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QUARTERLY REPORT

FOR THE MONTHS SEPTEMBER, OCTOBER, NOVEMBER, 1948

D.C. BARDWELL, Director

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CHEMISTRY DIVISION

QUARTERLY REPORT
FOR THE MONTHS SEPTEMBER, OCTOBER, NOVEMBER, 1948

D. C. Bardwell, Director

Date Issued: FEB 3 1949

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ABSTRACT OF QUARTERLY REPORT
CHEMISTRY DIVISION

The program of the Division as described in previous Quarterly Reports has gone ahead without major changes in emphasis. A considerable interruption of the normal work was caused by a concerted attack upon the radioactive particle problem which, at various times, involved most of the senior members of the Division.

It would be impossible to abstract completely the work of the quarter in a reasonable space so that only the results of principal interest are mentioned below.

Nuclear and Chemical Properties of the Heavy Elements - Conditions have been discovered for the existence of U(V) as an equilibrium (or at least quasi-equilibrium) species in aqueous solution. The region of optimum stability is between pH = 2 and 4, and the formula of the ion there is $UO_2(H_2O)_n^+$. Potentials have been measured for the oxidation to U(VI) and the reduction to U(IV). UCl_5 can be dissolved at pH = 2 to give an apparently stable solution of U(V), the process leading first to U(IV) and U(VI) which then react more slowly to give U(V).

About 5 mg. of americium of high purity have been prepared by ion-exchange techniques.

The equilibrium constants for the formation of a number of complex ions of thorium in aqueous solution have been measured by extraction into benzene containing TTA (thenoyltrifluoroacetone). The complexes studied were ThX^{+3} where X was NO_3, ClO_3, Cl, mono-, di- and trichloracetate, and IO_3, as well as ThX_2^{+2} where X was di- and trichloracetate, and IO_3, and finally $Th(IO_3)_3^+$.

Nuclear and Chemical Properties of Fission Products - One of the principal results of this quarter has been the success of the process for preparing Xe^{135}. It is now being produced in quantities sufficient for the desired neutron transmission measurements, the best sample having decreased the neutron beam by about 30%. The assay method which has been the subject of considerable effort for the past year has proved to be satisfactory.

A hard gamma emitter (greater than 2.2 Mev) has been found associated with iodine and appears to have a half-life of about 55 minutes.

General Nuclear Chemistry - The program for the preparation of gram quantities of very pure rare earths has reached a point where quantities ranging from 0.1 to 8 grams are available of each rare earth except Eu and 61. An example of the purity is given by Dy in which Inghram et al of the Argonne Laboratory found less than 1 part in 70,000 of any other rare earth.

A great deal of work over the last few years on the nuclear chemistry of the rare earths is summarized in the present report. Half-lives and energies

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Abstract of Quarterly Report (Continued)

of radiation are given for many of the pile-produced radioactivities. The ion-exchange separations developed here have made this work possible both in the preparation of pure starting materials as are described above and in the subsequent separation of the induced activities.

Radio-organic Chemistry - Carbon dioxide has been reduced to formic acid in yields of 71 to 88% by the use of lithium borohydride in ether solution, and some progress has been made toward elucidating the mechanism of the reaction.

The preparation of acetic acid by the carbonation of methyl magnesium bromide has proved to be satisfactory so far as the carbonation step is concerned (about 90-95% reaction of CO_2) but the isolation of anhydrous acetic acid has proved troublesome.

Applied Nuclear Chemistry - In the development of a process for separating fission-produced rare earths by ion-exchange, distribution data for europium between Dowex 50 resin and 5% citrate solution have been obtained, and the technique has been improved to the point where such distribution coefficients can be reproduced within 10%.

Physical Chemistry and Chemical Physics - A number of solvents has been found which are fluid at the boiling point of nitrogen and which will dissolve rare earth compounds. Solutions of $Nd(NO_3)_3 \cdot 6H_2O$ and $NdBr_3 \cdot 6H_2O$ at this temperature showed considerable sharpening of their absorption lines over room temperature, many lines being from 2 to 5 Å wide.

Radiation Chemistry - The work of the last two years on the decomposition of water and aqueous solutions seems to have reached a state where the results can be given quantitative interpretation in terms of a suggested mechanism. A final report on this work has been prepared.

Physical Measurements and Instrumentation - Further improvements have been made in the alpha range analyzer, specifically in the pulse-height discriminator. The instrument can now conveniently be used in the range of 10 to 10^5 counts per minute.

Analytical Chemistry - A separation of thorium from aluminum by extraction with TTA in CCl_4 has been worked out, so that aluminum can be determined colorimetrically without interference from thorium.

A polarographic method for uranium in process solutions has been developed giving a routine method for the concentration range from 10 to 200 micrograms per milliliter. This helps to bridge the gap between the colorimetric (200 - 1000 μg/ml.) and the fluorimetric (0.01 - 1.0 μg/ml) methods.

The Particle Problem - The following studies have been made by members of the Chemistry Division. A cyclone dust sampler later supplemented

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Abstract of Quarterly Report (Continued)

by filters was installed in the exit air from the pile. The presence and approximate sizes of radioactive particles, and their dependence on pile operating conditions were demonstrated. The presence of fission product gases and their decay products was shown by collection on a charged wire; a continuous monitor for these contaminants based on this method was built and is in operation.

Dust samples were collected at several points around the laboratory using a vacuum cleaner, and the bag was subjected to autoradiography to establish the presence of radioactive particles. Serious contamination of the air of the pile building was demonstrated in this way.

X-ray diffraction and electron and optical microscopy were used extensively in the identification of particles and in determining their sizes.

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I. Nuclear and Chemical Properties of Heavy Elements

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

Employing an aqueous phase of 0.5 M H^+ and an ionic strength of 0.5 and a benzene phase 0.25 M in TTA, the equilibrium constants for the following reactions were obtained using the TTA solvent extraction method. The ionic strength was maintained with $HClO_4$.

Equation	k
$Th^{+4} + NO_3^- = ThNO_3^{+3}$	4.73
$Th^{+4} + ClO_3^- = ThClO_3^{+3}$	1.84
$Th^{+4} + Cl^- = ThCl^{+3}$	1.76
$Th^{+4} + ClCH_2COOH = Th(ClCH_2COO)^{+3} + H^+$	1.33
$Th^{+4} + Cl_2CHCOOH = Th(Cl_2CHCOO)^{+3} + H^+$	5.74
$Th^{+4} + 2Cl_2CHCOOH = Th(Cl_2CHCOO)_2^{+2} + 2H^+$	12.7
$Th^{+4} + Cl_3CCOOH = Th(Cl_3CCOO)^{+3} + H^+$	8.23
$Th^{+4} + 2Cl_3CCOOH = Th(Cl_3CCOO)_2^{+2} + 2H^+$	26.7
$Th^{+4} + IO_3^- = ThIO_3^{+3}$	7.6×10^2
$Th^{+4} + 2IO_3^- = Th(IO_3)_2^{+2}$	6.2×10^4
$Th^{+4} + 3IO_3^- = Th(IO_3)_3^+$	1.40×10^7

The acid constants of di- and tri-chloracetic acids used were 0.05 and 0.2 respectively. No evidence for higher nitrate complexes was found at up to 0.5 M NO_3^-.

The iodate constants were obtained (in a manner similar to the others) from a curve of the distribution ratio of Th(IV) between aqueous and benzene phases as a function of iodate concentration in the aqueous phase. The curve was indistinguishable from a curve obtained previously by A. J. Fry, employing an aqueous nitric acid medium, after the latter was corrected for the nitrate complex. This correcting for the nitrate complex was accomplished by plotting (R/R_o-1) obtained with perchlorate medium and $(R/R_o-1)(1 + k_n[NO_3^-])$ obtained with nitrate medium against iodate concentration. Here R is the distribution ratio, R_o the ratio at zero iodate concentration and k_n is the nitrate complex

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constant as written in the table above. As can easily be verified, both of the functions plotted are equal to

$$k_1(IO_3^-) + k_2(IO_3^-)^2 + k_3(IO_3^-)^3,$$

where the k's are the three iodate constants given above, providing no additional complexes exist containing both nitrate and iodate. Since the two curves were indistinguishable, it is concluded that at up to 0.5 M NO_3^- and up to 2.36×10^{-2} M total iodate in 0.5 M H^+ no complexes exist which contain both nitrate and iodate.

The fluoride complex constants for the reactions

$$Th^{+4} + HF = ThF^{+3} + H^+$$

$$Th^{+4} + 2HF = ThF_2^{+2} + 2H^+$$

were determined in nitrate media at an ionic strength (equal to HNO_3 concentration) of 0.5. After correcting for the nitrate complex, the values obtained for the two constants were 5.3×10^4 and 3.5×10^7 respectively. Dodgen's values using a different method were 4.5×10^4 and 2.9×10^7. While the agreement is considered satisfactory, the values will be re-determined in perchlorate solutions where the reproducibility is appreciably better than with nitrate medium.

No corrections have been made in determining any of the above constants for complexing of Th(IV) by TTA in the aqueous phase.

Acetic and formic acids were also tried as complexing agents. In these cases another effect came into play making the results difficult to interpret. With 0.25 M TTA in the benzene and an equal volume of aqueous phase containing 0.5 M $HClO_4$ and the following amounts of organic acid, the results were

Acid	M	R = Th(IV)aq/Th(IV)org
Acetic	0	0.63
"	0.5	0.44
"	1.0	0.37
Formic	0.01	0.67
"	0.03	0.84
"	0.05	0.82
"	0.1	0.83
"	0.5	0.79
"	1.0	0.79

The difficulty in interpretation arises from the fact that the usual trend, i.e., a steady increase in the ratio R = Th(IV)aq/Th(IV)org with increasing complexing agent, is not observed here. Instead, the addition of acetic acid causes R to decrease, while formic acid causes a small increase at first followed by no further change or a very small decrease on further addition.

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Hydrolytic Behavior of Cerium (IV). Preparation and Properties of Polymeric Ce(IV).
(R. W. Holmberg and K. A, Kraus)

A) Polymerization of Ce(IV).

As has previously* been reported the properties of Ce(IV) solutions

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* Monthly report of the Chemistry Division for March, April and May 1948, ORNL-65

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of low acidity change slowly with time. This slow hydrolysis, which is almost certainly due to polymerization of Ce(IV), has been investigated in some detail using both spectrophotometric and pH measurements. For the pH measurements the glass electrode-vibrating reed electrometer equipment previously described was used.

