curve was taken in the same counting apparatus as the remainder of the work on a sample of pile-activated $Ba(NO_3)_2$ in solution. Figure 3 shows the absorption curve. The Ba^{139} range in Al was taken as 1130 mg/cm^2, corresponding to 2.3 Mev. Absorption in the cell, counter window, etc. was estimated as 104 mg. The Feather analysis shown in Figure 2 inset is based on data in excess of this 104 mg/cm^2. The indicated range is then 1290 + 104 = 1394 mg/cm^2, corresponding to a maximum energy of 2.8 Mev.

In Figure 3 there is also plotted the normalized absorption of the 85 min. component obtained by analysis of the decay of the fission Ba. This curve shows a several-fold larger γ-component than the (n, γ) activity, and a somewhat harder β-spectrum, the significance of which is not clear.

Discussion

Although the combination of HCl-ether precipitations and $Fe(OH)_3$ scavenging used is the basis for the usual radiochemical analysis for radio-barium in long-lived fission activity, it is not known that it gives sufficient decontamination from all short-lived fission products. Some chemical tests of this question are indicated.

Drawing # 6294



UNCLASSIFIED

Drawing # 6292

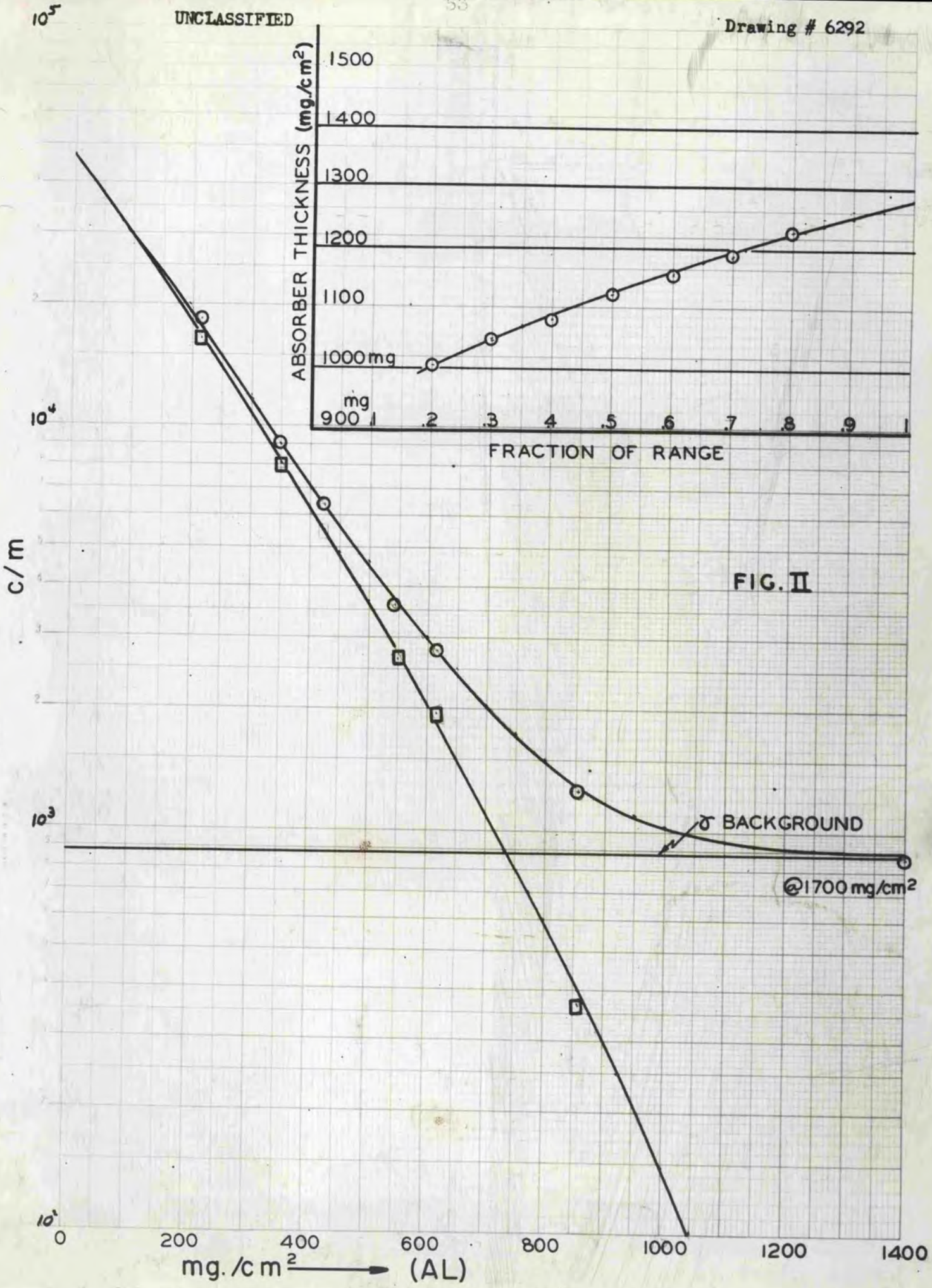
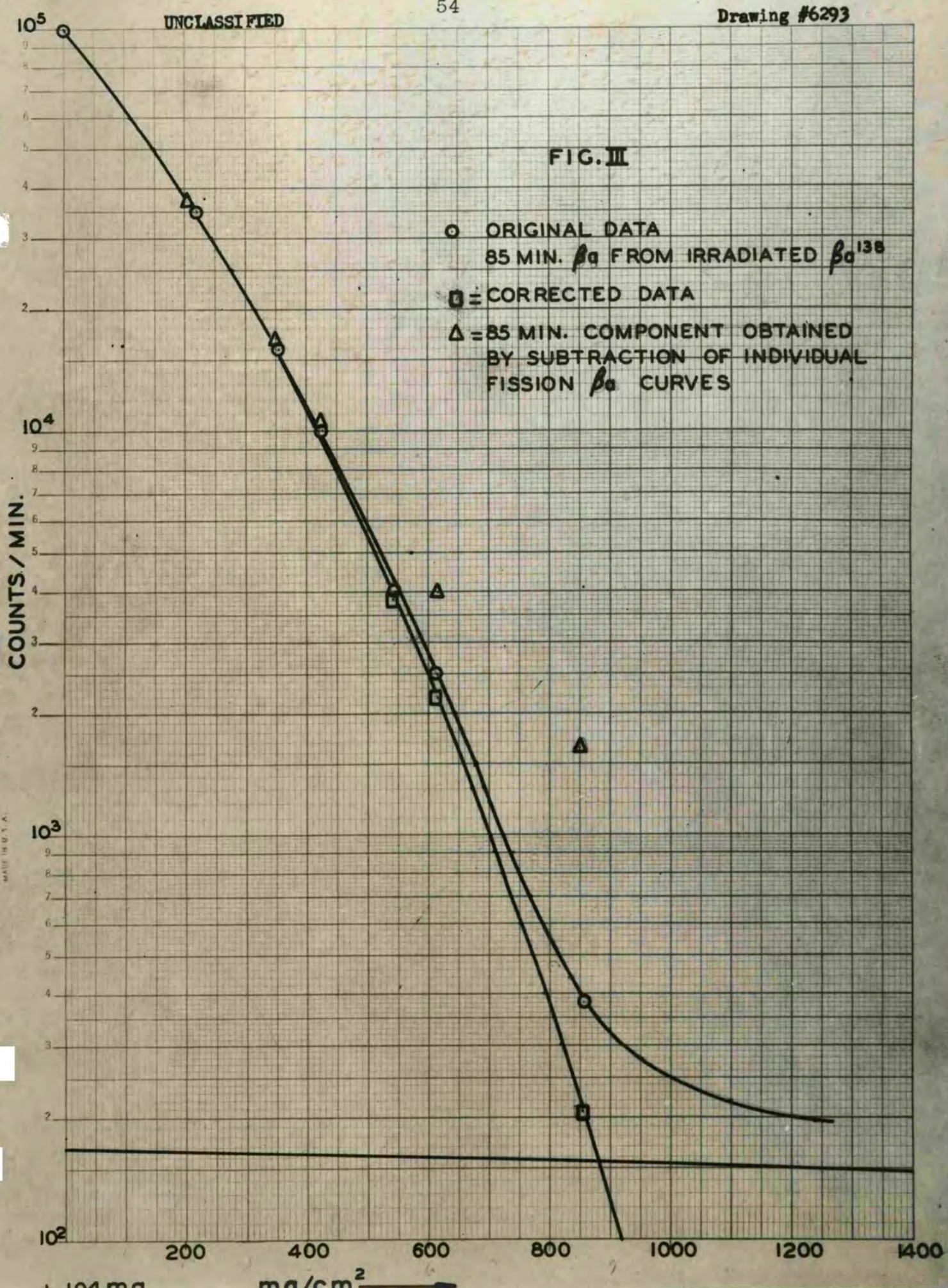


FIG. II

UNCLASSIFIED

Drawing #6293



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Solid Chemistry of Ruthenium - (M. D. Silverman, H. A. Levy)

The Crystal Structure of $KRuO_4$

Introduction: Previous work[1], using Debye-Scherrer powder patterns, revealed that $KRuO_4$ possessed a tetragonal structure and was isomorphous with scheelite ($CaWO_4$), KIO_4, $KReO_4$ and other crystals of this type. Either of two space groups, C_{4h}^6-$I4_1/a$ or C_4^6-$I4_1$, requires the following absences and these are confirmed by the experimental data: $hk\ell$ when $h + k + \ell$ is odd, corresponding to a body-centered lattice; 00ℓ when ℓ is not a multiple of 4. The former space group also requires one more set of absences, i.e., hk0 when h or k is odd. There are four molecules of $KRuO_4$ present in the unit cell with K and Ru occupying the 4-fold special positions a and b[2]. The sixteen oxygen atoms are placed in the g eneral positions (f). The two sets of 8-fold positions c, d, or e are ruled out because they do not lead to a chemically plausible structure and do not fit the experimental data.

Experimental Procedure: Single crystals were mounted on glass fibers and oriented properly by means of oscillation photographs. This procedure consisted of taking two 10-15° range oscillation pictures with the crystal in two positions 180° apart. By making one exposure longer than the other, it was possible to tell how the crystal was tipped from its axes. Adjustments were made by means of the goniometer head rocker arms until the crystal was lined up so that it rotated about the c or a axis.

Two series of photographs were obtained. The first series was made with rotation about the c axis of the crystal. Complete 360° rotation pictures were taken and then Weissenberg (moving camera) photographs were made of the equatorial, 1st, 2nd, and 8th layer lines. Since the crystal was rotated about the c axis, these consist of the hk0, hk1, hk2 and hk8 reflections, respectively. A second series was obtained by mounting and orienting another crystal so that rotation took place about the a axis. Complete rotation photographs were taken as well as Weissenberg pictures of the equatorial and 1st layer line. This gives all the $h0\ell$ and $h1\ell$ reflections, respectively. Three films were placed front to back in the camera for all these photographs (except orientation) to aid in the estimation of intensities.

Results and Calculations: Absolute structure factors were calculated for the hk0 reflections for a series of models, using assumed parameters. The initial model calculated was based on the parameters for potassium osmiamate, $KOsO_3N$,[3] which is isomorphous with potassium perruthenate and possesses lattice constants quite close to those of the perruthenate. None of the calculated early models fitted the experimental data well; hence, maps of a number of the planes were plotted to ascertain the effect of changing the x and y parameters for these hk0 reflections. The observed intensities were converted to absolute structure factors and these were compared with calculated values obtained by noting the forbidden areas on the maps of the reflecting planes. It was then possible to estimate the x and y parameters fairly well. These can vary between x = 0.37 - 0.38 and y = 0.238 - 0.240.

[redacted]

[redacted]

Employing the values of x = 0.38 and y = 0.238, absolute structure factors were then calculated for the h0ℓ reflections. Again, maps of the various planes were plotted, this time to estimate the z parameter. Although the most likely value of z appears to be about 0.79, there are several distinct discrepancies between the calculated structure factors and those obtained from observed intensities. These are for the 105, 107, 305 and 307 planes. These discrepancies may be due to either of two things or a combination of both(1): The atomic scattering factors used for Ru may well be too large, so that the effect of the oxygen atoms is not as large as it should be in the calculation of the structure factors(2), or errors were made in estimating the observed intensities due to having an undesirably large and irregular crystal for the h0ℓ reflections. It was noted that the reflections obtained on the photographs taken about the c axis were sharper and were not split, whereas those obtained for the h0ℓ series were split on a number of reflections. The results indicate that the data from the hk0 photographs are better than those from the h0ℓ reflections.

Program: Further efforts to refine the parameter values are underway. The better crystal has been remounted so that it can be rotated about the a axis, and a series of photographs of the h0ℓ reflections will be retaken to obtain better data.

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(1) ORNL-65
(2) "Internationale Tabellen zur Bestimmung von Kristallstructuren", Gebrüder Borntraeger, Berlin, 1935.
(3) Jaeger, F. M. and Zanstra, J. E. Proc. Acad. Sci. Amsterdam 35, 610 (1932).