As has previously been shown the rate of change of these properties, i.e., the rate of polymerization, is strongly dependent on the acidity of the solutions, increasing rapidly with decreasing acidity. At low acidities these properties change rapidly from the moment of preparation of the solutions (dissolution of ammonium hexanitrato cerate (HNC)) with no induction period noticeable. The family of curves shown in Fig. 1 is representative of this behavior. In this figure the average hydroxyl number "n" (for the formula $Ce(OH)_n^{+4-n}$) has been plotted as a function of time for a series of typical 2×10^{-3} M HNC solutions whose initial perchloric acid concentrations were between 8×10^{-4} and 4×10^{-2} M. It may be noticed that polymerization is very slow (practically not detectable in one to two hours) in ca 4×10^{-2} M $HClO_4$ at this Ce(IV) concentration.

At higher Ce(IV) concentration however, polymerization is still very pronounced at acidities where only negligible polymerization occurs at lower Ce(IV) concentration as shown in Table 1, clearly demonstrating that the rate of polymerization increases with Ce(IV) concentration.

Table 1

Polymerization of Ce(IV)

M $H_3O^+ \times 10^3$			M Ce(IV) $\times 10^3$	Hydroxyl number n		
Initial	t = o a)	t = 80		t = o	t = 5	t = 80
0.83	5.53	7.77	2	(2.35)	3.06	3.47
4.98	9.68	11.58	2	2.35	2.58	3.30
13.5	17.9	19.2	2	2.20	2.27	2.86
19.9	24.2	24.5	2	2.13	2.14	2.30
41.4	45.3	45.32	2	1.95	1.95	1.96
4.98	17.3	22.1	5	2.46	2.50	3.42
4.98	28.0	38.8	10	2.44	2.46	3.38

a) t represents time in minutes.

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It should be pointed out that the acidity of the solutions during polymerization is determined both by the initial acidity of the solutions (before dissolution of HNC) and the acid liberated through hydrolysis of the HNC. A considerable part of this hydrolysis occurs practically instanteneously on dissolution and the values of M H_3O^+ at t = o given in Table 1 are the acidities calculated from the pH measurements of the HNC solutions after extrapolation back to the time of dissolution. These acidities of course are strongly dependent on the concentration of Ce(IV) and the extent to which rapid hydrolysis of Ce(IV) occurs determines the lower limit of the acidity of the solutions.

The polymerization reaction of the more concentrated, and thus fairly acidic solutions is clearly autocatalytic as can be seen from Fig. 2 and Table 1, indicating that the initial rate of polymerization is controlled by a hydrolytic intermediate which is present only in low concentrations at the higher acidities and furthermore indicating that polymerization can also occur directly through reaction of the polymeric particles with low molecular weight hydrolysis products.

These results on the polymerization of Ce(IV) based on determination of the hydroxyl number are closely paralleled by the spectrophotometric properties of the solutions as shown in Fig. 2 for an autocatalytic and a non-autocatalytic reaction. The relationship between the two types of observations actually is even closer than could be anticipated since there is apparently a linear relationship between the hydroxyl number and the extinction coefficients near 400 mμ as illustrated in Fig. 3 for 0.01 M Ce(IV) solutions. Preliminary checks indicated that the same straight line relationship also applies for the polymerization of the more dilute Ce(IV) solutions investigated, i.e., that it applies for auto-catalytic and non-auto-catalytic polymerizations equally well. However, since the results on the more dilute set of solutions are considerably less reproducible a more detailed check of this relationship will have to await simultaneous pH and spectral measurements which are planned.

B) Reduction of Ce(IV) Polymer with Iodide.

It is well known that Ce(IV) normally is rapidly reduced by iodide ions. Since through this reduction the highly acidic Ce(IV) is replaced by Ce(III) which does not hydrolyze except at very much higher pH, the reduction is accompanied by a decrease in acidity according to the equation

$$Ce(OH)_n^{+4-n} + nH_3O^+ + I^- \longrightarrow Ce^{+3} + 2n\ H_2O + 1/2\ I_2$$

Conversely the rate of reduction of hydrolyzed Ce(IV) can be followed by suitable pH measurements.

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Solutions of Ce(IV) were permitted to polymerize for varying periods of time and then treated with five-fold excess of (solid) NaI. The acidity of the solutions was determined and from these measurements the hydroxyl number calculated. The results are shown in Fig. 4. As was to be expected the rate of reduction of Ce(IV) by I^- decreases as the time permitted for polymerization increases. Of particular interest, however, is the fact that with all the solutions studied the reduction of a certain percent of Ce(IV) is practically instantaneous although the bulk of the reduction is slow. Furthermore the percent of "instantaneous" reduction decreases with time of polymerization though it is still considerable after 2 hours of polymerization. It appears that polymerization does not involve simple growth of the particles, but rather that even in advanced stages of polymerization considerable concentrations of a low molecular weight component (e.g., trimer) co-exist with the high molecular weight component (or components).

C) Depolymerization by Nitric Acid.

Some experiments are in progress on the rate of depolymerization of Ce(IV) by strong acid. At the present time only experiments on depolymerization in 1.3M HNO_3 have been carried out for 0.01 M Ce(IV) solutions. Using a spectrophotometric method of analysis it was found that depolymerization in 1M HNO_3 is quite slow (ca 45% depolymerization in 24 hours) if polymerization had been permitted to proceed for 140 min. at an average acidity of 3.5×10^{-2} M H_3O^+.

Isolation of Americium from Plutonium Waste Solutions

G. W. Smith, K. A. Kraus

Work on the isolation and purification of americium has continued. Using resin adsorption techniques preliminary purification of ca 10 mg of americium has been completed and ca. 5 mg of americium of high purity have been prepared.

Chemistry of Aqueous Solutions of Uranium (V)

F. Nelson, K. A. Kraus

Several phases of this work have now been completed and written up (ORNL-188 and 189). However, since it may be some time before these reports are generally available, the main results of this work are summarized below.

1) The optimum stability range of U(V) is between ca pH 2 and 4.

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2) Further confirmation of the formula $UO_2(H_2O)_n^{\circ}$ for U(V) in these solutions has been obtained.

3) The diffusion coefficients of UO_2^{+} and of UO_2^{++} are practically the same.

4) Solutions of UO_2^{+} (also containing U(IV) and U(VI)) can be prepared by dissolution of UCl_5. The primary solution products (formed practically instantaneously) are U(IV) and U(VI) which near pH 2 react reasonably rapidly with each other to yield U(V).

5) Equilibrium mixtures of U(IV), U(V) and U(VI) have been prepared near pH 2.

6) From potential measurements of such equilibrium mixtures the formal potentials E_{45}, E_{46} and E_{56} of the U(IV)/(V), U(IV)/(VI) and U(V)/(VI) couples have been determined near pH 2 for 0.1 M Cl^- solutions. These potentials are $E_{45} = -0.072$ V, $E_{46} = -0.067$ V, and $E_{56} = -0.062$ V at an acid concentration of $[H_3O^{\circ}] = 7.29 \times 10^{-3}$ M.

7) Combining the potential data near pH 2 with the known hydrolytic properties of the various oxidation states of U the formal potentials $E_{45} = -0.58$ V, $E_{46} = -0.32$ V, and $E_{56} = -0.062$V have been estimated for 1M $HClO_4$ solutions.

8) Although U(V) solutions, stable for hours, can be prepared near pH 2.5 evidence for "autocatalytic" acceleration of the disproportionation of U(V) into U(IV) and U(VI), probably due to polymerization of U(IV), has been obtained.

9) Disproportionation of U(V) in 0.1 M Cl^- follows a second order rate law at any one acidity. The rate constant is roughly proportional to the first power of acidity.

Work is continuing at present on a more precise determination of the kinetics of the disproportionation reaction and of the reaction of U(IV) with U(VI), on the potentiometry of the equilibrium systems, and to determine if these "equilibria" are true or metastable equilibria.

Isolation Procedures for Pa^{231}

G. E. Moore, K. A. Kraus

Various isolation procedures for Pa^{231} are under investigation. The results will be reported in the subsequent quarterly report.

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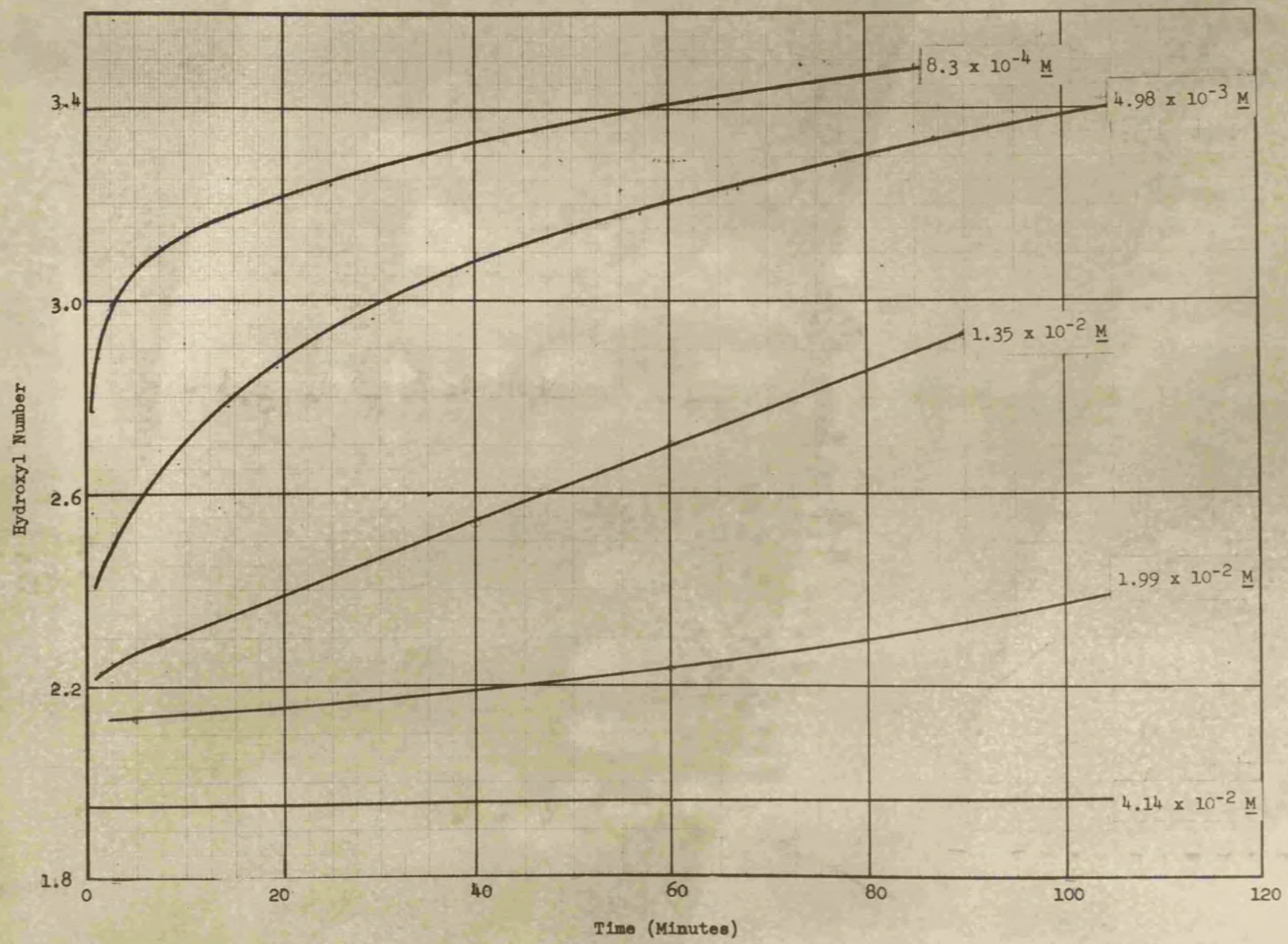