[redacted]

Effect of heavy particle radiation on water and aqueous solutions -(A. O. Allen, J. W. Boyle, J. A. Ghormley, C. J. Hochanadel, D. M. Richardson) P.A. CX5-20

Calorimetric measurements of energy imparted to various materials by radiation in Hole 12 of the pile have been completed, and the results analyzed in terms of the contributions to the total energy of fast neutron collisions, γ-ray absorption and radioactivation of the materials (if any). The complete report of this work is being prepared and will be issued as ORNL-129.

Data obtained over the past two years on the decomposition of water and aqueous solutions in the pile, and the kinetics of the back reaction between dissolved hydrogen and hydrogen peroxide under pile radiation have been assembled and analyzed. A report on this subject is being prepared and has been assigned the number ORNL-130.

The work on the decomposition of tritium water under its own radiation has also been written up as report ORNL-128.

The work on decomposition of concentrated H_2SO_4 and solutions of UO_3 under pile radiation is also being written up as an ORNL report.

Work was begun on determining the rate at which the combination of hydrogen and oxygen to water occurs at high temperatures when catalyzed by an aqueous slurry of U_3O_8. D. M. Gillies, in report MDDC-647, has shown that the U_3O_8 in such a slurry is reduced rather rapidly by gaseous hydrogen at 250° C or above, and is also oxidized rather rapidly by gaseous oxygen at the same temperature. It would seem that if both gases are present, the reduction and oxidation should occur simultaneously, so that the slurry should act as a catalyst for the reaction of the gases. This may indicate a possibility for operating a homogeneous slurry pile without the trouble due to formation of gas bubbles, provided the U_3O_8 is a sufficiently active catalyst to recombine the product gases as fast as they are produced by the action of fission fragments and other radiations on the water moderator. The question is whether the U_3O_8 is a sufficiently active catalyst, and if so, whether its activity will be retained over long periods. It appears possible from Gillies' work that a gradual drift of the composition of the oxide toward UO_3 will occur, with resultant recrystallization of the oxide particles and loss of catalytic activity. These points are to be determined experimentally by placing a mixture of hydrogen and oxygen gases over a U_3O_8 slurry in a rocking autoclave maintained at temperatures of 250° C or over. Available pressure vessels are designed to withstand 10,000 pounds pressure, but it is planned to keep the total pressures below 2,000 pounds. Apparatus is almost completely set up. All operations will be conducted behind a 2' sand bag barrier for safety. If the results of the experiments are not promising, the problem should be dropped; but if the results do appear promising, experiments should be run in the pile to see whether a slurry of enriched U_3O_8 in water exposed to pile neutrons at a high temperature will actually evolve gas.

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The System Uranyl Sulfate - Water and the Behavior of Aqueous Solutions of Electrolytes at the Critical Temperature - (C. H. Secoy)

I. Solubility of uranyl sulfate in water above 250° C. In previous reports solubility data for uranyl sulfate in water have been given up to 250° C. These data have now been extended to the critical temperature of water, 374.4° C.

Experimental: The technique employed was to heat solutions of known initial concentration in sealed silica tubes recording the temperature at which the appearance or disappearance of a phase occurred. The tubes had a 2 mm. bore and 4 mm. wall thickness and were approximately 12 cm. long. The technique of filling the tubes, degassing the solution, evacuating and sealing the tubes has been described elsewhere. (CNL-18)

A stainless steel cylinder, 3" in diameter and 13" long, wound with a heating coil over its entire length, was used as a heating block. The silica tube rested at the center of the block and could be viewed through narrow slots in opposite sides of the block with the aid of a light source placed behind the apparatus. The entire assembly was clamped in a horizontal position in a rocker mechanism which oscillated through a vertical arc of about 30° causing the liquid contents to flow back and forth in the silica tube. In the two liquid phase region free flow was always obtained at temperatures well below those at which phase changes were observed. An explosion shield with Plexiglass windows could be attached to the rocker.

Temperature was measured by means of an iron-constantan thermocouple using a Type K-2, Leeds and Northrup potentiometer. The hot junction of the thermocouple rested on top of the silica tube at its midpoint. Since a finite temperature difference between the contents of the tube and the outside of the tube would be expected, the thermocouple was calibrated against the critical change of carefully purified acetic acid (321.6°), propionic acid (339.5°), chlorobenzene (359°), water (374.4°), and bromobenzene (397°).

Correction for Weight of Water in the Vapor Phase: The maximum volume of vapor above the solution was about 0.22 cc while the volume of solution used varied from about 0.10 to 0.20 cc. At high temperatures the loss of water to the vapor phase would materially change the composition of the liquid and a correction in compositions is necessary. The vapor pressure of the saturated solution was measured, using an isotensiscope method, at several temperatures from 25° to 70° C. Two bulbs, one containing water and the other saturated uranyl sulfate solution over an excess of salt crystals, were attached to the arms of a small U-tube differential manometer. The whole apparatus was agitated in a constant temperature bath and the difference in mercury levels in the U-tube, with appropriate zero-point corrections, gave the vapor pressure lowering due to the solute. The data are given in Table I. No other vapor pressure data are available..

[redacted]

TABLE I

Vapor Pressure of Saturated Uranyl Sulfate Solutions

T, °C.	Mole Fraction N_2	P, observed mm. of Hg	van't Hoff factor i
25	0.0688	4.60	2.814
30	.0694	5.82	2.635
35	.0700	7.41	2.510
40	.0708	9.56	2.441
50	.0724	15.6	2.329
60	.0744	24.9	2.240
70	.0765	39.4	2.204

In order to make an extrapolation to 181°, (the transition temperature trihydrate-monohydrate) the van't Hoff factor, i, was calculated and plotted against temperature (see Figure I). The values of i fall rapidly with increasing temperature and seem to approach the ideal value, 2. Such an extrapolation is undoubtedly questionable but in view of the fact that the resulting correction in the concentration of the solution up to 181° is less than the probable experimental error, it seems justified as a first approximation.

An examination of the phase diagram (see Figure II) indicates a triple-point at B, 374°, at which the three phases in equilibrium would be solid monohydrate, a liquid phase consisting of salt saturated with water, and another liquid phase consisting of water saturated with salt. Furthermore, the aqueous liquid phase was found invariably to undergo critical transformation at 374°, the critical temperature of pure water, provided that the volume of aqueous liquid bore the proper ratio to the volume of the vapor. This means that the aqueous liquid phase must be essentially pure water at the critical temperature. The partial pressure of water vapor at this temperature is, therefore, that of pure water. If the gas phase is assumed to contain only water vapor, the vapor pressure of the monohydrate saturated solution must also be equal to that of pure water since the two phases are in equilibrium. Thus, having established a value for the vapor pressure of the saturated solution at 181° and at 374°, one can draw a typical vapor pressure curve between these points as representing the vapor pressure of the monohydrate saturated solution.

In the two-liquid phase region, three phases are present and the system is monovariant. The temperature, therefore, fixes not only the composition of each phase but also the vapor pressure of the system. The lower critical solution temperature is 294° and the concentration about 30% UO_2SO_4. Assuming that the deviation from Raoult's law is independent of concentration, one can calculate the pressure of the 30% solution from the estimated value for the monohydrate saturated solution at this temperature. Again the pressure must rise with increasing temperature and reach that of water at 374°.

This is, at first sight, a crude approximation. However, the resultant corrections in the concentration of the solutions are most significant in the

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high temperature and high concentration region, i.e., in the vicinity of point B. (Figure II). This is the region where the approximated vapor pressures are most nearly correct and at the point B must be precisely correct. Error in the approximations could only result in shifting the curves slightly in this region and would not alter the fundamental nature of the phase diagram.

Discussion: The data are summarized in Table II in which the initial or overall composition of the contents of the tube as obtained by chemical analysis is given in the first column. The second column gives the composition of the liquid phase at the temperature of phase separation. These values were calculated from the initial composition and the vapor pressure of the solution estimated as described above.

In the two liquid phase region the equilibrium could be approached from either direction and the temperatures established with precision. These temperatures are believed to be correct to the nearest tenth of a degree. However, for the points on the solid phase solubility curve, equilibrium was reached much more slowly. Free flow of the solution was not obtained and the stirring was negligible. These points were approached with the temperature falling at a very slow rate (usually about two hours for the final degree) and the approach was repeated several times at even slower rates. The values reported are believed correct to the nearest degree.

At temperatures above 374° the system becomes one in which a gas is dissolved in a solid under pressure. The melting point of the solid is lowered by the presence of the dissolved gas so that a liquid state is possible. A univariant system can exist, the phases being solid salt, liquid salt saturated with gas, and gas. However, such a system would be very pressure dependent and the techniques employed in this work are not adequate to study the system in this range.

The point B has the character of a triple-point. At lower temperatures we may have equilibrium between the two liquid phases at concentrations less than that at B, or equilibrium between the salt liquid phase and solid monohydrate at concentrations greater than that at B. At higher temperatures we have only the equilibrium between the aqueous gas phase and solid monohydrate. Although this point was not realized experimentally, the data indicate that it occurs at the critical temperature of water. If this is true, it must be by virtue of the fact that the vapor pressure of the monohydrate saturated solution becomes equal to the critical pressure of water at this temperature.

Summary: The system uranyl sulfate - water displays a two liquid phase region with concentrations up to 82.7% UO_2SO_4. The lower critical solution temperature is 294° and the critical concentration is 30% UO_2SO_4. The aqueous phase undergoes critical transformation at the critical temperature of pure water indicating that it is pure water at this temperature.

The solubility curve of solid $UO_2SO_4 \cdot H_2O$ is followed to its intersection with the two liquid phase region. This intersection has the character of a triple-point and occurs at 374.4° and a concentration of 82.7% UO_2SO_4.

[redacted]

TABLE II

Solubility of Uranyl Sulfate in Water

% UO_2SO_4 Initial	% UO_2SO_4 Corrected	Temperature ° C.	Phase Appearing or Disappearing	Critical Temp. of Aqueous Phase
0.77	1.1	335.1	Liquid Salt	
3.15	3.6	319.4	" "	
5.86	6.8	310.1	" "	
12.30	13.8	299.9	" "	374.3
20.40	22.5	295.8	" "	
31.65	34.6	295.5	Aqueous	374.0
40.72	44.2	297.5	"	374.2
48.06	52.2	302.3	"	374.2
55.45	60.1	308.2	"	
58.64	63.7	312.5	"	374.4
60.60	65.9	316.2	"	
62.32	68.0	320.5	"	
67.43	75.2	339.6	"	
71.00	80.8	363.0	"	
72.60	81.7	365.	Solid Monohydrate	
72.85	80.2	347.	" "	
73.49	77.8	311.	" "	
73.94	76.7	287.	" "	
76.02	76.3	181.	" "	
76.66	76.7	152.	" " (metastable)	

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Drawing # 5935

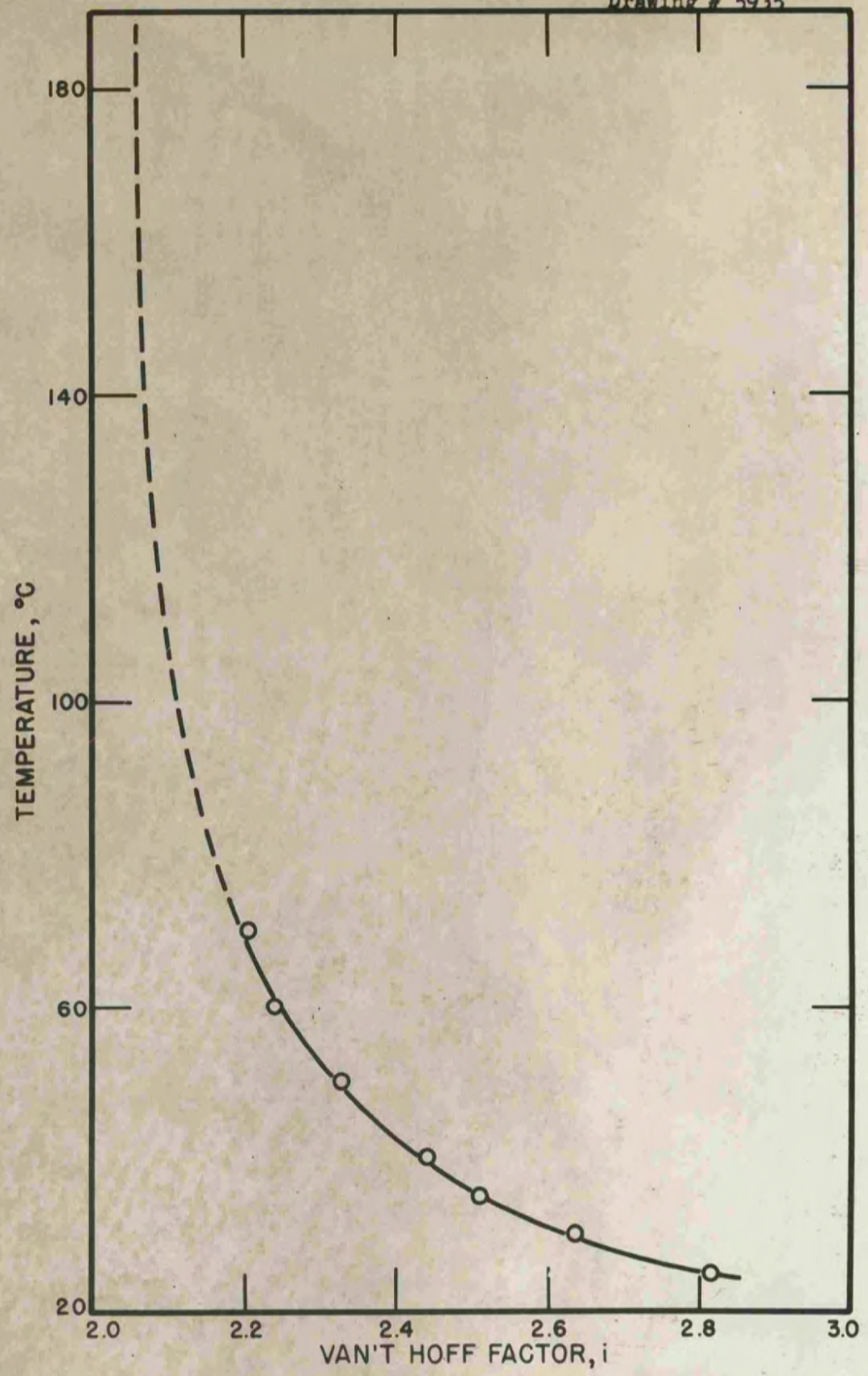

FIG. I
VARIATION OF THE VAN'T HOFF FACTOR WITH TEMPERATURE

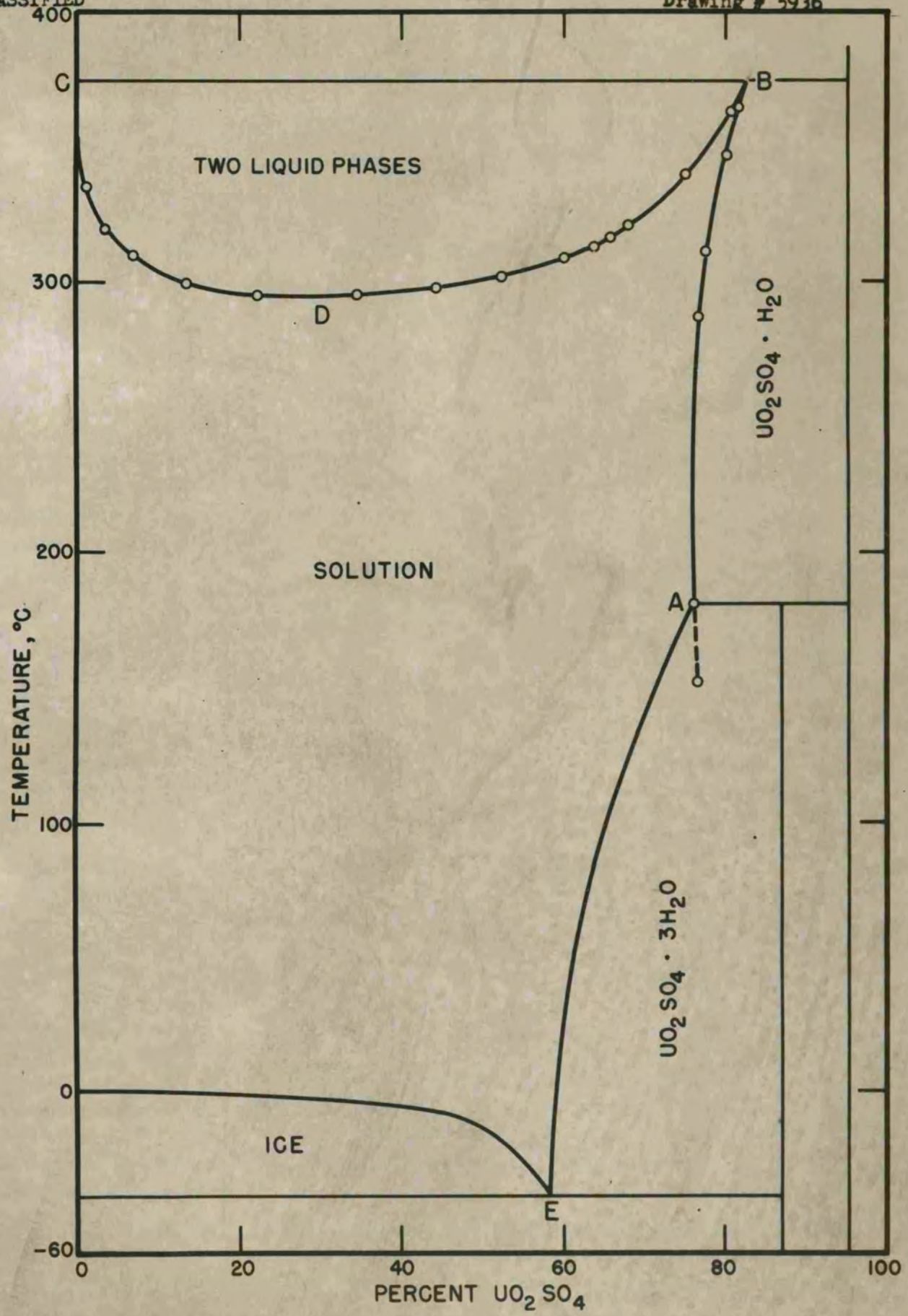

FIG. II

PHASE DIAGRAM FOR SYSTEM URANYL SULPHATE-WATER

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II. Behavior of Aqueous Solutions of Electrolytes at the Critical Temperature. The behavior of the uranyl sulfate system at the critical temperature gives rise to questions concerning the behavior of solutions of electrolytes in general. Although no extended study of such systems has been made, there is considerable qualitative and semiquantitative information in the literature. Several types of phenomena may occur either below or above the critical state. Irreversible chemical change involving reactions of decomposition or hydrolysis may take place. Irreversible precipitation of oxides, hydroxides, hydrated oxides and oxy-salts have been reported in certain cases. In cases where no evidence of chemical change is noted, the formation of a solid or liquid phase may occur either below or above the critical phenomena. Finally, the solute may remain in solution and the solution undergo a critical phenomena similar in all respects to that of the pure solvent. The critical temperature of the solution is, in all known cases, higher than the critical temperature of the pure solvent; however, no adequate theoretical relationship between the elevation of the critical temperature and the concentration of the solution is known. Table III briefly summarizes the observations that have been reported in the literature as well as those made in this laboratory. In most cases only one or two concentrations have been observed and the phase relationships are far from complete. The table merely indicates the type of phenomena that might be expected for the salts listed.

TABLE III

I. Salts whose aqueous solutions are stable and show no phase separation. Critical temperature is elevated.

$NaCl$, KCl, KBr, KI, $RbCl$, KNO_3, $CaCl_2$

II. Salts whoseaqueous solutions are stable and show phase separation.

A. Critical temperature is not elevated:

Na_2SO_4; solid phase
K_2SO_4; solid phase
$MgSO_4$; solid phase
UO_2SO_4; liquid phase

B. Critical temperature is elevated:

$BaCl_2$; liquid phase first, then solid
Rb_2SO_4; liquid phase
$CuSO_4$; solid phase
$SrCl_2$; liquid phase

III. Salts whose aqueous solutions show irreversible or very slowly reversible chemical change.

$CuCl_2$, $CoCl_3$, $UO_2(NO_3)_2$, UO_2Cl_2

The alkali halides, which display high solubility in the fluid state above the critical temperature, stimulate conjecture concerning the character of such solutions. Preliminary work with absorption spectra is underway by which it is hoped some information about the molecular state can be obtained. Neodymium chloride has been selected for initial study since it yields exceptionally sharp absorption bands in the visible and ultraviolet. The work has not progressed far enough to give any indication as to whether or not revealing information will be obtained.

 [redacted]

Spectra of the Heavy Elements and Rare Earths in Crystals and Solutions - S. Freed, F. J. Leitz, Jr.)

Further study has been made of the preparation of solutions fluid at 77° K for absorption spectral observation. These solutions are composed of heavy element or rare earth compounds as solutes and a solvent consisting of a hydrocarbon mixture to give the required low melting point and an additive such as alcohol to give appreciable solubility of the solute. Such solutions must be prepared at reduced temperatures and in the absence of water. Accordingly, the preparation is conducted in a Dewar flask attached to a high vacuum line.

In the upper part of the Dewar, D, is situated a mixing chamber, E, which can be cooled with a jet of liquid nitrogen - cooled gaseous nitrogen and into which the organic constituents of the solution may be distilled in the absence of any foreign gas. For spectral observation these solutions are then transferred in the Dewar through a capillary tube, B, to a capillary optical absorption column, A, which is coaxial with the Dewar.

In the absorption spectra experimentation the optical path through the Dewar is defined by the capillary column A. A-1, 2, 3, and 4 are flat Corex windows. Corex gives greater transparency than pyrex glass in the ultraviolet, and four windows being required since a pair of windows separated by a vacuum is needed at each end of the column to prevent frosting at low temperatures. Windows A-2 and 3 are inset in the column to minimize the likelihood of trapping a bubble on their faces which would interfere with the optical path through the solutions.

The Dewar with its mixing chamber and capillary side-room, C, is connected to the high vacuum system through the ground joints attached to the control stopcocks G-1, 2 and 3. Flexibility of these three joints is achieved by means of 3 mm. glass helices on the vacuum line.

A typical solution recently investigated consisted of 1-2 mg of uranyl acetylacetonate in a solvent comprised of ~ 1/2 ml butyl alcohol, ~ 4 ml iso-pentane, and ~ 8 ml propylene. The 2:1 ratio of propylene to iso-pentane gave a less viscous solution at 77° K than the 1:1 mixture formerly used.

Distillation of the butyl alcohol and then the iso-pentane into the uranyl salt previously added to the mixing chamber proceeds smoothly with the chamber at -20 to -90° C. Distillation of the propylene from a gas cylinder to the mixing chamber is sufficiently rapid and smooth at or below -90° C than at any appreciably higher temperature. The resulting solution had a low viscosity and could be readily transferred to the capillary column by cooling the latter to a temperature lower than that of the mixing chamber. This transfer was prevented during the preparation of the solution by electrical heating of the capillary column.

This mode of solution preparation was found rather satisfactory, but unfortunately the spectrum of this particular solution was not very informative. After a matter of hours a flocculent precipitate appeared in the capillary column and this may have been partially responsible for the unsatisfactory spectral results. This type of investigation will be repeated and next be applied to solutions of rare earth acetyl acetonates.

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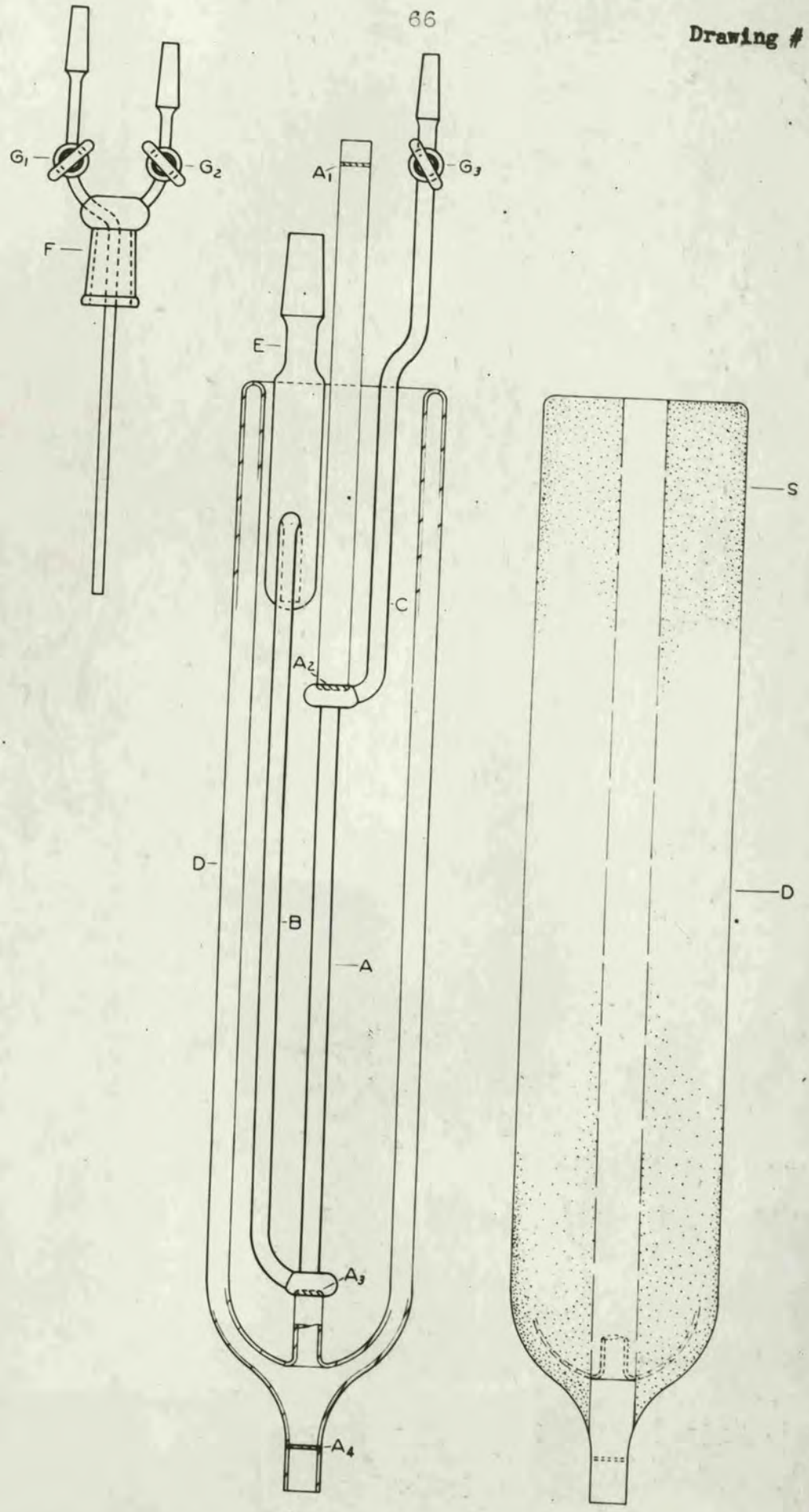
Drawing # 6291



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Cloud Chamber Studies - P. A. CX4-1 (R. Livingston)

The recent major problems in the cloud chamber work have been photography, the bad effects of the neutron beam on track quality and the difficulty in getting sharp tracks after prolonged running.