Figure 1

Rate of Polymerization of Ce(IV) at Various Initial Perchloric Acid Concentrations

0.002 M $(NH_4)_2 Ce(NO_3)_6$
1M ClO_4^-

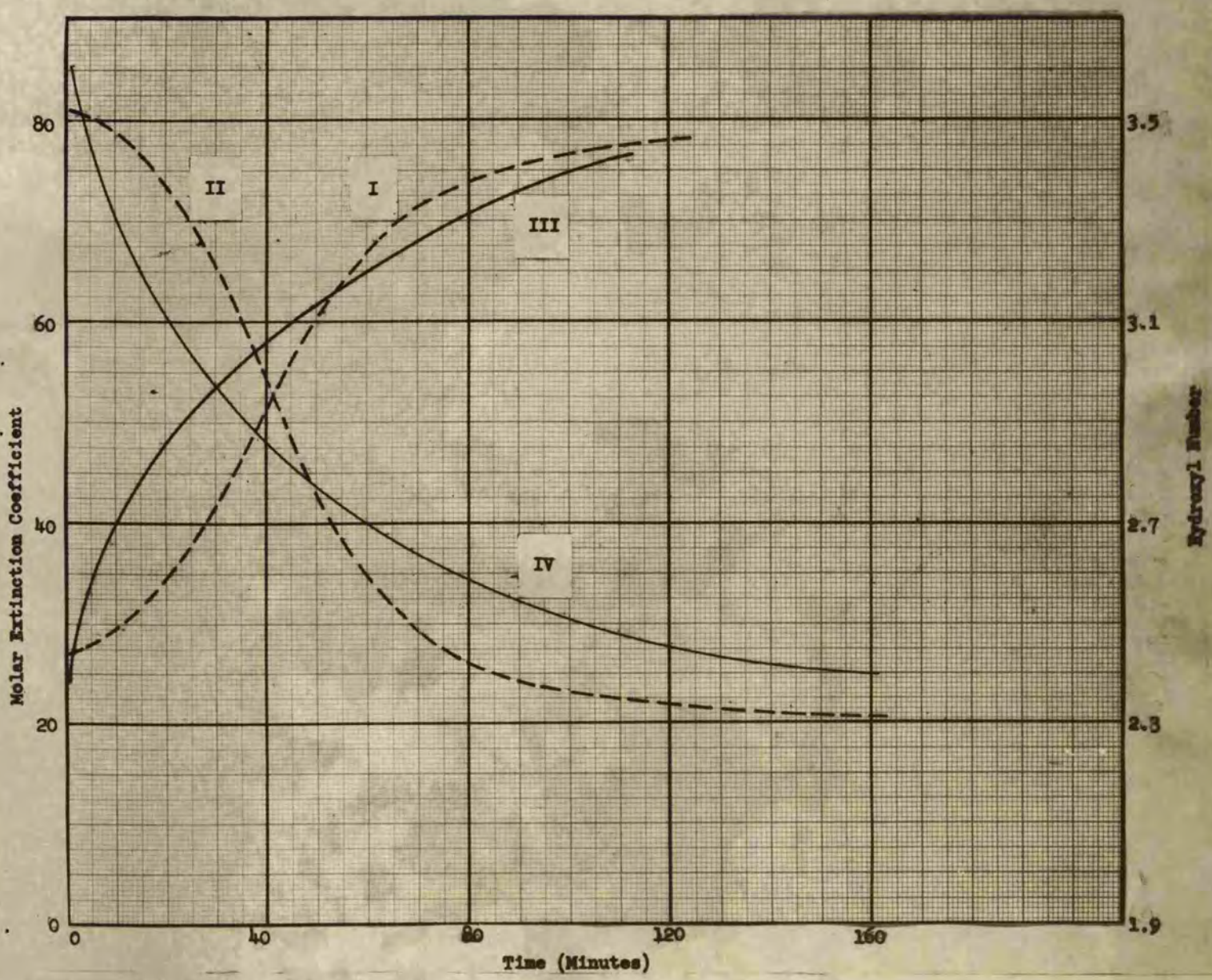

Figure 2

Polymerization of Ce(IV)
(Initial acidity: 0.00497 M $HClO_4$)

1) 0.01 M Ce(IV) - Hydroxyl number
2) 0.01 M Ce(IV) - Extinction coefficients at 410 m
3) 0.002 M Ce(IV) - Hydroxyl number
4) 0.002 M Ce(IV) - Extinction coefficients at 410m

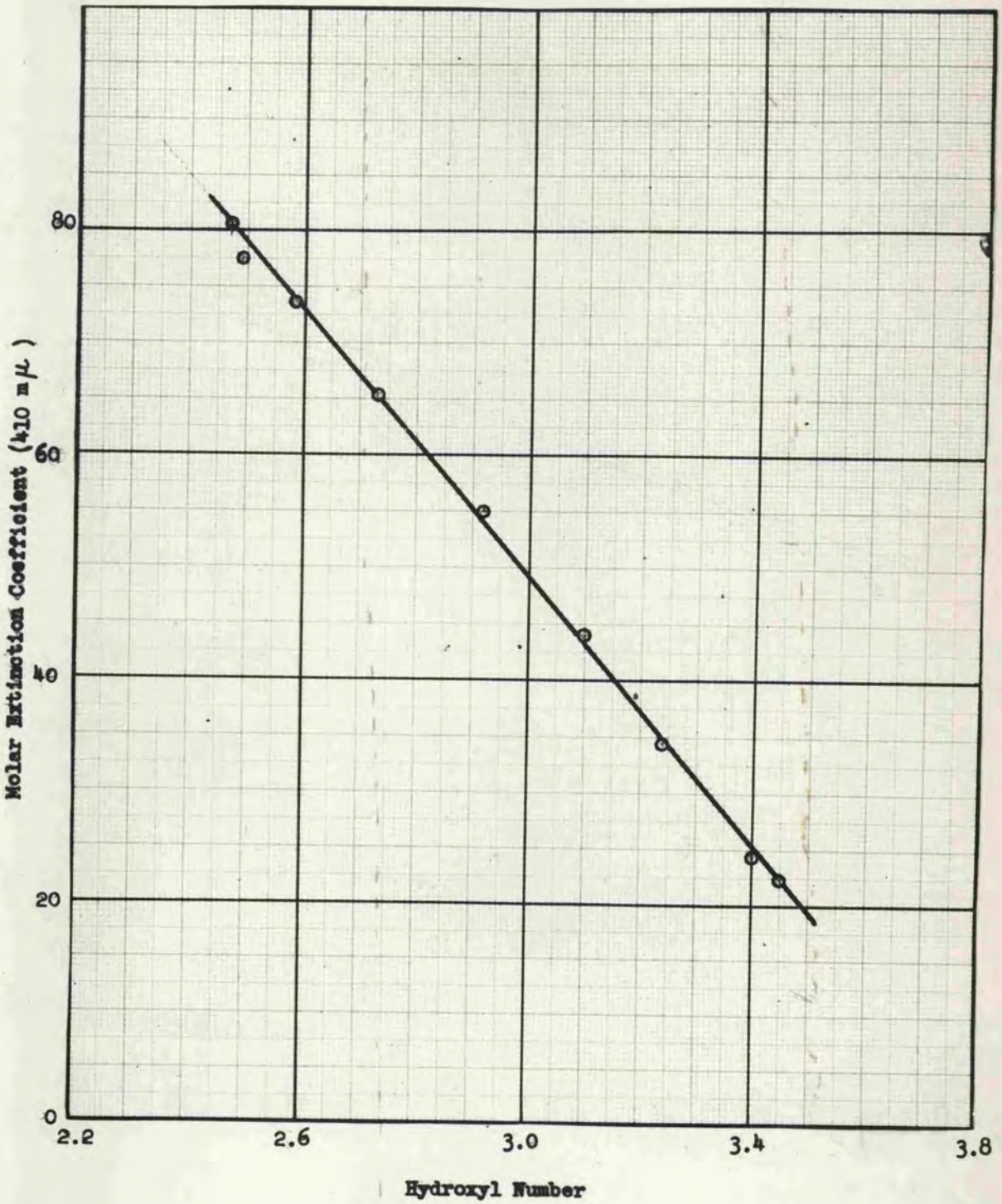

Figure 3

Relationship between hydroxyl number and Extinction coefficient at 410 mμ during Polymerization of Ce(IV).