The photographic problem has been reasonably well solved. A number of commercial photographic emulsions were tried. Eastman's Linagraph Ortho was found far superior to the Super XX that has been in use. It has considerably more contrast and is faster than Super XX. It's resolution is also good. The new method of lighting described in the last quarterly report has been put into use. In this method light is scattered through 70° rather than 90° in order to get from the track droplets to the camera. The smaller angle scattering gives a substantial increase in track brilliance and hence contrast. Adequate illumination intensity is provided by two new stroboscopic lights with improved optics described in Rev. Sci. Instr. 19, 271 (1948). Suitable exposures have been made at f16 on Linagraph-Ortho film. In recent work the contrast has decreased which probably means that the platinum black background in the chamber needs replacement.

The effects of the neutron beam on the cloud chamber operation have been greatly reduced. The effect was largely caused by the neutrons in the beam rather than the gammas alone. Apparently, the neutrons were striking the walls of the chamber and producing a large number of gammas in the chamber by n-γ processes. A series of pictures of the beam were taken on X-ray film backed with an indium foil. It was found necessary to raise the cloud chamber 1/4" and to place a beam collimating slit between the pile wall and chamber. A 1 1/2" thick bismuth plug was also placed at the beginning of the graphite stringer in the pile shield. Upon making these changes the bad beam effects practically disappeared. Two to four fissions still appear per chamber expansion.

Continual operation of the cloud chamber for several hours usually results in the tracks becoming very broad and diffuse. The effect was first attributed to convection currents due to large thermal gradients. All electrical equipment that produced much heat was moved away from the chamber, but no improvement was noted. The effect was finally found to be caused by the sweep field electrode. This electrode is a grid of nickel wires against the top plastic window of the chamber. The plastic, fluorothene, is a very good insulator. The chamber filling mixture is also a good insulator. Apparently, ions collect on the plastic between the sweep electrode wires. When the sweep voltage is interrupted, an electrostatic field continues to appear in the chamber due to the collected ions. To eliminate the effect one method tried was to reverse the polarity on the sweep electrode between successive expansions. The result was not satisfactory. The method to be tried next will be to decrease the high insulating property of the plastic window by an extremely thin evaporated metal film. The difficulty with this method is the danger of complete fluorination of the metal by the cloud chamber filling mixture.

[redacted]

Calorimetry of Radioactivity - (G. H. Jenks, F. H. Sweeton, J. A. Ghormley)

I. Study of Half-life and Average Energy of Tritium Disintegration

A sample of tritium gas diluted with normal hydrogen has been analyzed for tritium content with the gas density balance, and condensed on palladium in an ampoule suitable for use in the β-calorimeter. Following calorimetric measurements on the tritium, condensed on palladium, it was quantitatively converted to water and transferred to a quartz ampoule. In this form the heat evolution of the sample was again measured.

A determination of the rate of He^3 evolution from the sample is now being carried out. Using the results of these measurements, it will be possible to calculate accurate values for the half-life and average energy of the decay.

Analysis of sample for tritium content - The gas density balance and the associated gas controlling system, which were designed and constructed for use with the tritium sample, have been discussed briefly in a previous quarterly report and will be described fully in a report now in preparation.

The general procedure followed in determining the relative proportions of tritium and normal hydrogen in the sample was to compare the pressure of the tritium sample necessary to balance the arm of the gas density balance with the pressure of normal hydrogen necessary to balance it. In practice, repeated observations were made of these quantities, alternating a measurement of the tritium sample with a measurement of a sample of normal hydrogen. Between determinations, the tritium sample was repurified by repassing through palladium. The following table shows the balancing pressures determined for the various samples.

Date	Time	Gas	Pressure (mm Hg) Hydrogen	Pressure (mm Hg) Tritium
6/15	7:54 PM	H_2, freshly filtered	307.3_3	
6/16	7:56 AM	H_2, same	307.0_3	
6/17	9:19 AM	H_2, freshly filtered	306.6_7	
	10:10 AM	H_2, same	306.7_5	
	2:15 PM	Tritium, filtered		154.2_6
	5:08 PM	H_2, freshly filtered	307.1_1	
	6:02 PM	Tritium, refiltered		154.8_7
6/18	3:56 PM	" "		155.1_7
	6:30 PM	" "		155.5_8
	7:34 PM	" , same		155.4_5
	9:03 PM	" , refiltered		155.6_6
	10:57 PM	" "		155.7_1
6/19	2:00 AM	H_2, freshly filtered	306.7_8	
		Best values	306.8	155.7

Very good reproducibility was obtained with normal hydrogen, but a slight increase in the balancing pressure of tritium occurred with repeated filtering through palladium. This increase was easily shown to be due to an increase in

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foreign gases in the apparatus when in contact with tritium. The foreign gases were removed when the gas was refiltered through palladium. The amount of foreign gases arising in this manner became steadily smaller and reached a negligibly small amount during the last two measurements on tritium.

Following the final measurement of the density of the tritium gas, the volume of the sample was measured and the gas then condensed on palladium contained in a pyrex ampoule.

The possibility existed that the quartz bulb of the gas density balance altered in dimensions when different balancing pressures were applied. Calculations, using the elastic modulus of quartz, indicated that a significant change in the buoyancy of the bulb might occur in changing from a pressure of 300 mm to 150 mm.

To establish the magnitude of the effect experimentally, a comparison of the balancing pressure of normal hydrogen and helium was made. The density of helium is approximately the same as that found for the hydrogen-tritium mixture and the comparison should therefore give an accurate measure of any necessary correction.

The helium used for the comparison was obtained from a tank supply. Its density, determined directly by weighing in a 5-liter flask, was found to be 0.1789 g./l., 0.2% greater than the literature value for helium density. Balancing pressures obtained for this helium and for normal hydrogen are shown below.

Time	Gas	Pressure (mm Hg)	
		Hydrogen	Helium
11:18 AM	H_2 - freshly filtered	299.1	
3:52 PM	He - from bulb		152.0
4:59 PM	H_2 - same	300.05	
5:58 PM	He - from bulb		152.4
6:39 PM	H_2 - same	300.3	
7:03 PM	He - from bulb		152.5
	Best values	300.3	152.5

The density of helium as measured by the gas density balance, was then 0.1771, 1.0% less than the density measured directly by weighing. The correct balancing pressure for the tritium-hydrogen mixture was therefore 1.0% less than that observed directly.

The results of the measurement of the amount of tritium in the sample are summarized as follows:

Fraction of tritium in sample	0.4970
Volume of sample	5.173 ml STP
Volume of tritium in sample	2.571 ml STP
Estimated error in value for volume of tritium	± 1.4%

[redacted]

Heat evolved from tritium sample - The heat evolved from the sample of t tritium adsorbed on palladium was measured using the β-calorimeter. The data are shown below:

Calibration			Tritium	
Run No.	Watt Input	Rate (arbitrary units)	Run No.	Rate (arbitrary units)
1	2.200×10^{-4}	1.182	1	1.191
2	2.200×10^{-4}	1.177	2	1.169
3	2.200×10^{-4}	1.166	3	1.168
			4	1.191
		av. 1.175 ± 0.3% av. error		av. 1.[illegible] ± 0.5% av. error

Energy of tritium sample: 2.214×10^{-4} watts ± 0.6% probable error

A value of 5.68kev. for the average energy per disintegration has been reported by this group. The preliminary value computed for the half-life of tritium is then 12.5 years.

Following the above measurement, the sample of tritium was converted quantitatively to water and collected in a small quartz ampoule suitable for use in measuring the disintegration rate of the sample.

Several calorimetric measurements of the heat evolution from the sample of tritium water were made. The results of the measurements were dependent to some extent on the time, prior to the measurement, that the sample had been at liquid nitrogen temperature. In general, the heat evolved showed an increase during the run, starting out with an energy less than that obtained from the same volume of tritium adsorbed on palladium and increasing to some apparently constant value. For three measurements the final value was equal to, or a fraction of a percent less than, that of the tritium on palladium. For two of these runs the sample had been at room temperature for several hours before freezing in the calorimeter. In the third case, the sample was at liquid nitrogen temperature 64 hours before assembling in the calorimeter.

For the three other runs which were made, the sample had been frozen at -195° C. varying lengths of time, in one case 150 hours, before the calorimetric determination was made. For each of these cases, the final heat evaluation was about 2.5% higher than the tritium-on-palladium value. None of these runs was carried out for as long a time as the former three, and it is possible that these values would have changed further with time.

The variations of the results with the tritium water sample were considerably greater than the experimental error of the calorimeter. There is good indication that when the sample was freshly frozen a fraction of the decay energy did not appear in the form of heat. Is is reasonable that some energy would be stored in the ice as trapped electrons and as chemical energy. That storage of energy does occur is indicated by the observation that gas resulting

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from decomposition appears on melting tritium water which has been held at -196° C. In one sample in which 15% of the hydrogen was tritium, the yield of electrolytic gas after 6.5 hrs. at -196° C. accounted for 0.5% of the total decay energy. Since some recombination of intermediate products probably occurred on melting, this would be only a lower limit for the fraction of the decay energy which would not appear as heat in the calorimeter measurements. No explanation has been found for the cases in which the heat evolution was greater than that of the tritium on palladium.

Calorimetric measurements on the sample have been suspended so that a disintegration rate determination may be made.

II. Attempt to Measure the Energy of a Sample of C^{14}

In connection with a program, initiated by this laboratory, to standardize the relative and absolute counting of C^{14}, we agreed to attempt to measure the energy of the sample from which the counting standards would be made. The sample available consisted of about 100 m c. of C^{14} in the form of $BaCO_3$. Approximately 2% of the carbon in the sample was C^{14}, so that the total sample had a volume of about 20 ml. As the calorimeter was designed to hold about 1 c c. samples, a modification was required.

Procedure: A stainless steel ampoule, 25 m m. in diameter and 50 m m. in length, was designed to contain the C^{14} in the calorimeter, and a modification of the calorimeter Dewar large enough to hold the steel ampoule was constructed. The heat capacity of the modified calorimeter was thus about five times greater than that of the original calorimeter, and the diameter of the neck of the Dewar, which is the main factor in determining the heat leak, was larger by the same amount.

Calibration runs with the calorimeter proved it to have a background larger by about a factor of five than was found with the smaller calorimeter. For the small amount of heat which would be evolved from the C^{14} sample ($\sim 3 \times 10^{-5}$ watts), this background heat leak would be slightly larger than that of the samples. Under these conditions, an accurate determination of the energy of the sample would be very difficult, if not impossible, and we have abandoned attempts to study it.

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Analytical Chemistry

Polarographic and Electrolytic Studies (L. B. Rogers, J. C. Griess, D. P. Krause, H. H. Miller)

All phases of this work have been completed and the results have been included in the following project reports:

ORNL-81 - "Pentavalent Manganese", H. H. Miller and L. B. Rogers.

ORNL-91 - "A Study of the Separation of a Trace of Silver from a Macro Amount of Palladium by Electrolysis", J. C. Griess and L. B. Rogers.

ORNL-99 - "The Electrodeposition Behavior of a Simple Ion", L. B. Rogers and A. F. Stehney.

ORNL-100 - "Comparison of Polarographic Curves Obtained with a Rotated Micro Electrode and a Stationary Electrode", H. H. Miller and L. B. Rogers.

ORNL-117 - "An Instrument for Controlled-Potential Electrolysis", R. W. Lamphere and L. B. Rogers.

ORNL-118 - "The Electrodeposition Behavior of a Trace of Silver", L. B. Rogers, D. P. Krause, J. C. Griess and D. B. Ehrlinger.

ORNL-121 - "Electroseparation of Technetium from Rhenium and Molybdenum", L. B. Rogers.

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[redacted]

Spectrophotometric Determination of Aluminum in the Presence of Iron Using Ferron - W. H. Davenport

This investigation has been completed and the report (ORNL-83) has been issued and is available.

Ammonium Thioglycolate as a Colorimetric Analytical Reagent for Uranium in the Presence of Various Anions - W. H. Davenport, P. F. Thomason

This method has just been completed and the report is being submitted for publication as a project report. Briefly, it has been found that ammonium thioglycolate gives an intense orange-yellow color with uranium^{+6} in a basic solution. This color is suitable for the spectrophotometric determination of uranium in the presence of a number of anions that interfere with other colorimetric methods. Several cations, Fe, Ni, Co, and Cr, interfere, however organic complexing reagents such as tartaric or citric acid may be used to minimize some of these interferences.

Colorimetric Determination of Selenium with Pyrolle - F. J. Miller, P. F. Thomason

Selenium in an acid solution containing ortho-phosphoric acid forms a greenish-blue color with pyrolle. This has been made the basis for the colorimetric determination (1) of selenium. It was found necessary to develop the color in an ice bath as room temperature produced an unstable colored solution which intensified on standing.

Aliquots of acid solutions containing 5 to 40 micrograms of selenium are pipetted into 25 ml. volumetric flasks. Ten ml. of o-phosphoric acid are added to the flasks which are cooled in an ice bath. The o-phosphoric acid is rinsed down with distilled water and 0.5 ml. of 1% solution of pyrolle in ethyl alcohol is added. The solution is made to volume with distilled water and mixed thoroughly. The color is allowed to develop five minutes in the ice bath and then read immediately in a Coleman spectrophotometer at 445 mu. wavelength versus a reference solution containing everything but selenium. The concentration of selenium is found from a standard calibration curve obtained from solutions made by dissolving selenium metal in concentrated sulfuric acid.

As this method will be used for the relatively pure solutions obtained by the radioisotope production group, interferences were not thoroughly investigated, however, it is known silicic acid gives a similar reaction.

Determination of Uranium in the Presence of Potassium Dichromate by the Thiocyanate Method - E. K. Hanig, P. F. Thomason

The colorimetric determination of uranium with thiocyanate as given by Currah and Beamish (2) has been used quite successfully with process solutions containing thorium, iron, aluminum, and uranium. However, the proposed redox process will require a rapid colorimetric method for the determination of uranium in the presence of 0.1 molar potassium dichromate. Heretofore on a few isolated samples, the chromium was volatilized with perchloric and hydrochloric acids. This procedure is not feasible for a routine method. Therefore an investigation

(1) R. Berg and M. Teitelbaum, Mikrochem., Emich, Festschr. 23-6, (1930).
(2) J. E. Currah and F. E. Beamish, Anal. Chem., 19, 609 (1947).

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was made to determine the amount of uranium that could be accurately found by the thiocyanate method in the presence of 0.1 molar potassium dichromate. It was learned that 5 milligrams of uranium per ml. was the lower limit for an accurate determination as this permitted a 100 λ aliquot to be analyzed. The slight blue color of this amount of chromium when it was reduced by the stannous chloride in the procedure did not absorb appreciably at the 380 mu. wavelength. However, when the concentration ratio of chromium to uranium was increased to 29.4 mg. of $K_2Cr_2O_7$ (0.1 molar) to 1 mg. of U per ml. the absorption by the chromium resulted in a 10% error.

As these solutions are also expected to contain 0.65 molar aluminum, it was decided to attempt to separate the uranium from the potassium dichromate by precipitating the aluminum and uranium with carbonate-free ammonium hydroxide. It was found that as little as 400 micrograms of uranium per ml. could be determined by dissolving the centrifuged precipitate in HCl and repeating the precipitation twice. The results obtained were within ±3% which is the experimental error of the straight thiocyanate procedure.

Analytical Apparatus Development - H. L. Hemphill, P. F. Thomason

Improved Fusion Device - The plans for a modification of the fusion device (CML-23) used for the fluorimetric uranium analysis have been submitted to the engineering group. The modification should eliminate the frequent loss of samples caused by the erratic movement of the stainless steel spider which holds the fusion dishes in the burner flame. Threaded lavite tips will be used to fasten the platinum loops to the stainless steel spider. This should eliminate the deterioration of the stainless steel spider caused by the intense burner heat.

Automatic Temperature Control for the Distillation of Silicon Tetrafluoride

The volumetric determination of fluorides (1) usually requires a separation from other elements by the steam distillation of hydrofluosilicic acid which is absorbed in weak sodium hydroxide. The fluoride can then be titrated with a standard thorium nitrate solution using sodium alizarin sulfonate as an indicator.

The flask containing the fluoride sample, concentrated H_2SO_4, and a few glass beads must be kept at 135° C. for distillation. It is difficult to rigidly control the temperature with either a gas burner or a hot plate, therefore an aluminum jacket containing a nichrome heating element that is thermostatically controlled was made to fit the flask. This unit maintains the temperature to 135° C. ±0.5° C. and facilitates the analyses of routine samples by the water analysis group.

Colorimetric Determination of Tellurium with Thiourea - E. K. Hanig, P. F. Thomason

Tellurium reacts with thiourea (2) in an acid solution forming a yellow color whose intensity is proportional to the amount of tellurium, hence suitable for its estimation. Crossley (3) recommended a turbidimetric method using

(1) H. H. Willard and O. B Winter, Ind. and Eng. Chem. Anal. Ed., 5, 7 (1933).
(2) Pietro Falciola, Ann. Chim. Applicata. 17, 359 (1927), A. A. 3580 (1927).
(3) P. B. Crossley, Analyst; 69, 206 (1944).

[redacted]

[redacted]

stannous chloride to reduce the tellurium in the presence of thiourea. However it has been found that measuring the transmittance of the yellow colored solutions with a spectrophotometer is more reliable for the estimation of tellurium than the turbidimetric procedure.

A sample containing 200 - 1000 micrograms of tellurium is pipetted into a 25 ml. volumetric flask and 5 ml. of 10% thiourea aqueous solution are added. The solution is made to volume with 4 N HCl and the transmittance measured in a Beckman spectrophotometer at 380 mμ after allowing the solution to stand 10 minutes for color development. The amount of tellurium is obtained from a calibration curve made in the same manner using tellurium metal dissolved in HNO_3 as the standard.

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The Decay Scheme of Zirconium and of Columbium[95] - J. E. Hudgens, W. L. Lyon

A complete study of the decay scheme of these isotopes has been completed and the preparation of reports of the data obtained are in progress.

A Radiochemical Method for Plutonium - F. L. Moore, J. E. Hudgens

A rapid quantitative method for the analysis of plutonium has been developed and a report is being written. The method is based on a solvent extraction of the plutonium and a good separation from the usual stable and radioactive sample constituents can be achieved.

A Colorimetric Method for the Determination of Zirconium - R. H. Powell, J. E. Hudgens

The separation of a radioactive element from other radioactive elements in a sample is facilitated in the usual radiochemical procedure by adding a known weight of an inactive element isotopic with the radioactive element being sought. Precipitation type reactions can then be utilized to separate the element from other radioactive elements in the solution. A weighable form of the element is then prepared and weighed to enable the quantity of the element which has been lost in making the separations to be determined. Since it is usually necessary from the solubility and convenience standpoints to precipitate several milligrams of carrier in order that the precipitate may be weighed on an ordinary analytical balance the corrections for self scattering and for self absorption become appreciable. As a solution to this problem we have in the case of zirconium sought a colorimetric method of high sensitivity in order that the necessity of ashing a cupferron precipitate of zirconium and of using more than 0.2 milligrams of zirconium may be eliminated.

The most widely used colorimetric method for the determination of zirconium utilizes the color produced with alizarin. The method as described by Liebhafsky and Winslow (1) is time-consuming, requires accurate pH adjustments and the volumes of the solutions which are measured on the spectrophotometer are larger than is desirable. In the Liebhafsky and Winslow method the alizarin dye is added and the color formed in a basic medium. The solution is then adjusted to neutrality, made acid (pH 0.8) prior to the dilution with ethanol and the transmission determined on a Beckman spectrophotometer using a 5 centimeter cell and a 5600 Å wave length.

Experiments have been performed in which alizarin red S has been compared with alizarin as the color producing reagent. The lakes produced with alizarin faded more rapidly than did those formed with alizarin red S, however, higher concentrations of zirconium can be determined with alizarin since the transmittance curve obeyed Beer's Law over a slightly more extended range.

Studies of the rate of formation of the color have shown that intense and stable lakes were formed by adjusting the hydrochloric acid concentration of the zirconium solution to 6 M, diluting the volume to 0.5 milliliter and adding 0.5 milliliter of an alcoholic solution of alizarin red S. The solution

(1) Liebhafsky, H. A., and Winslow, E. H., J. Amer. Chem. Soc. 60 1776 (1938).

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thus formed was allowed to stand 12 minutes before diluting to volume with ethanol. The pH of the ethanol was adjusted to 2 pH units before using. The transmittance of the colored solution was read on a Coleman Model 14 spectrophotometer twenty minutes after the dye had been added to the zirconium solution. A 1 centimeter cell was used and the transmittance was measured at 5600 Å through a PC-4 filter.

Standard curves have been determined by forming the color with known quantities of zirconium. The slope of the curve thus obtained obeys Beer's law over the region which corresponds to 25 to 100 micrograms of total added zirconium, and an accuracy of ±2% should be readily obtainable.

Further work on this problem will be directed toward the discovery of methods of separating zirconium from the usual stable and radioactive sample constituents.

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Diffraction and Microscopy

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

About three quarters of the time of this section has been spent in work for K-25 which (at the request of their security department) is not reported here. The remainder of the time has been spent on the following problems:

(1) Ion exchange resins

In co-operation with G. E. Boyd, the study of the physical characteristics of a variety of ion exchange resins has continued. It is possible that the data being collected may aid in the interpretation of the behaviour of the different materials.

(2) Fibrous fractures in beryllium

Fibrous fractures in some recently manufactured extruded beryllium have been examined for the Technical Division to determine, if possible, the existence of, and the nature of foreign material at the fracture surface. The nature of these fractures is shown in Fig. 1, and it can easily be seen that they have a very marked effect on the mechanical properties of the metal.

The fracture surface has been examined by electron diffraction both here and at K-25 (R. Sherman), but only a few faint bands were found on occasional areas. These bands are insufficient for identification, but it can be concluded that the foreign material is amorphous and does not show crystal growth at 800°C., because the beryllium is extruded at approximately this temperature. Also, it did not appear probable that very hard materials such as beryllium oxide would behave as this material does in the extrusion process. From this type of reasoning the presence of carbon was suggested as a possibility. G. E. Boyd pointed out that this could be checked by deuteron bombardment in a cyclotron. At the request of the Technical Division this has been done by E. Creutz (refer to letter dated August 13, 1948 from E. Creutz to A. Weinberg) and, although the results were not conclusive, he suggests the possibility of calcium or magnesium fluoride. Spectrum analysis of a fibrous fracture and a normal one by C. Feldman showed slightly greater trace amounts of aluminum, calcium and magnesium in the fibrous surfaces as compared to the normal fracture surface. Neither carbon nor fluoride could be found.

If either calcium or magnesium fluoride were present in a relatively pure state, they would recrystallize at 800°C., and could easily be found by electron diffraction. However, as M. Bredig has pointed out, it is probable that a glass would be formed from a mixture of fluorides and this could melt at 800°C. It is easily seen that foreign inclusions of this nature could act in the same way as the unknown material does in the extrusion process.

(3) Corrosion fibers on beryllium

The corrosion fibers on beryllium metal specimens have been examined by electron diffraction for J. E. Draley. Good patterns were obtained in all cases but the materials could not be identified since there are very few recorded patterns of beryllium compounds. The data are recorded in C.F. 48-7-1 and in C.F. 48-8-350.

For technical reasons one of the patterns was made by R. Sherman of K-25.

(4) Miscellaneous

About the normal amount of time has been spent on photographic prints, record photographs of corrosion specimens, lantern slides, etc.

[redacted]

Fig. 1

Plate No. ME 205
Showing nature of fracture in extruded beryllium billet.