0.01M HNC
4.98×10^{-3}M $HClO_4$

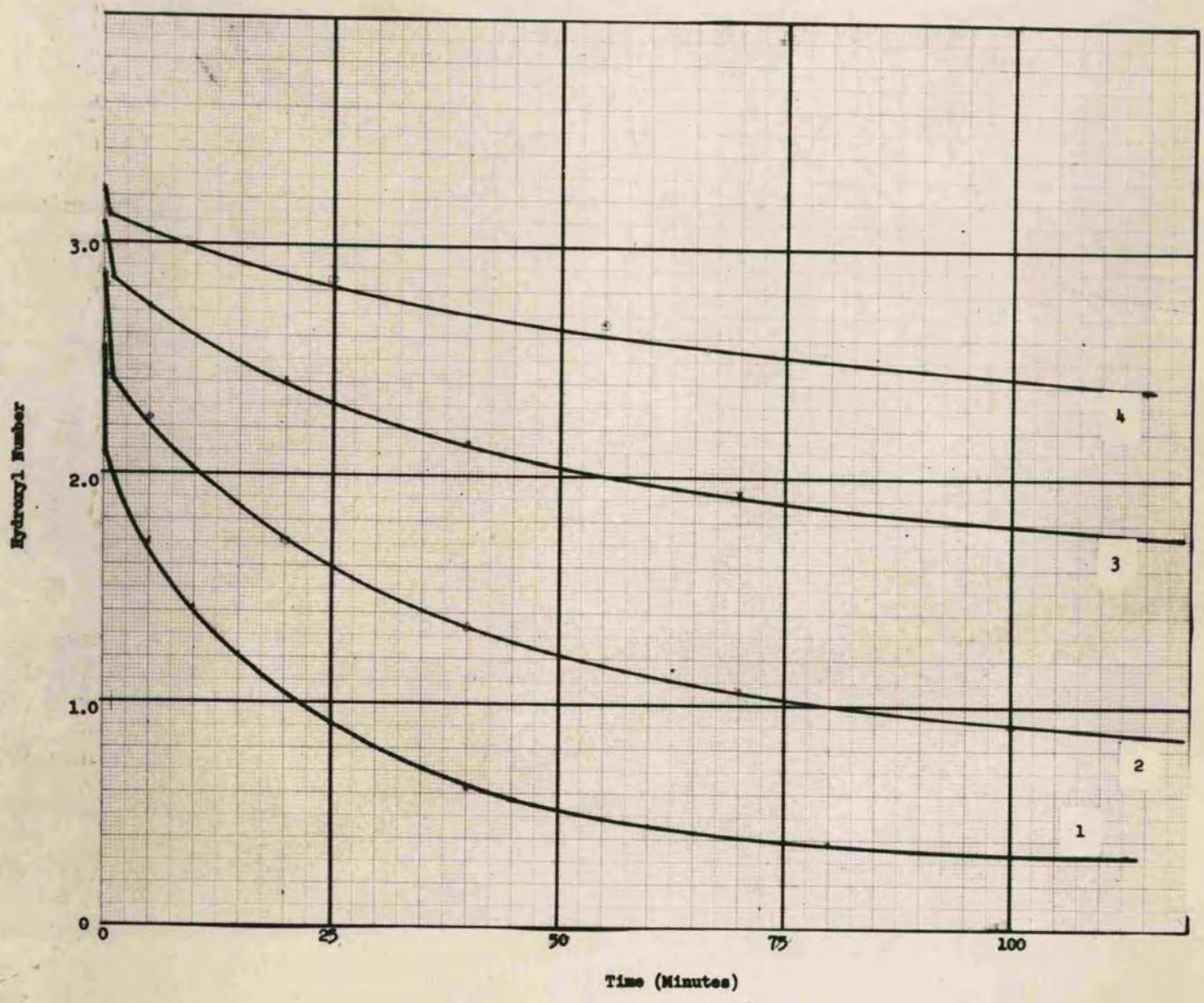

Figure 4

Reduction of Ce(IV) Polymer by Sodium Iodide

2×10^{-3} M HNC
4.98×10^{-3} M $HClO_4$
1×10^{-2} M NaI

1 Reduction after 10 min. of polymerization
2 Reduction after 20 min. of polymerization
3 Reduction after 60 min. of polymerization
4 Reduction after 125 min. of polymerization

Phase Rule Studies - C. H. Secoy [redacted]

Solutions of Electrolytes at Temperatures above Criticals: Many electrolytes, particularly the uni-univalent type, have been found to display a high degree of solubility in the gas phase above the critical temperature with water as the solvent. Those polyvalent electrolytes on which observations have been made do not behave in this fashion giving instead the formation of a new solid or liquid phase below the critical temperature of the solvent. Since the vapor and liquid phases approach identity as the temperature approaches the critical value, there is no reason to expect a discontinuity of any sort in the solubility curve at the critical temperature.

Early in this quarter experiments were planned to study the absorption spectra of a salt which would remain in solution through the critical change. Spectra were to be observed of both the liquid and vapor phases just below the critical point and of the gas phase above the critical temperature. It was desirable to select a solvent with a low critical temperature and a solute which would give a reasonably sharp spectrum. A solution of neodymium chloride in methyl alcohol was selected as a likely possibility.

Anhydrous $NdCl_3$ was prepared by heating the hydrate in an atmosphere of dry HCl, at first gradually and finally to complete fusion. This dehydration was carried out with the salt in the solubility tube which was attached to a vacuum system. Commercially available absolute methyl alcohol was treated with magnesium turnings and fractionated twice in a 12-plate column under anhydrous conditions. The required amount of alcohol was then distilled under vacuum into the solubility tube. Neither the dry salt nor the alcohol was exposed to the atmosphere at any time.

Solutions containing about 2 to 3% $NdCl_3$ gave nice spectra at room temperature. However, upon being heated in the heating block and rocker mechanism described elsewhere (ORNL-98) a solid phase appeared at about 110°. The amount of solid phase increased as the temperature increased, and finally the liquid went through the critical change at 240°, the critical temperature of methyl alcohol. Apparently very little, if any, of the salt remained in solution at the critical temperature. Furthermore, the separation of the solid phase was not reversible upon cooling. An X-ray diffraction study of this solid, carried out by Dr. M. A. Bredig, indicated that it was not $NdCl_3$, NdOCl, nor SiO_2. It is highly probable that it is a methoxy salt of neodymium, but nothing more has been done to determine its identity.

Since this system failed to meet the requirements demanded for such a study, it seems rather improbable that one will be found. Other possibilities might include liquid ammonia as a solvent. If one could find a highly soluble 1-1 electrolyte with a sharp absorption spectra, this work would justify continuation.

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Vapor Density in the System Uranyl Sulfate - Water: In an earlier report (ORNL-98) measurements of the solubility of uranyl sulfate in water at temperatures up to the critical temperature were described. In this work the only composition determination that was made experimentally was the over-all composition of the system. On the basis of several admittedly questionable assumptions, the true composition of the liquid phase was estimated. Newer results indicate that the assumptions were not only questionable but, at least in one respect, erroneous. Therefore, it becomes necessary, in order to complete the previous work, to obtain the necessary experimental data to fix the composition of each phase.

The composition of the solid phases has been determined and reported previously. Therefore, only the liquid-vapor equilibrium is involved. It does seem safe to assume that the vapor contains no appreciable uranyl sulfate. Therefore, all that remains to be done is to determine the vapor pressures and volumes of the liquid and vapor phases respectively. Measurement of the latter has been partially completed and apparatus has been constructed for the vapor pressure measurements. However, it seems best to withhold the data until the experiments are completed. At that time a report will be issued giving the newly obtained data and corrected values for the composition of the liquid phases.

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

Xenon Cross Sections as a Function of Energy

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

The mechanical and chemical operations in the cell are now under a considerable measure of control. The chemical processes have sufficiently paralleled those on the laboratory scale that it has proved possible to provide I^{135} in capillary tubes in quantities adequate for neutron measurements.

Three series of neutron transmission experiments have been made at the pile but there has not yet been time to evaluate the results with precision. So far, transmission has been measured with neutrons having energies at 0.03, 0.06, 0.10, and 0.15 and also at 0.20 electron volts. The Xe^{135} content in the best sample has decreased the neutron beam by about 30%.

The method of assay of Xe^{135} has measured up to expectations. The results of the assays and their precision will be discussed in a later report.

Chemical experiments are under way to increase the final yield of Xe^{135} and thus improve the precision and range of the neutron measurement.

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Completion of the Test Program on the $(I-Xe)^{135}$ Cell Equipment: (G.W. Parker, G.M. Hebert, G.E. Creek with A.R. Brosi and S. Freed)

I. Introduction:

In the last Quarterly Report, ORNL-176, a general description of the process equipment for the rapid separation of I^{135} was presented together with a group of sketches illustrating the chemical operations and most of the mechanical manipulating devices, some of which were still in tentative status. At the present time, an optimistic status has been reached on the complete process which has been proved by the successful completion of two intermediate level runs. Refinements are still being sought. However, full scale operation is now possible.

Since about September 15, almost all of the cell equipment has been either under test or under revision following an indication of unsatisfactory performance. The major steps in the performance testing program are discussed under four headings:

II. Outline of Test Program

1. Correction of Inadequate Off Gas Vacuum
2. Test of the Oxidation-Distillation Step and Control of End Point, Distillate Volume and Chemical Yield
3. Trial PdI_2 Transfer and Remote Operation of the Centrifuge
4. Test of Centrifuge Stripping, Wafer Handling, Sealing and Shielding

1. Correction of Inadequate Off Gas Vacuum

The vessel off-gases such as dissolver hydrogen, hydrogen chloride, xenon and krypton, and the xenon, krypton and iodine lost from the distillation process are expected to be dangerously radioactive. They will be confined as completely as is possible within the limits set by the available off-gas pipes to the chemical fume stack by means of a slight negative pressure maintained in the vessels through an ejector jet. All the acidic gases will be scrubbed through an alkaline column.

In the early test dissolvings #3 and #4, Table I, the volume of gas and water vapor exceeded the total available ejector capacity, resulting in the flow of vapors onto unprotected equipment and into the unshielded cell ventilation duct. In order to overcome this deficiency of gas flow it was necessary to replace the smaller shielded line to the roof with a new system of maximum pipe size. Meanwhile, it has also been decided advisable to install moderate shielding on the large ventilation duct for the protection of personnel normally working nearby.

Subsequent dissolvings have been adequately controlled through the larger gas system and by periodically draining and cooling the scrubber columns.

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Table I (Cold Dissolvings)

Dissolver Performance

Cold Run No.	No. Slugs	Time Dissolved Hrs:Min.	% Dissolved	Off Gas Performance
1	2	1:15	94	OK
2	2	1:00	90	OK
3	4	1:00	85	Failed
4	6	1:15	88	Failed
New Off-Gas System Installed				
5	6	1:00	88.5	OK
6	6	1:00	87	OK
7	6	1:00	88	OK

Note: Since the rate of decay of the 6.7 hr. iodine is approximately 10% per hour, it was decided to increase the dissolving time by about 1/4 hour, expecting thereby to obtain about 93% total dissolution of metal as in runs 8 and 9.

8	6	1:15	92	OK
9	6	1:15	94.5	OK

2. Test of the Oxidation-Distillation Step and Control of End Point, Distillate Volume and Chemical Yield

The oxidation of the UCl_4 is controlled by means of a buffer oxidant of a ferrous-ferric mixture which aids in preventing over-oxidation of the iodine by the dichromate which must provide most of the oxidizing power. The observation of an end-point of the UCl_4 titration in the presence of an adequate reserve of ferrous iron is possible through the use of a potentiometer connected to platinum and tungsten electrodes.