Mag. 1X

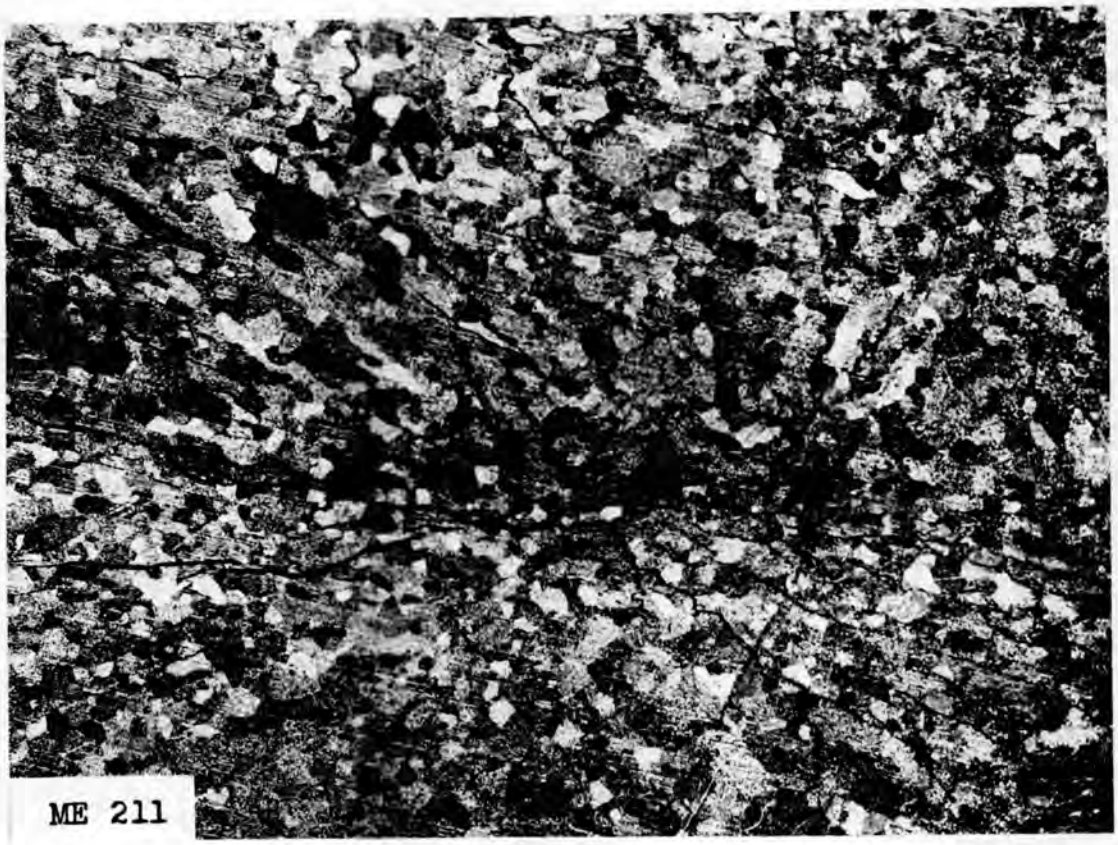
Plate No. ME 211
Transverse section showing radial cracks on billet of extruded beryllium. It is along these cracks that fractures take place during machining.

Mag. 6X Etchant 5% H_2SO_4

[redacted]

[redacted]

ME 205



ME 211

[redacted]

X-Ray Diffraction
(M. A. Bredig)

1) Crystal Structures of Beryllium Oxide.

In the last report, two alternative interpretations of the x-ray powder patterns of high-fired beryllia samples were discussed. It was pointed out that a preliminary microscopic examination failed to reveal any optically isotropic phase. It thus did not bear out the first assumption of a cubic beryllium oxide phase having sphalerite (zincblende) structure.

However, in view of the rather striking coincidence of some of the x-ray lines with lines to be expected for a cubic zincblende structure, it seemed desirable to have the matter of optical anisotropy checked by an expert petrographer. Dr. R. A. Hatch, of the Electrotechnical Laboratory of the U. S. Bureau of Mines at Norris, Tennessee, kindly undertook a careful microscopic-optical examination of a sample (XR-178) submitted to him by the writer. It contained, according to an estimate based on the x-ray pattern, about 50% of the new beryllium oxide phase. The result of this examination, confirming the previous microscopic finding, was that an optically isotropic (cubic) phase could not be present in more than trace amounts, far below 1%. Dr. Hatch's findings also confirmed the presence, in amounts varying between 15 and 25% in his preparations, of an optically anisotropic phase different from hexagonal beryllium oxide. (The discrepancy with the 50% figure above is probably due to uncertainties in the estimate from x-ray diffraction patterns.) The refractive indices of the new phase were found as 1.755 and 1.770, i.e., considerably higher than those of hexagonal BeO, 1.719 and 1.733. The crystals are biaxial positive, and of orthorhombic, or monoclinic, symmetry. They were reported to exhibit pinacoidal cleavage.

These findings lead to the final conclusion that not a cubic, zincblende, structure is present in high-fired beryllia, but a phase of considerably lower symmetry, most probably produced and established by an impurity.

In the search for the "foreign" substance that might be responsible for the observed new structure in beryllia, a number of samples were given high-temperature heat treatment under the supervision of W. W. Galbreath Jr. of the Power Pile Division at the Norris Laboratories. The x-ray examination of several dozen of such samples showed that the new phase occurred, in mixture with the hexagonal one, on heating beryllia at, or above, 2000°C, when carbon in the form of graphite or beryllium carbide was not excluded. It was never produced at temperatures of 1900° C, or lower. In view of the experimental difficulties, the accuracy of the figure 2000° C is subject to some doubt.

Of special interest was the last series of samples (of June 4th, 1948), in which the influence of the graphite of the furnace tube and cartridge were eliminated by the use of beryllia crucibles containing the specimens. Only in the one specimen in which 10% beryllium carbide, Be_2C, had been added to pure BeO (Sample No. BR-14) did the new phase occur, in an estimated amount of 25%. It was absent in samples of pure BeO, and of BeO containing 2% graphite, 2% graphite ash and 3% alumina. The amount of graphite added apparently was not high enough to form a sufficient quantity

of carbide for even partial conversion of the BeO to the new phase. It was also somewhat surprising to note that in the disk containing originally 10% Be_2C, the new phase was absent in a surface layer of 1 to 2 millimeter thickness of light-grey color. The interior of this pellet, which did contain the new phase (approximately 15%) was darkened by what appears to be graphite, produced by the decomposition of a major portion of the beryllium carbide added, possibly by reaction, with the water used as binder. It is hoped to eliminate in future experiments this decomposition, and to obtain the new phase in higher concentration. In order to learn the reasons for the present limitation to amounts, of the new phase, not exceeding 25 to 50%, longer heating periods and rapid quenching from various temperatures, including fusion, will be tried, so that equilibrium conditions may be ascertained.

The formation of beryllium carbide at the contact zone between BeO and graphite under the conditions of the experiments was established through its x-ray pattern. However, in addition, one very strong line and several medium strong ones with spacings 2.415, 2.209, 1.732 and 1.435 Å, of an additional phase, have been observed several times, beside the cubic phase of Be_2C. Its nature remains to be determined.

2) X-Ray Diffraction Study of Pile-Irradiated Metals.

D. S. Billington, of the Metallurgical Division, submitted approximately 30 samples of beryllium, magnesium, aluminum and copper, and of a binary copper-beryllium alloy (2% Be) to which he had given various mechanical and heat treatments. Some of these samples had been exposed to radiation in the X-10 pile for 3 weeks. The x-ray diffraction spectrometer was employed for a quick first survey. No effects of irradiation upon the width of the x-ray diffraction lines were observed in magnesium, aluminum and copper, but it is possible that small effects may be found in the reflection range above a Bragg angle of 45°, which was inaccessible with the present spectrometer. A rather strong effect was observed in two samples of the copper beryllium alloy, one hardened by cold work, the other, in addition, by aging. The line breadth of the (111) reflection increased from 0.57° and 0.50°, respectively, before irradiation, to 0.80° (2 θ) afterwards. Much smaller effects were observed with other samples, representing the same type of alloy, but different heat treatments. While it is much too early to draw any reliable conclusions from these few results, they seem to suggest that irradiation produces more distortion of the crystal lattice in hard materials than in soft ones, and particularly in those hard ones in which a certain amount of energy of distortion is stored from preceding cold work. This work is being continued in co-operation with the Metallurgy Division.

3) Miscellaneous Work.

a) Identification of highly radioactive particles:

The Health Physics Division submitted a number of highly radioactive particles, ranging in size from approximately 100 to 400 microns. X-ray diffraction patterns of individual particles showed the presence of uranium dioxide as a major constituent of four of these samples, while a fifth one

contained only minor amounts of UO_2, beside an amorphous material not identified. The particle size of the UO_2 is of the order of 800 Å, and in homogeneous distribution of intensity over the Debye-Scherrer rings indicates that it must have originated by oxidation and orientated growth, from one, or very few uranium metal grains. These results lend support to conclusions reached by Health Physics as to the origin of the particles.

b) Compounds of Barium and Ruthenium Oxides:

In mixtures of barium and ruthenium oxides, with ratios varying from 1:2, 1:1, 2:1, to 3:1, to which M. D. Silverman had given various heat treatments, at least 5 different crystal phases were observed by x-ray diffraction. A characterization, by their x-ray patterns, will be given in a later report. Much more work will be required to determine the composition and conditions of formation of these phases.

c) A small number of samples were examined in connection with their use in neutron diffraction studies (C. G. Shull).

Instrument and Physical Measurements

Modifications of the Sweep Type Differential Alpha Energy Analyzer (E. Fairstein)

Introduction:

The alpha energy analyzer described by J. H. Parsons in report Mon C-416 is essentially an electronic recording alpha spectrometer, and can be used to determine energies and relative abundance of a series of alpha emitters when these emitters are prepared as a deposit on a thin metal plate.

This report describes the changes made in the present model which result in a considerable simplification of the circuit and improvement of operation.

Amplifier changes:

Much of the filtering in the amplifier was found unnecessary and has been dispensed with. The rise time of the amplifier has been made longer than the collection time in the chamber. This minimizes effects of changes in collection time due to straggling of the pulses. The rise time is limited by the relatively large valued feed back compensating condensers. Differentiation is used in two places to eliminate the effects of hum and improve the signal-to-noise ratio. A diode restorer is used at the cathode-follower grid to eliminate undershoot. The stepped gain control was replaced by a continuous control. It is felt, however, that a control with course and fine adjustments of the Thompson-Varley type would result in greater convenience of adjustment.

The cathode-follower input was adjusted for optimum signal-to-noise ratio. A shorting electrode held at the floating grid potential by a battery was added to prevent voltage shocks to the grid while samples are being changed. This results in improved reproducibility of results and a considerably shorter stabilizing time after a sample change.

Signal generator:

The built-in signal generator was found to be unnecessary and was removed. Necessary circuit adjustments are made from the pulses produced by the sample which is being analyzed.

Anti-coincidence circuit:

The "slit-width" control (Δ E control) was replaced by one which permits adjustment in one-tenth volt steps from zero to one volt.

The sensitivity switch was replaced by a continuous linear control with a calibrated dial. A graph of sensitivity versus total counting rate with slit-width as a parameter can be prepared in order to insure that the curves drawn will occupy a convenient chart range without numerous trial and error adjustments.

At narrow slit-widths, instability in the trigger-pairs necessitates frequent rebalancing. To facilitate this adjustment, the balancing controls and 'scope jacks were brought to the front panel in the position previously occupied by the signal generator adjustments.

An output shorting switch permits quick discharge of the recorder tank condenser. A zero adjustment was also mounted on the side of the recorder.

A voltmeter was provided to indicate the position of the pulse height selector. This aids considerably in re-adjustment following a sample change.

Power supplies:

The D. C Filament supply was eliminated.

The amplifier power supply was changed to eliminate the need for reference batteries. Much of the filtering was unnecessary and has been removed. The hum level and regulation are negligibly low.