The above titration has been carried out on all of the afore-mentioned dissolvings and the potentiometric curve has also been compared with that observed with the more dependable but less adaptable platinum-calomel electrodes. This was done with the advice and assistance of A. R. Brosi, who has reported on a careful study of this method of oxidation.

While repeating some of the oxidations, elemental sulfur of prohibitive quantities appeared in the distillate of the later ones and was assumed to arise from impure ferric sulfate. Fortunately this condition was found to be easily corrected by simply boiling the slightly acidified solution of ferric salt before use.

In Table II is a summary of the early experience obtained in distilling the tracer iodine from the oxidized mixture.

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TABLE II

Chemical Yields of Iodine

Run No.	Time for Oxidation	Time for Distillation (Limited by the violence of the reaction)	Vol. of Distill.	% Yield
4A (3 slugs)	1 hr.	1 hr.	250 ml.	50%
4B (3 slugs)	1 hr.	1 hr. 40 min.	600 ml.	78%
5 (6 slugs)	1 hr.	1 hr.	180 ml.	50%
		1 hr.	1068 ml. (no reflux)	16%
		2 hrs.	1248 ml.	66%
6 (6 slugs)	55 min.	1 hr. 40 min.	245 ml.	78.5%
		20 min.	280 ml. (no reflux)	11.6%
		1 hr.	167 ml.	5.2%
		3 hrs.	592 ml.	95.3%
7 (6 slugs)	1 hr. 10 min.	1 hr.	650 ml.	78.6%
		1 hr.	725 ml.	12. %
		2 hrs.	1375 ml.	90.6%

A. Improved Fractionation of Iodine and Aqueous Distillate

From these data it was obvious that a better fractionation of iodine and water was required (since the maximum permissible distillate volume is about 100 ml) and also that the time for distillation was too long. Hence a higher rate of heat input was also desirable provided a very high reflux ratio could be maintained to prevent accumulation of distillate.

It was therefore decided to increase both the condenser capacity and the total wattage of heat. By taking advantage of the total cell height available, using increased counter current water flow, and adding a feature which proved to be very important, a central cold finger, it was possible to eliminate all aqueous distillate from the iodine vapors. After a suitable period of reflux in which the iodine is fairly completely removed from the bulk solution, a prescribed amount of distillate (about 75 ml) is collected by reducing the cooling water.

B. Increase in Electrical Heat to the Distillation Vessel

Data on the removal of iodine activity from the distillation vessel by vigorous boiling have consistently indicated that the rate of distillation of iodine is influenced only by the heat input with other conditions constant, including amount of iodine carrier, volume of uranyl solution and ratio of oxidizing and reducing reagents.

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In order to provide at least as high a vaporization rate as was consistent with the improved condensing capacity, it was necessary to replace the 600 watt quartz covered electrical immersion heaters with specially built 1000 watt units. Combined with the 1000 watt infrared lamps, a total of about 7400 watts is now available of which the condenser has been able to match about 90%.

In the following table is a summary of some of the later runs in which the distillate volume and heat input have been satisfactorily improved.

TABLE III

Iodine Recovery with Improved Condenser

Cold Run No.	Time for Oxid.	Time for Distill.	Volume of Distill.	% Yield
10	1 hr.	1:05 (all carrier added at start)	300 (without cold finger)	85
11	Same soln. as No. 10	0:45 (iodine carrier added to maintain equilibrium concentration)	0 (complete fractionation)	80
		1:00	90 (distillate allowed to collect)	
12	Same soln. as No. 10	1:30* (carrier added throughout distillation)	50 (distillate allowed to collect)	90%

*Note: Distillation for 1 hour and 30 minutes has been decided as optimum based on the 10% decay per hour and the observed increase in yield.

3. Trial PdI_2 Transfer and Remote Operation of the Centrifuge

A number of trial centrifugations have been made after the preparation of PdI_2 following a distillation of low level tracer iodine from the uranium solution. Since the complete centrifuging operation was not possible, comparisons were made of percent of total activity in the decanted supernatant from the small precipitation vessel and in the dissolved PdI_2 and the washings. In this way it was possible to establish an average yield figure based on a comparison of the total activity in each fraction.

Similarly, yield figures have been obtained on the first low level I^{135} runs which were assayed by A. R. Brosi with the high pressure ion chamber for the hard gamma ray associated with I^{135}.

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TABLE IV

Overall Chemical Yields

Intermediate Run No.	I^{135} Radio-activity Source	Total Chemical PdI_2 Yield
1	10 g Metal, 11 hr. Bombardment	55%
2	1 X slug, 1 hr. Bombardment	Yield not Determined due to Leakage*
3	1 X slug, 1 hr. Bombardment	34% (about 250 mc I^{135})

*In the intermediate run No. 2, a minor mechanical failure on the capillary decanting pipettes made it necessary to attempt to seal the sample without complete removal of solvents. Later this resulted in leakage from the capillary and the sample could not be assayed.

B. Experience in Time Requirements for the Chemical Separation of 6.7 hr. I.

In Mon-432, p. 75, an early estimate of the most probable time lapse before the zero time of trapping xenon in the PdI_2 crystals was outlined in fair detail. This estimate ranged from 3¼ to 5 hours. Since that time it has been found that in all cases the longer period allowed for each step has been necessary and that all the major chemical operations have been extended for from 1/4 hrs. to 3/4 hrs. Therefore, zero time has actually been found to be approximately 7½ hours from discharge time. After this time the decay loss is approximately 60%.

C. The Major Factors Affecting the Final Yield of I^{135} in the Wafer

In a memorandum of March 15, 1947 discussing the subject, "Amount of Xe Required for the Xe^{135} Cross Section Experiment", M. Shapiro, in a detailed account of how the number of I^{135} atoms per X-slug is calculated, arrived at the figure:

(1) 1.37×10^{16} atoms I^{135}/slug after 24 hours' bombardment at the center of the pile or at max. flux.

Related to specific activity of radium of 1 curie/gram and using a half life of 1590 years, this number of I^{135} atoms represents in curies:

(2) No. of atoms x λ/d/s/curie = No. of curies/slug

$$\frac{1.37 \times 10^{16}}{3.7 \times 10^{10}} \times \frac{0.693}{6.7 \times 3600} = 10.7$$

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The following variations, however, have been observed which diminish this ideal yield.

(a) the pile loading and power is actually nearer

$$\frac{3700 \text{ KW}}{40,500 \text{ slugs}} = .094 \text{ KW/slug or } 94\% \text{ of max.}$$

(b) Practical exposure time has been cut to ~ 20 hours which is equal to 87.5% of sat. or 95% of that from a 24 hr. bombardment.

(c) The flux region available for these slugs averages about 90% of max. for the center slug of 8. The outer slugs probably receive only 85% of maximum. The average slug then, must receive only about 90% of the maximum for that row.

(d) <u>Correction for Bombardment</u>

The overall correction then for these variations from the ideal maximum gives:

$$.94 \times .95 \times .90 \times 90 = .72 \text{ or } 72\% \text{ of } 10.7 = 7.7 \text{ c/slug}$$

at discharge time.

(e) <u>Correction for Decay during 7½ hours of processing through</u>

1.12 half lives = 45% yield, or 45% of 7.7 c = 3.5 c/slug

(f) <u>Correction for chemical yield</u>

Dissolution, maximum	=	90%
Distillation, maximum	=	88%
Precipitation, maximum	=	90%
Centrifugation, Estimate	=	75%

Maximum total chemical yield = 55%

55% of 3.5 c/. = 1.8 c/slug or 10.8 c/six slugs

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4. Testing of the Centrifuge Stripping, Wafer Handling, Sealing and Shielding Operations

A. The Centrifuge Stripping Operation

While this has been one of the last techniques to be successfully mastered, it is normally the first in the sequence of the remote handling operations. The order of operations illustrated in the isometric sketches shows first the removal of the tare centrifuge cup in order to provide space for the elevated pipettes, which must be lowered to permit passage of the wafer tong carriage over the centrifuge housing.

The second operation illustrates the difficult removal of the fluorothene funnel, which is separated after loosening by rotation and by lifting it away from the locked down cup and wafer. The necessity for locking down the centrifuge cup and wafer in a way that is adaptable to the remote procedures required extensive revisions after several unsuccessful designs.

B. The Wafer Handling Operations

The third remote operation is that of removing the wafer from its locked down position in the cup, and separating it from the filter pedestal which fits into the lower taper bushing and supports the tiny inside filter in the capillary tube.

The most reliable technique found for holding down the wafer during the separation from the funnel is by means of a heavy soft metal spring, which is simply bent open by the lifting force of the wafer tong. The filter pedestal is separated by being pulled off, since it will not pass through the opening in the wafer supporting plates, which are also locked in with a set screw.

The wafer is first placed on a vacuum-holding turntable, requiring very accurate positioning of the wafer tong by indicating micro switches. After sealing, the wafer is lifted off of the turntable and released in the cut-out section of the shield drawer.

C. Test of the Wafer Sealing Operation

Prior to the assembly of the centrifuging unit, the capillary is carefully checked for tightness between the thin koroseal gaskets, the tapers and the glass tube ends, and for sealability of the tapers with the aluminum plugs. After a successful test, the selected plugs are kept for reuse in the final sealing. Each end of the wafer is tested to hold at least 20# air pressure on the gaskets and on the plugs. Aluminum, of moderate hardness, accurately tapered and burnished, is used for the plugs. A small amount of vacuum type silicone grease is used to insure gas tightness.

Satisfactory sealing has been general with the single exception of the second intermediate level run indicated in Table IV, which was known to be incompletely freed of solvents.

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D. Loading the Drawer into the Wafer Shield

In order to remove the drawer without exposure, the wafer shield is elevated and placed against a small opening in the 3" lead inner cell door. By means of an attached rod the drawer is slowly drawn into the shield, after which the rod is detached. In an effort to provide extra safety, a gas tight blister cap has been made to fit over the openings around the ends of the drawer. Through attached valves in the sides of the blister, it is possible to circulate a gas for the collection and measurement of suspected xenon leakage from the wafer.

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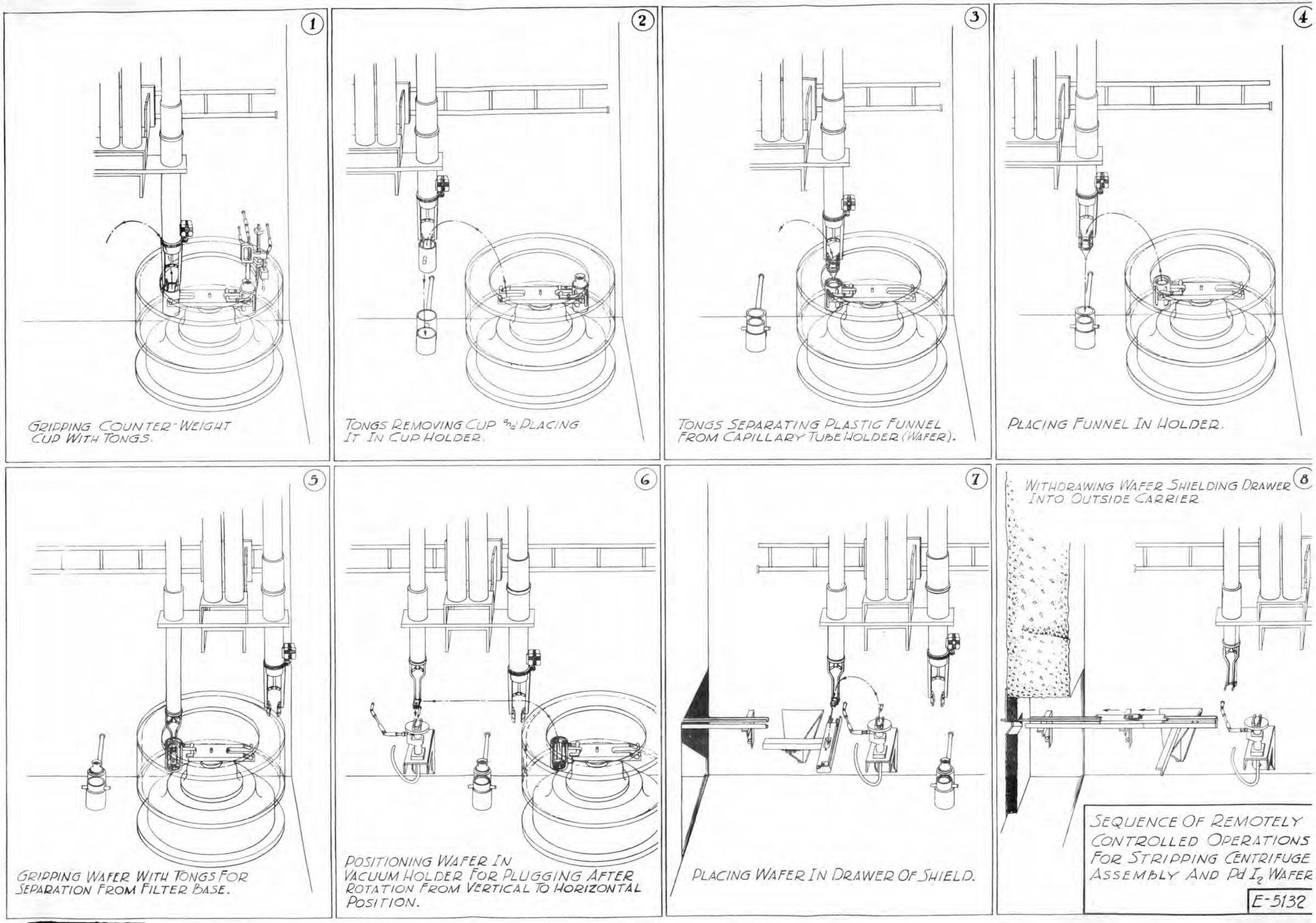
1
GRIPPING COUNTER-WEIGHT CUP WITH TONGS.
2
TONGS REMOVING CUP and PLACING IT IN CUP HOLDER.
3
TONGS SEPARATING PLASTIC FUNNEL FROM CAPILLARY TUBE HOLDER (WAFER).
4
PLACING FUNNEL IN HOLDER.
5
GRIPPING WAFER WITH TONGS FOR SEPARATION FROM FILTER BASE.
6
POSITIONING WAFER IN VACUUM HOLDER FOR PLUGGING AFTER ROTATION FROM VERTICAL TO HORIZONTAL POSITION.
7
PLACING WAFER IN DRAWER OF SHIELD.
8
WITHDRAWING WAFER SHIELDING DRAWER INTO OUTSIDE CARRIER
SEQUENCE OF REMOTELY CONTROLLED OPERATIONS FOR STRIPPING CENTRIFUGE ASSEMBLY AND Pd I_2 WAFER
E-5132

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Nuclear Chemical Studies in the Fission Product Region: (G. E. Boyd)

Cross-sections for the Production of Radionuclides of Element 43: (E.F. Motta)

The chief effort during the quarter now elapsed has been directed toward the calculation of the cross-sections for the production of the Tc radio-isotopes by energetic deuterons on the calutron enriched stable Mo isotopes currently available. Since (d,n), (d,2n) and (d,3n) reactions appeared to occur in varying proportions depending upon the deuteron beam energy, a group of three linear simultaneous equations relating the cross-section for each reaction to the observed yield of activity has been set up for each target isotope and then solved by the method of determinants. Distinct differences in the predominance of a given reaction depending upon the energy were observed: (1) with nominal 14 MeV deuterons (DTM) the main reaction was (d,2n) together with small amounts of (d,n) and probably no (d,3n) products; (2) with nominal 20 MeV particles (UCRL), the (d,3n) reaction was quite evident although the (d,2n) reaction was the more abundant. If data at 10 MeV taken at the Ohio State cyclotron [cf. M. L. Pool and D. N. Kundu, Bull. Am. Phys. Soc., 23, [J9] (1948)] can be normalized, it may be possible to construct crude excitation functions for these reactions. Since the nuclear charge was held constant (Z = 42), whereas the mass number varied from 92 to 100, these curves may show up differences in neutron binding energies in this region of the periodic table.

Neutron Irradiation of Tc^{99}: (F. E. Motta)

Several irradiations of a one milligram quantity of Tc^{99} extracted from pile irradiated molybdenum were carried out in order: (a) to test the assignment of the cyclotron produced 80 second period to Tc^{100}; and (b) to determine the activation cross-section for Tc^{99}. In two experiments, periods of 120 and 90 s. were observed, the latter being considered the more reliable since the sample was intensively purified between the two irradiations. In spite of the purification, the presence of small amounts of Mo and Ru were indicated by the characteristic 14 m and 18 h periods found in the gross decay curve. A highly provisional value of about .05 b was estimated for the capture cross-section. Further purifications and irradiations are planned.

Search for the Long-lived Ground State of Tc^{97}: (G. E. Boyd)

A search for the radiations emitted by the ground state of Tc^{99} is being made in connection with a re-investigation of the radiations emitted by the 90 d. Tc^{99} isomer. The emission of element 43 Kα X-rays in the decay of the 90 d. activity has been confirmed by critical absorption measurements with Zr, Cb and Mo foils. The presence of unconverted 97 KeV γ-radiation has not yet been proved despite repeated attempts, suggesting that the conversion is well over 50%. Evidence for appreciable conversion in the L-shell, as well as in the K-shell, has been indicated by the observation of Lα X-rays by absorption in beryllium. If the ground state decays by orbital electron capture, as might be expected from a variety of considerations, Mo X-rays should also be noted in the "old" Tc samples. Thus far, even using a strong sample prepared by extracting all of the pure Tc^{97} produced in a 20 g. $Ru(OH)_3$ irradiated in the pile for seven months, no Mo X-rays have been observed. Possibly then, the half-life for the decay of the ground state of Tc^{97} by K-capture is greater than 10^6 y.

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Search for Zr^{93}: (Q. V. Larson and G. E. Boyd)

Nuclear stability estimates and the high spin of stable Cb^{93} appear to indicate that the radionuclide Zr^{93} might possess a very long half-life. Accordingly, a search is being made in a number of old exchange column oxalic acid solutions each of which initially contained several hundred millicuries of 65 d. Zr^{95}. These elutriants were treated first to remove appreciable amounts of long-lived Ru and Ce, then the Zr was extracted into benzene by means of TTA (using Ce hold-back) and finally a small quantity of $BaZrF_6$ was precipitated and mounted for the counting study. Despite the fact that the 65 d. Zr^{95} had decayed through as many as twenty half-lives, it appeared as the predominant Zr activity. Aluminum and lead absorption curves were highly characteristic of the 65 d. activity so that not more than 10% of a second Zr activity could have been present. The decay of these samples will be followed. However, on the basis of the relative fission yield of Zr^{93} and Zr^{95} and the decay time and the amount of 65 d. activity still observed, it has been concluded that if Zr^{93} is long-lived: (a) its half-period must be of the order of 10^6 y., or greater; or (b) its beta radiations must be less than 0.1 MeV in energy.

The foregoing considerations may be in error, of course, and Zr^{93} may possess a short half-life. Sometime ago (2/4/46), E.E. Motta carried out several pile neutron irradiations of some spectrochemically analyzed ZrO_2 and observed (using a 6 minute bombardment) a strong 2.0 minute period which could be followed over six half-lives before merging into a second approximately 30 m. component. This observation appears to agree with the previous finding of a 2.5 m. period produced in Cb presumably by an (n,p) reaction at the Chicago cyclotron (Nedzel, et al., CC-2299, October, 1944). Currently short neutron irradiations of the calutron separated Zr isotopes are being conducted.

The Radionuclides of Columbium: (G. E. Boyd)

It has been possible to isolate and identify the radioisotopes of columbium of mass number 90 through 98 formed by (d, α) and (d, α n) reactions on the calutron separated Mo isotopes incidental to the program during the past 15 months for the production, characterization and mass assignment of the element 43 radio-nuclides which was conducted by means of a series of deuteron bombardments from the 60 inch cyclotrons at the Department of Terrestrial Magnetism, Carnegie Institution, Washington, D. C. (DTM) and at the University of California Radiation Laboratory (UCRL). Certain information gained from these studies may be communicated at this time, although a final analysis of the decay curves, absorption curves, etc. has not yet been completed:

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1) Cb^{90} - A 15 h. period in columbium decaying with the emission of positrons as shown by magnetic deflection was found to be produced in maximum yield upon the irradiation of the Mo^{92} preparation with nominal 14 MeV deuterons (DTM). The reaction then is Mo^{92} (d,α) 15 h. Cb^{90}. Absorption measurements in Al and Pb indicated: (a) a maximum β^+ energy of ca. 1.7 MeV; (b) three gamma rays of 0.04, 0.25 and 1.66 MeV, respectively. An 18 h. positron emitting activity in Cb had been assigned tentatively to mass 90 by Jacobson and Overstreet (CC 2345, December 1944).