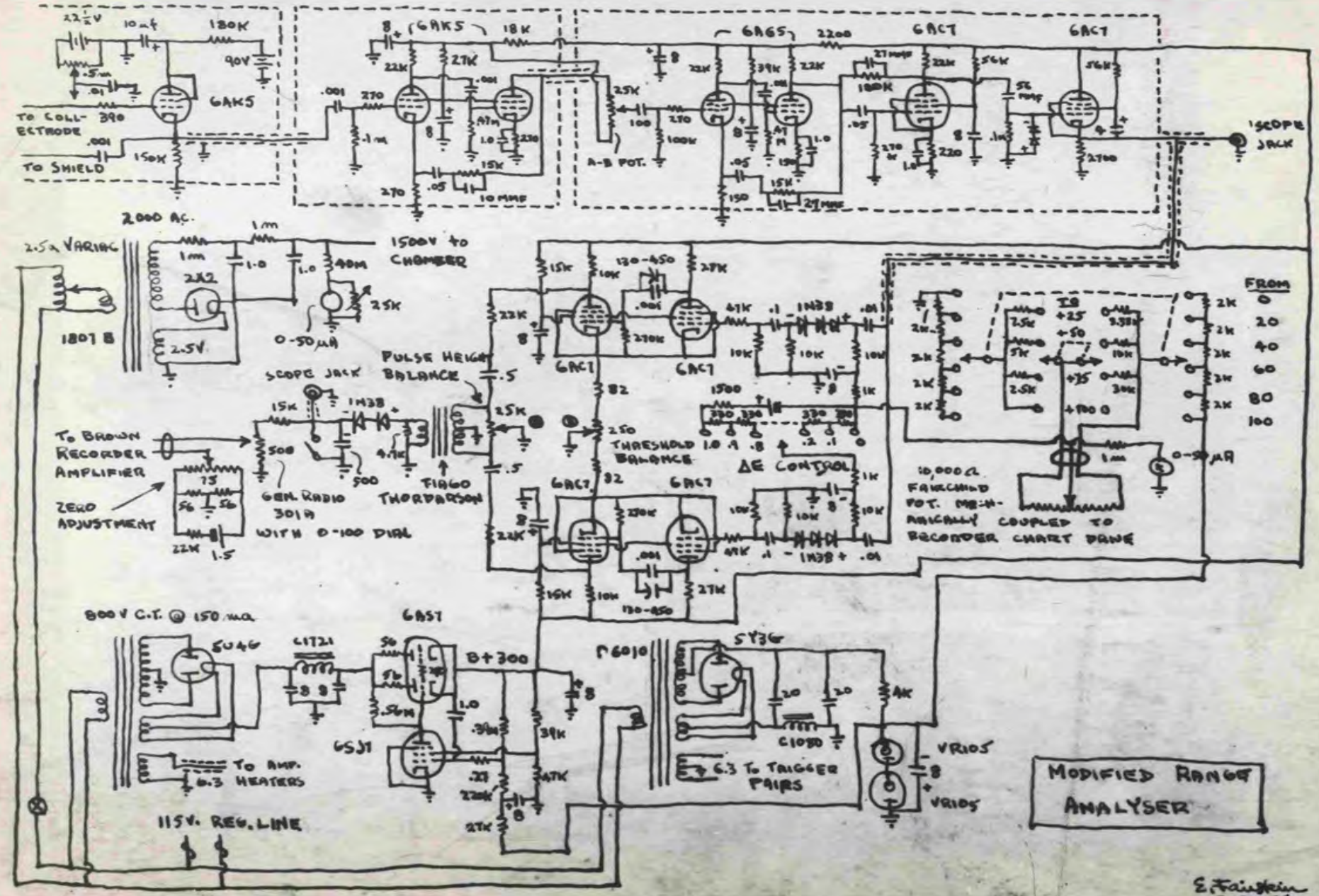
At present, the cathode-follower still uses batteries. These were not eliminated because a new unit is being planned which will eliminate the need for a cathode follower.

Automatic cut-off:

The automatic cut-off circuit was found to be more of a hindrance than an aid and was eliminated.

Future work:

A completely new unit is being planned which will be considerably smaller and less expensive than the present one. The anti-coincidence circuit will consist of two Schmitt trigger pairs feeding into a variation of the rate meter circuit described by Elmore and Sands in Chapter four of the LA-1002 report. Anti-coincidence will be produced in the integrator and drifts in the trigger pairs will have no effect on the signal amplitude or zero position. The overall resolution time will be less than ten microseconds, permitting samples of 100,000 cpm to be used with a coincidence loss of less than one percent.


MODIFIED RANGE ANALYSER
TO COLLECTRODE
TO SHIELD
6AK5
6AC7
6AS7
6SJ7
5U4G
5Y3G
1807 B
2X2
2000 AC.
2.5A VARIAC
1500V to CHAMBER
0-50 μA
SCOPE JACK
PULSE HEIGHT BALANCE
THRESHOLD BALANCE
ΔE CONTROL
TO BROWN RECORDER AMPLIFIER
ZERO ADJUSTMENT
GEN. RADIO 301A WITH 0-100 DIAL
FIAGO THORDARSON
10,000 Ω FAIRCHILD POT. MECHANICALLY COUPLED TO RECORDER CHART DRIVE
FROM
0
20
40
60
80
100
800 V C.T. @ 150 ma
B+300
TO AMP. 6.3 HEATERS
115V. REG. LINE
6.3 TO TRIGGER PAIRS
VR105
E. Fairstein
8-27-46

Fast Coincidence Circuitry
(R. A. Dandl)

In the process of developing coincidence circuits with resolution times of 10^{-7} sec or less, without losing true coincidences, the following circuits were investigated.

1 compensated Schmitt trigger pairs:

Since the greater part of the gain of the positive feed-back circuit intrinsic in a trigger pair is best located in the first half or conducting side, it is desirable to apply the most effective compensation to this plate circuit with its larger plate resistor and longer RC time constant.

The trigger circuit shown in Figure 1 seemed satisfactory for some types of pulse shaping. The pulses obtained were square, of ten to fifteen volts amplitude, and had rise times of less than 10^{-7} sec.

2 coincidence detector:

Since the usual type of coincidence circuit requires some sort of pulse shaper, its resolution time (T') is limited by the rise times of the amplifiers feeding it. Two coincidence pulses differing greatly in amplitude will initiate shaped pulses separated in time by at least the rise times (T") of the amplifiers. (Actually T' minimum was found to be 2 T" if no coincidence pulses were lost). Another disadvantage of the usual coincidence circuit is the gain required to let the smaller pulses through the shaping circuits.

As a result of these considerations the coincidence circuit shown in Figure 2A* was investigated and was found to have many advantages. The

*Coincidence circuit by Baldinger, Huber and Myer, RSI July, 1948.

two most important advantages are: operation on low voltage pulses (0.1 volt) and the elimination of pulse shapers. However this coincidence circuit being of the bridge type, requires a differential voltage detector of the type shown in Figure 2B.

Present plans involve its use with two channels, each containing a proportional Beta counter and a fast low gain amplifier. Sample amplifier stages using four terminal compensation, were tested and a 50 megacycle amplifier with a gain of twelve seems to be a good compromise, providing the proportional chamber can deliver four tenth volt pulses without being operated in the geiger region.

UNCLASSIFIED

Drawing # 6297

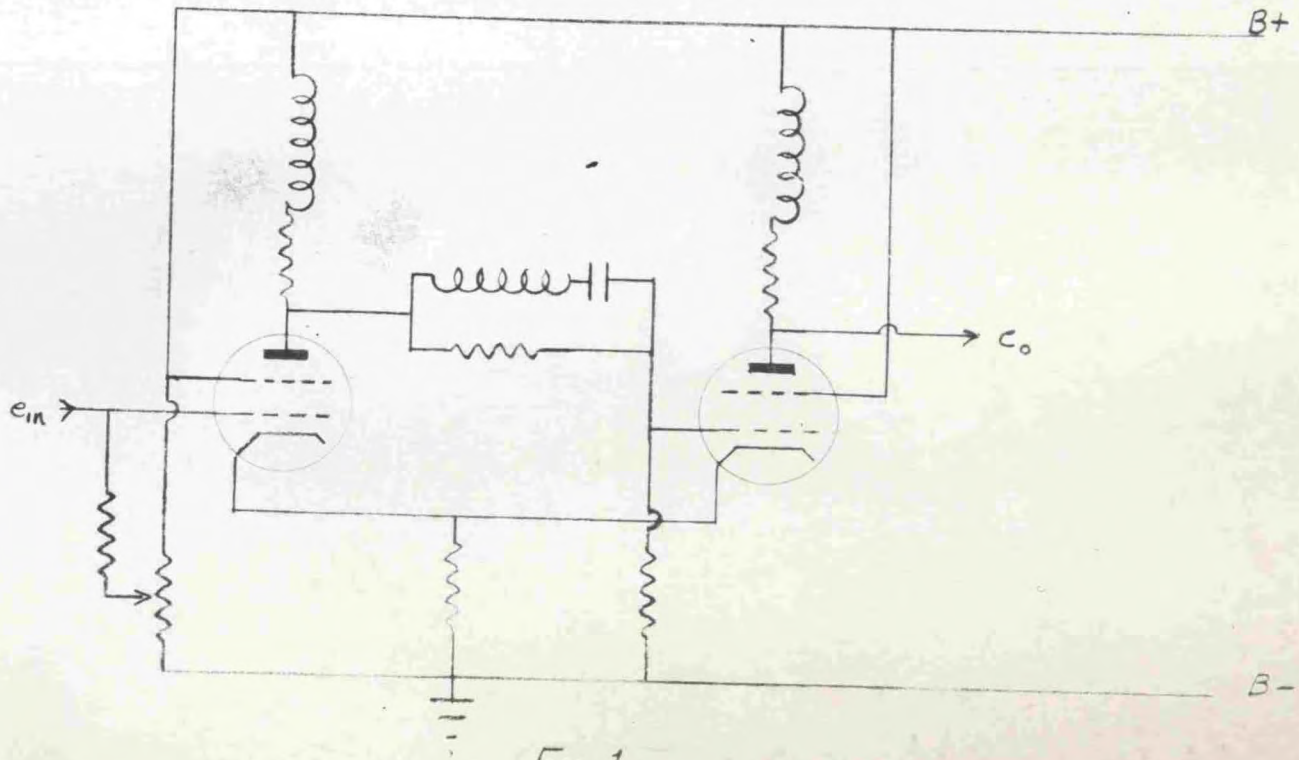


Fig. 1.

Compensated Schmidt Trigger

Drawing # 6293

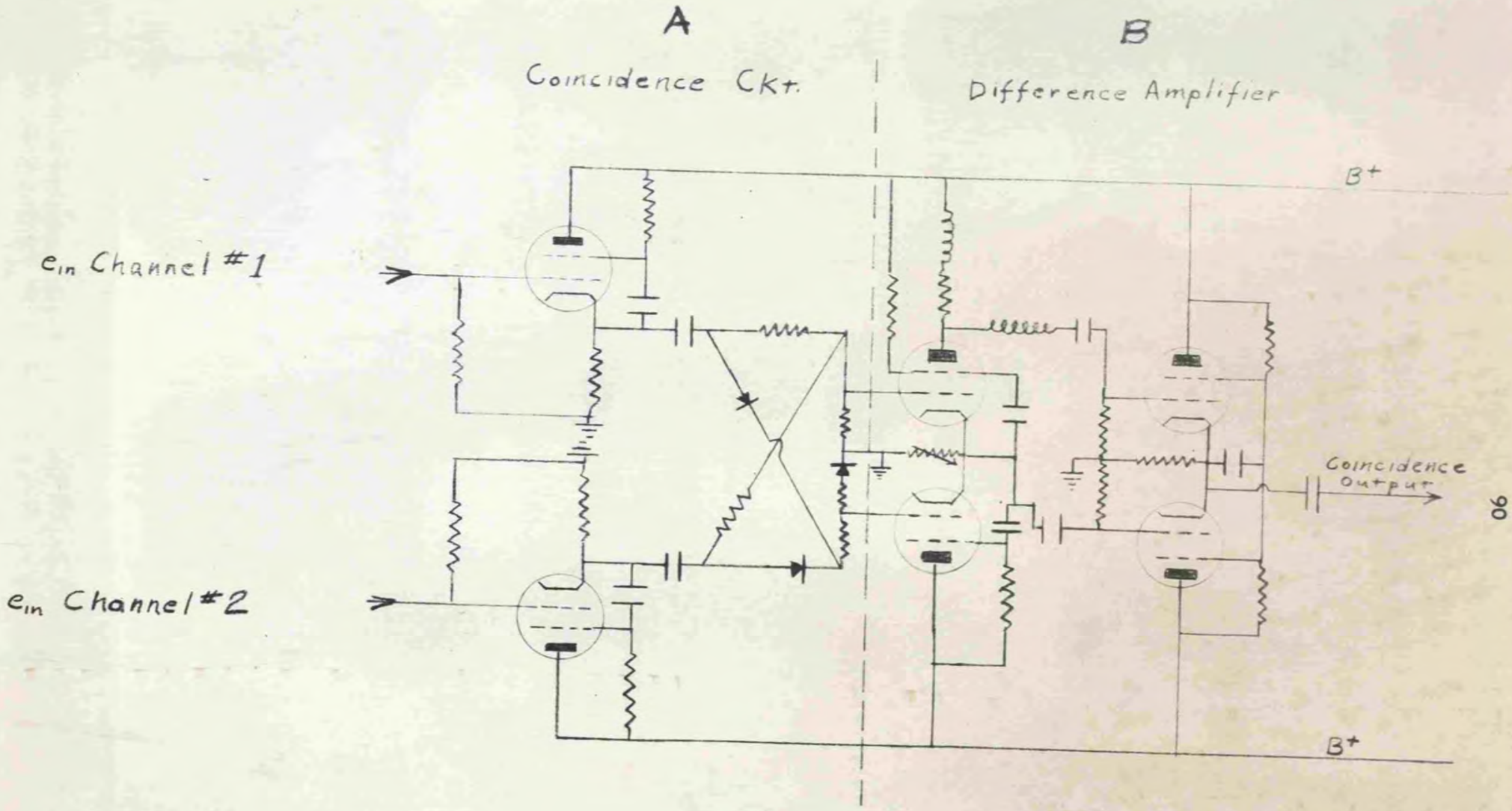


Fig. 2.

Coincidence Detector

 [redacted]

A Proportional Beta Counter
(E. Feirstein, C. J. Borkowski)

Introduction:

A circuit has been developed for determining the counting rate of weak beta emitters which is much less complicated than those presently in use. It is meant to be used with a flow-type proportional chamber, and the operating voltage is in the range usually associated with alpha-counting.

The unit can also be used for alpha counting with a reduced chamber voltage.