2) Cb^{91} - A 64 d. period decaying with the emission of e^- and Cb X-rays was produced in maximum yield with the Mo^{94} sample (UCRL) presumably by a (d,αn) reaction. The 0.94 MeV γ-ray reported by Moquin and Pool, [Phys. Rev., 65, 60 (1944)] was not found. Samples containing appreciable amounts of the 35 d. Cb^{95} show this γ until over 300 d. total decay, however. Presently it is proposed that the 64 d Cb^{91} decays by isomeric transition to a very long-lived ground state. It is of interest that the nucleus of Cb^{91} possesses 50 neutrons.

3) Cb^{92} - The previously well-characterized 10 d. period in Cb was found to be produced with maximum yield in the irradiation of Mo^{94}. The observed negative beta and gamma radiations and energies thereof were in substantial agreement with that found in earlier work. None of the 21.6 h. period assigned as an independent isomer of Cb^{92} by Wiedenbeck [Phys. Rev., 70, 435 (1946)] was observed in these bombardments.

4) Cb^{93} - Deuteron irradiation of Mo^{95} did not lead to any activities in Cb which could be assigned to mass 93. The 42 d. period reported by Wiedenbeck [Phys. Rev., 68, 1 (1945)] was not observed.

5) Cb^{94} - No period which could be assigned to Cb^{94} was observed in the irradiation of Mo^{96}. Since the chemical separations and purifications required 60-100 minutes, the well-established 6 m. isomer was not seen.

6) Cb^{95} - The definitely established 90 h. and 35 d. periods in Cb were produced in maximum yield in the deuteron irradiation of Mo^{97}. Good agreement with the reported radiations and energies was realized, although the reported Cb K_α X-ray characteristic of the 90 h. isomer was not observed. The relative yield of the 90 h. isomer was much greater than has been found in the slow neutron fission of U^{235}.

7) Cb^{96} - A 2.6 d. period emitting negative beta particles but no gamma radiations was observed in maximum yield in the deuteron irradiation of the Mo^{98} preparation. The maximum energy of the beta rays determined by absorption in Al was ca. 1.1 MeV. Previously, a 3 day period in Cb had been assigned tentatively to mass 98 by Jacobson and Overstreet (vide supra).

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8) Cb^{98} - Deuteron irradiation of the Mo^{100} preparation gave rise to a strong 30 m. period in Cb which was shown by magnetic deflection to decay with the emission of negative particles. A smaller amount of a 65 m. period (probably the known Cb^{97}) was formed also. A characterization of the energies of the radiations was not made. Further work seems desirable since our observation of a 30 m. activity at mass 98 contradicts the report of Katcoff (LAMS-765, August 1948) that, "any new Cb fission products with an appreciable yield must have shorter half-lives than four minutes".

The Radio-nuclides of Tin (C. M. Nelson)

As a preliminary to a study of the fission product activities formed in the Cd, In, Sn region of the periodic table some effort was devoted during the past quarter to the pile neutron irradiation of the calutron separated tin isotopes. First, a ten minute bombardment of a purified sample of the naturally occurring mixture of tin isotopes, followed by rapid counting, showed 10 m., 37m. and 27.6 h. periods in high relative yields. Irradiation of Sn^{124} gave a predominant 11 m. period together with smaller amounts of a 3 h. and a 42 h. activity. Irradiation of Sn^{122} gave a predominant 35 m. activity which grew in a ca. 15 m. Sb daughter; smaller amounts of a three hour activity and a longer activity were formed also. Irradiation of Sn^{120} gave a predominant 27 h. activity together with a small amount of 10 m. Sn. Irradiation of Sn^{119} appeared to give a relatively long period in low yield. On the basis of the foregoing observations the following provisional assignments are proposed: 11 m. Sn^{125}; 35 m. $Sn^{123} \longrightarrow$ ~15 m. Sb^{123} m.; 27 h. Sn^{121}.

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III. General Nuclear Chemistry

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

General Summary: (B. H. Ketelle)

During the past two years a continuing study of the activities induced in the rare earths by pile neutrons has been conducted. The rare earths which were irradiated were, in many cases, previously highly purified by chromatographic separation on ion-exchange columns(1). Following irradiation the earths were separated again on ion-exchange columns as described elsewhere(2). A preliminary study of the radiation characteristics of the active isotopes has been carried out and it is possible at this time to compile a considerable part of the observations on the half-lives in the following Table: (see Table). Because several earths have been present in each study it has been possible to begin with the heaviest rare earth, lutecium, which is eluted from the column first and identify each earth successively. In one series of studies all of the earths from lutecium through cerium have been studied. Since the relative spacing of the peaks should be related to the ion size one feels confident that the assignment of the activities to the several elements is correct. It is recognized that the half-lives here reported agree closely with certain half-lives reported by other workers who assumed that the activities observed were those of the principal element irradiated. However, one has only to look through the literature on the nuclear chemistry of the rare earths to find an abundance of examples where the experimentor has been misled by the presence of a small amount of another rare earth impurity which has a high activation cross section. Furthermore, the element assignments made from the order of elution from the column are in agreement with the isotopes whose masses have been established by mass spectrographic separation. The maximum energies of the beta groups have been determined by absorption curves. These values are in agreement with values reported elsewhere. Since many of these isotopes have complex decay schemes, it is felt that these values may be subject to considerable error and only the values determined on the thin lens spectrometer are reported.

Study of the Active Isotopes of Gd and Tb: (B. H. Ketelle)

The assignment of the activities found upon irradiating Gd and Tb has been difficult because the starting materials may be cross-contaminated and because the Gd isotope of mass 161 decays to an active Tb isotope of the same mass. In the present study the decay curve of slow neutron irradiated Gd without separation is represented by four half-lives, 3.6 min., 17.9 hr., 6 d., and 225 d. Activities corresponding to these half-lives have been reported by Krisberg, Pool and Hibdon(3), and by other workers. (See ORNL-65, p. 94). Upon irradiating the Tb obtained from the U.S. Bureau of Standards, half-lives 140 min. and 72.5 d. were obtained. This Tb yielded Dy lines upon spectrographic analysis so the short-lived activity is undoubtedly Dy^{165}. No six day activity was found in this material.

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(1) Darwin Harris has generously furnished these materials (vide supra).
(2) B. H. Ketelle, G. E. Boyd, J. Am. Chem. Soc. 69, 2800 (1947).
(3) Phys. Rev. 74, 44 (1948).

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Summary of Half-lives and Radiation Characteristics
of Rare Earth Activities Produced by
Pile Neutron Irradiations

(Energy values determined with thin lens spectrometer)

Element	Total No. of half-lives	Average half-life	Beta energy	Gamma energy	Total No. of half-lives	Average half-life	Beta energy	Gamma energy	Total No. of half-lives	Average half-life
Ce	2	30.5 hr.(1)								
Pr	4	14.1 d.(1)			7	18.9 hr.(1)				
Nd	5	11.4 d.(1)								
61	7	49 hr.(1)								
Sm	26	46 hr.(2)								
Eu	18	9.5 hr.(3)								
Gd	34	17.9 hr.(2)			2	225 d.(2)				
Tb	41	72.5 d.(9)			3	7.5 d.(1)				
Dy	17	140 min.(2)								
Ho	54	27.2 hrs.(6)								
Er	85	9.4 d.(7)	0.33±0.01	None	37	7.5 hrs.(7)	71% 1.05±.03 6% 1.49±0.05 22% 0.67±0.03	0.305±0.010 0.113±0.005 0.805±0.025		
Tm	14	129 d. (3)	0.98±0.01	83 kev	3	680 d.(5)	0.100	None		
Yb	31	32.5 d.(5)			10	103 hrs.(1)			36	2.0hrs.(3)
Lu	10	6.8 d.(1)			4	3.9 hrs.(1)				

*Figure given in parentheses following the half-life denotes the number of separate samples measured.

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When Gd was irradiated and a complete separation of Tb was made from the Gd, the Tb sample decayed through 3 half-lives with a half-life of 7.5 d. This value will be decreased when the sample has been followed sufficiently long to subtract the 72.5 d. Tb activity due to cross contamination. This activity has a β energy of about 0.5 Mev and γ ray of an undetermined energy. (This value will be known when the activity of the long-lived Tb can be subtracted). The separated Gd sample decayed with a half-life of 17.7 hrs. and this activity has leveled off to an activity of long half-life. In previous studies where short bombardments of Gd were made prior to separation, this long-lived component has been found to have a half-life of 225 d. as shown in the following table. This separated Gd sample did not show the 6 day half-life found in the non-separated Gd. From this, one must conclude that the ~ 6 d. Tb must be the daughter of a short lived Gd which had decayed before the Tb separation was made or of a very long-lived Gd which has not produced a measurable amount of 6 d. activity in the separated Gd sample. A study of the activity obtained on irradiating column separated Gd for 3 min. showed the presence of a 3.6 min. component with a beta energy of 1.5 Mev and a γ energy of .37 Mev and possibly a softer γ. Further studies are in progress to establish the absence of this activity in possible contaminants.

Since the 225 d. activity is probably the same activity separated by Inghram, Hayden and Hess(4), we have the 3.6 min. and 17.9 hr. activities of Gd, and the 6 d. Tb to assign mass numbers. The calculated energy instabilities of Gd^{159} and Gd^{161} are 0.91 and 1.78 Mev respectively. If the 3.6 min. activity above-mentioned decays by simple beta decay followed by the γ its energy change is about 1.9 Mev. This agreement with 1.78 and the probability that the parent of the 6 d. Tb which must be Tb^{161} is short-lived leads us to assign the 3.6 min. activity to Gd^{161}. The 17.9 hr. activity is probably Gd^{159} since with a beta energy of 0.9 Mev and a γ of 0.35, its energy is in fair agreement with the calculated value. Since Pool was unable to obtain this activity by n,p reaction on Tb^{159}, further work is in progress to clear up this uncertainty.

Further Studies of the Radiations of 129 d. Tm^{170}: (B. H. Ketelle)

Aluminum absorption curves of the thulium activity produced by radiative neutron capture on ion-exchange column purified stable thulium indicate a maximum beta energy of 1.0 Mev and a very small amount of a harder component. The maximum beta energy reported in CNL-37 was found to be 0.98 ± 0.1 Mev by measurement on the thin lens beta ray spectrometer. There was evidence also of a conversion line at low energy. Therefore, the source was further purified on a Dowex 50 column under conditions which would have removed adjacent rare earths, if they were present. No impurities were detected. The purified source was then used to make further studies. The γ ray energy deduced from the L conversion line would correspond to 83 Kev. A stronger source was obtained and the photoelectron peaks were studied with several radiators. The results are tabulated below.

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(4) Phys. Rev. 71, 60 (1947).