Problems involved in an amplifier to be used for beta counting:

Since beta emitters produce a continuous energy spectrum, it is necessary that an amplifier used for beta counting be able to handle a wide range of signal voltage. The requirements of a wide plateau for stable operation complicates the problem further. The amplifier is required to saturate without blocking or producing spurious responses.

Consider the following situation:

An interstage coupling condenser of .001 mfd is used with a grid resistor of one megohm in front of a tube where positive pulses occur. This results in a time constant of 1000 microseconds. If the tube is biased to the normal value of two or three volts, the occurance of a fifty volt pulse will drive the tube well into the grid current region. The input resistance of the stage under these conditions is about 1000 ohms. If the pulse lasts five microseconds, the coupling condenser charges to about forty volts. When the pulse disappears, the discharge of the coupling condenser causes the stage to be cut off for as long as 2000 microseconds, during which time low amplitude pulses cannot pass through the amplifier. This phenomena is known as blocking and results in a decrease in counting rate as the chamber voltage is increased. This effect can be eliminated by the use of a diode restorer and minimized by the use of an unby-passed cathode resistor, which will permit a certain amount of cathode follower action.

In a many-stage amplifier, multiple differentiation can occur unless extreme measures are used to eliminate it. This results in pulse overshoot. If the overshoot is sufficiently great, it will cause a double count, since it is in the same direction as the desired signal. The best way to eliminate this is to limit the amplifier to three stages and carefully choose the values of the coupling condensers.

[redacted]

[redacted]

Noise is a relatively insignificant consideration. The amplifier noise places a lower limit on the plateau threshold, but since a ten percent increase in operating voltage will offset nearly a 1000% improvement in amplifier noise, it is hardly worthwhile to spend a lot of time in decreasing the noise below a reasonable value.

Description of the circuit presented in this report:

A three stage amplifier is used with no compensation or feedback, except for the unby-passed cathode resistor in the second stage. Leaving the by-pass condenser off decreases the noise and prevents grid blocking. Differentiation is used at the very input to narrow the pulses. Differentiation is also used at the output to eliminate the effects of hum and minimize the effects of amplifier noise. The back-kick which results is not serious because the Schmitt trigger pair into which the amplifier feeds will respond to positive pulses only. The second differentiation also considerably decreases the resolving time of the trigger pair.

The rate-meter output circuit shown produces positive pulses of approximately fifty volts amplitude and two and one-half microseconds duration. The output impedance is never more than 300 ohms, due to the cathode follower. The rate meter for which it is intended is based on the circuit described by Elmore and Sands in chapter four of the LA-1002 report.

The scalar output produces negative pulses of approximately fifteen volts amplitude and one microsecond duration. This will drive a Higginbotham scaler. For rate-meter work, a 300 volt power supply is necessary. For scalar work, 225 volts is sufficient. A regulated supply is unnecessary and was not used in testing the unit.

The pulse height selector is adjusted to the point where amplifier noise pulses just stop counting.

All the tubes are operated at much less than their rated power dissipation.

Results:

The plateau length is approximately twenty percent of the plateau threshold voltage with an overall slope of two percent.

The resolution time was not measured, but oscillograms indicate that it should be less than six microseconds (one percent loss per 100,000 counts per minute).

[redacted]

[redacted]

It may be possible to decrease the plateau slope and improve the resolution time by the use of diode restorers at appropriate places in the circuit. No data are available on this point at the present writing.

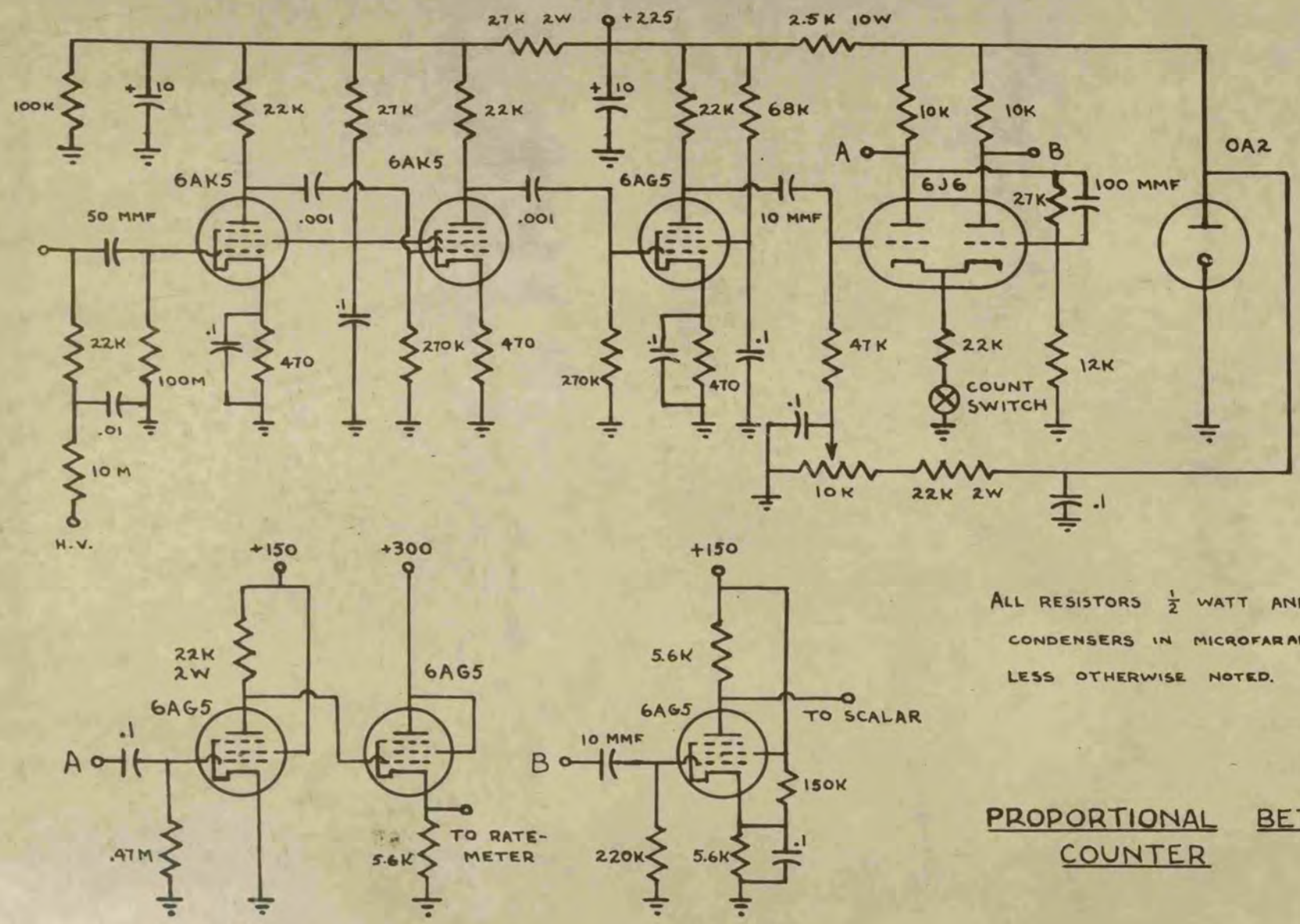
Future work:

It was suggested by R. A. Dandl that an additional tube whose plate current is supplied by the screen resistor of one or more stages of the amplifier and whose signal voltage is supplied by a fraction of the chamber voltage might be used to extend the plateau by causing the amplifier gain to vary inversely as the chamber voltage. Preliminary tests indicate that this is feasible, but exact data are not yet available.

The use of a cathode coupled amplifier pair ("long tail pair") for the second stage may result in a flatter plateau. A stage of this type was tried and gave results at least as good as the present circuit, but an accurate comparison has not yet been made. The conventional stage was chosen for its simplicity.

[redacted]

Drawing # 6296



ALL RESISTORS $\frac{1}{2}$ WATT AND ALL CONDENSERS IN MICROFARADS UNLESS OTHERWISE NOTED.

RATE-METER OUTPUT

SCALAR OUTPUT

PROPORTIONAL BETA COUNTER

E. Faustem
8-24-48

[redacted]

4. ANALYTICAL SERVICE

Summary of Analytical Work for Quarter
May 15 to August 15, 1948

	Radio-chem. Dev.	Ionic Dev.	Radio-chem. Anal.	Ionic Anal.	Water Anal.	Pilot Plant Control	Lab. and Semi-Works Control	Production Analyses	Spectro-graphic Analyses	Total
Personnel (8/15/48)										
Tech.	6	5	10	2	1	5	2	6	4	41
Non-Tech.	1	1	9	3	4	23	8	18	0	67
Physics Div.			70	19					14	103
Chem. Div.			162	5			48		261	476
Technical Div.			4656	128	1146	11432	7208		19	24589
Production			2633		258			5066		7957
Power Pile				29						29
Metallurgy					22					22
Biology									13	13
Health-Physics			60							60
Misc.				4	15				81	100
			7581	185	1441	11432	7256	5066	368	33349

Spectrographic Group - C. Feldman, A. J. Estepp, M. Murray, J. Gillespie

In addition to the spectrographic analyses indicated in the above table, the following development work was done in this group:

1. A working curve for Hf in Zr was prepared by the porous cup method using pure ZrO_2 (< 200 ppm Hf) obtained from the National Bureau of Standards as base material. The present curve covers the range (Hf x 100)/Zr = 0.065 - 8.0. The intensity ratio Hf II 2641.406/Zr II 2761 for a given mixture was found to remain essentially constant when the total sample concentration was varied between 1.5 and 6 mg. Zr/ml. This confirms previous studies made with a less sensitive procedure.

[redacted]

[redacted]

2. A technique was developed for preparing metallic Pd standards spiked uniformly and accurately with known trace amounts of Ag. The Pd is dissolved, Ag^+ added to the solution and the metal precipitated with formaldehyde. The metallic powder is then mixed with graphite, pelletized, and sparked.

3. A special graph paper was designed which will permit the construction of calibrated intensity scales directly from % transmission data by an entirely graphical method. On this graph paper, abcissae correspond to log intensity; ordinates are proportional to the log of the Seidel function W, where $W = \frac{100}{\% \text{ trans.}} - 1$, but calibrated in terms of % transmission. The Seidel function was chosen for this purpose because it is linear between 5% and 97% transmission at most wavelengths, thus favoring uniform relative accuracy over a wide intensity range.

4. A 20 minute procedure was developed for decontaminating spectrochemical spark chambers. Before use, the inside parts of the chamber are painted with an alcoholic solution of Carbowax 1540. After exposure, the contaminated parts are placed in a 5% ammonium citrate solution. The containing vessel is placed in a hot sink, and tap water is run into it for about 15 minutes. This removed both Carbowax and activity. Lacquered lava pieces reading 90 mR were found to read less than 2 mR after treatment.

5. The curve-straightening method for preparing working curves when base materials free of the impurity being studied are not available was extended to the estimation of Cs in Nb. A determination made with the aid of such a curve agreed to within 10% with a pile activation determination whose accuracy was estimated as ± 15%.

Radiochemical Analyses - C. L. Burros, G. W. Leddicotte, R. Slusher, H. H. Miller R. Sampley, D. I. Gilbert, J. Gill, A. B. McBride, D. J. Coombe, W. Brooksbank

The major load for this group continues to come from the Hot Pilot Plant and the Radioisotope Development Group in the Production Division. It has been necessary to increase the personnel of this group somewhat recently to handle the expected increased work due to the Technical Division program on the Redox Process.

Ionic Analyses - D. E. LaValle, W. Wolkowitz

Ionic analyses have been at a low ebb in this quarter with the exception of aluminum-uranium alloy analysis. The ferric sulfate analytical method for uranium in these alloys has greatly lessened the time required for each analysis, but it may be some time before the backlog of samples can be cleaned up completely unless more equipment can be obtained.

Water Analyses - J. H. Edgerton

Most of the work of this group continues to come from Technical Division groups during corrosion work. An improved method for determination of very small

[redacted]

[redacted]

amounts of aluminum and iron has reduced the time required for these analyses and has greatly improved the accuracy of these determinations.

Pilot Plant Control Group - E. J. Frederick, W. T. Mullins. E. W. Sharp, H. A. Parker, L. C. Henley

This group has finished the work on the 25 process and is now engaged in preparations for work on the Redox Process. It is expected that the Pilot will start on the Redox Process about September 15.

Lab and Semi-Works Process Analyses - L. T. Corbin, G. R. Wilson

This group is now engaged in analyses for the initial Redox runs and is experiencing some difficulty in some of the methods used. This will probably require considerable overtime work for a short period, but will not justify additional personnel for an extended period.

Production Analyses - E. I. Wyatt, T. G. Harmon, B. J. Ginocchio, C. M. Goolsby

The analyses of routine preparations of radioisotopes has proceeded smoothly in this period. Rising activity levels are creating new problems in preventing personnel exposure particularly in the determination of non-volatile solids. It is hoped that a Mettler balance recently purchased will help to solve the problem, when properly protected with lead shielding. This balance is admirably adapted to remote control applications because it does not require external weights and hence minimizes exposure of personnel.

[redacted]