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Radiator	γ-ray Energies Corresponding to K line	L line	Th line
U		84 kev	80 kev
Fe	81 kev		
Cu	84		
Cb	84	80	
In	85	83	
LaF_3	83	80	

In order to establish that the conversion electrons were originating from a heavy rare earth the photoelectrons produced by the K X-ray on copper were studied. Their X-ray energy, 50 kev, is in reasonable agreement with the known energy of the ytterbium X-rays considering that the peaks obtained were very near the window cut off. As further confirmation of the belief that the 83 kev originates from the same nucleus as does the 0.98 Mev beta ray, the activity has been studied on the coincidence apparatus in collaboration with Francis McGowan. The results show a high coincidence rate between conversion electrons and betas and indicate that if the γ ray is delayed that its half-life is less than 0.1 microsecond.

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Radiations of Hf^{181} (B. H. Ketelle)

A sample of HfO_2 of purity in excess of 99% was irradiated in the pile and its radiations studied on the thin lens spectrometer. The conversion lines falling at or just below the beta ray endpoint make a rather long extrapolation necessary on the Kurie plot. However, the maximum beta energy is reported as 0.41 ± 0.01 MeV. Because this source was about 1-2 mg/cm^2 thick, the conversion lines were shifted somewhat. K lines corresponding to γ ray energies of 128, 343, 472 and 602 KeV were observed. The last peak was very low but appears to be real. Photoelectron peaks with several radiators were obtained as follows:

Radiation	K	L
U	343 478	
Ta	128 344 480	131
Au	140* 344 480	132 346 481

*Very close to window cut off

These values are in good agreement with the values given by Cork, Shreffler and Fowler[5] as follows: .1325, .3442 and .4787 but are lower than the values reported by Jensen[6] at Iowa State College.

It is noteworthy that absorption curves lead one to believe there is a γ of about 0.6 MeV and some evidence is found above for conversion electrons corresponding to this energy. A careful search failed to give evidence to any photoelectron from uranium or gold.

(5) Cork, J. M., R. C. Shreffler and C. M. Fowler, Phys. Rev. 72, 888 (1947)
(6) See A. F. Voight and B. J. Thamer, AECD 2083

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IV. Radio-Organic Chemistry

[redacted]

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

Summary

Carbon dioxide has been reduced to formic acid in yields of 71-88% by the action of lithium borohydride in ether solution. Study of the reaction under various conditions has given some insight into the mechanism of the reaction. Studies on the isolation of the acid are under way.

Difficulties encountered in the preparation of methanol by lithium aluminum hydride reduction of carbon dioxide have been partially overcome by careful purification of solvents used in the process. Tracer-level experiments in the routine preparation of formaldehyde give preliminary indications of a satisfactory yield in the present process. Acetic acid has been prepared in yields of 95%. Isolation methods tried so far have not been completely successful.

Considerable progress has been made in the preparation of ring-labeled benzoic acid. The carbonation of γ-phenylbutyric acid has been carried out in 90-95% yields. The conversion of this to α-tetralone has been accomplished in yields of 85-90%. The oxidation of β-methylnaphthalene to phthalic acid has given difficulty. The lithium aluminum hydride reduction of p-methyl-cinnamic acid has yielded an unsaturated alcohol rather than the expected p-methyl hydrocinnamyl alcohol.

The attempted preparation of styrene through a series of reactions involving phenylacetic acid was abandoned, as a consequence of the poor yields of this acid obtained by the carbonation of benzyl magnesium chloride. A second reaction scheme involving benzoic acid gives considerable promise of success.

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

Formic Acid (J. G. Burr)

Discussion of Results

Carbon dioxide has been reduced to formic acid in yields of 71-88% by the action of lithium borohydride in ether solution. Over a series of five runs, the yield of formic acid has averaged 79%, based on the carbon dioxide absorbed by the hydride solution. The absorption of carbon dioxide has averaged 81% of the carbon dioxide charged. The unreacted carbon dioxide was recovered in each run by absorption in saturated barium hydroxide solution, and may be reused.

The procedure employed consisted of measuring a known quantity of standardized lithium borohydride solution into a reaction vessel which was connected to a system containing a source of dry carbon dioxide (obtained

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by acidification of barium carbonate). The carbon dioxide was swept with dry nitrogen into the solution which was maintained at 0°. The unreacted carbon dioxide was absorbed in two traps filled with saturated barium hydroxide.

At the completion of a run, the reaction product was hydrolyzed with dilute sulfuric acid, and the formic acid was determined by one of two methods:

(1) The dilute acid solution was submitted to continuous ether extraction, and the ether extract was titrated with standard sodium hydroxide. It was found that a very considerable amount of boric acid was also extracted by the ether, giving a poorly defined titration end point.

(2) The alternative, and superior method was by means of alkaline permanganate oxidation[1]. This may be carried out upon the solution resulting from the alkalimetric titration, which is boiled down to less than one-half the original volume to remove ether and methanol which would also be oxidized by the alkaline permanganate. It was found simpler, however, to make alkaline the original water solution of the reaction product and boil this down to about one-quarter of the original volume, dilute to a known volume, and oxidize an aliquot. After the oxidation, a known amount of oxalic acid was added. This was back titrated with permanganate.

The formic acid has been identified in one aliquot by preparation of the S-benzyl-thiuronium salt. Of the other products which would be expected to result, formaldehyde and/or methanol, formaldehyde has been found in one case to the extent of 3% of reacted carbon dioxide, and in other cases to be completely absent. Presumably, then, methanol is the other reaction product formed.

It was first assumed that the mechanism of formate production was analogous to the reduction of carbon dioxide to methanol[2], i.e. according to the equation:

$$4CO_2 + 3LiBH_4 = LiB(OOCH)_4 + 2LiBO_2$$

However, it was discovered that during the reaction a certain amount of boron is converted to a volatile compound which appears in the barium hydroxide absorption traps as boric acid. Presumably this volatile boron compound is a boron hydride, B_2H_6.

Several mechanism alternatives to the one above can be written which might account for the simultaneous production of formic acid and methanol by this reduction of carbon dioxide:

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

(2) Nystrom, R. F., J. Am. Chem. Soc., 70, 441 (1948)

[redacted]

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1. The two products may be produced by simultaneous and competitive reactions.

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

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

This mechanism demands that volatile boron compounds be formed containing one mol of boron for each mol of formic acid. This equality has been approached within experimental error in several of the runs, but the data havenot been found to be reproducible. (See Table 1) The mechanism also demands that the formic acid be formed as lithium formate. During these reactions a precipitate does appear. This precipitate was isolated in a nitrogen atmosphere, washed with ether several times and dried in a stream of dry nitrogen. Upon decomposition by dilute acid, 1.0 mol of gas is evolved per mol of formic acid in the precipitate. The precipitate contains 0.78 mols of boron (determined by alkalimetric titration in the presence of glycerine) per mol of formic acid. The precipitate thus appears to be a mixture of several substances. This may occur partly through metathesis:

$$LiB(OCH_3)_4 + 4LiOOCH \longrightarrow LiB(OOCH)_4 + 4LiOCH_3$$

since the lithium boromethoxides are ether soluble. However, there is insufficient boromethoxide produced to account for all the formic acid by this method. The formate ion may react in part at the moment of formation with a boron hydride:

$$OOCH^- + BH_3 \longrightarrow BH_3(OOCH)^-$$

and a portion of the formate may be present as lithium formate. As can be seen, from Table I, the material balances are approximately consistent with this picture.

2. Another possible mechanism for the reaction consists of the initial reduction of carbon dioxide to methanol (as a boromethoxide), which then acts as the agent for the reduction of more carbon dioxide to formic acid.

$$6CO_2 + 5LiBH_4 \longrightarrow 2LiBH(OCH_3)_3 + 3LiBO_2$$

$$LiBH(OCH_3)_3 + CO_2 \longrightarrow LiB(OCH_3)_3(OOCH)$$

This was suggested by the discovery[3] that the trimethoxy lithium borohydride will reduce carbon dioxide to formic acid in 60% yield. This mechanism however does not explain the formation of volatile boron compounds during the reaction. It has been found that a solution of 4.5 mmols of lithium borohydride to which 5 mmols of methanol had been added would absorb carbon dioxide as well as an untreated solution, and would reduce it to formic acid in 71% yield. If, however, ten mmols of methanol was added to a similar

(3) Schlessinger, Private Communication

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solution, the absorption of carbon dioxide fell off very sharply, and the absorbed carbon dioxide was reduced to formic acid in only 41% yield. These results are not consistent with this proposed mechanism.

3. A third explanation follows the same lines as (1) except that methanol is produced not by a competitive reaction, but by further action of the lithium borohydride upon formate ion. This explanation has been discounted by experiments which show that pure lithium formate is not reduced by lithium borohydride, alone or in the presence of methanol.

The yield of formic acid was not increased by use of excess carbon dioxide, and considerably lowered by use of excess of lithium borohydride. Elevation of reaction temperature from 0° to 30° did not increase the yield, but did reduce the amount of carbon dioxide reacted. The reaction does not proceed at temperatures much lower than 0°C.

Experimental

The dry, solid lithium borohydride, a product of the General Electric Company, gave an analysis of 43.2% boron (theoretical is 53.9%), and active hydrogen equivalent to 71% lithium borohydride. This shows an excess of boron probably present as lithium borate. The reducing solution was prepared by dissolving the dry solid in ether and separating the solution from the solid which does not dissolve. The concentration of this solution, as determined by evolution of hydrogen upon acidification with dilute sulfuric acid, was 1.15 mmols lithium borohydride per ml. It was stored in a closed system protected from the carbon dioxide and water in the air.

Reduction of Carbon Dioxide to Formic Acid -- Ten ml. of dry ether was placed in a special reaction flask, and 3.52 ml. of 1.42 M lithium borohydride ether solution (5.0 mmols) added. The flask was connected to the reaction system, and swept with dry nitrogen. Carbon dioxide was then generated from 0.985 g. (5 mmols) of barium carbonate during one-half hour, dried by passage through a trap at -80°, and a second trap filled with Drierite, and swept by a slow stream of nitrogen through the borohydride solution during one to one and one-half hours. The borohydride solution was maintained at zero degrees by an external ice bath during the entire period. Volatilized ether was returned to the reaction solution by a cold finger filled with dry ice. A heavy powdery white precipitate formed in the reaction solution. The off-gases were passed through two traps containing saturated barium hydroxide solution. At the end of the reaction period, the reaction flask was surrounded by a hot water bath, and a vigorous nitrogen sweep was continued until all ether had been volatilized and driven through the barium hydroxide solution, and the residue in the reaction flask was dry. The system was then connected to an apparatus for measuring gas by water displacement, and 10 ml. of water was admitted to the dry residue in the reaction flask. Forty ml. of gas was evolved (25°)(1.6 mmols). Addition of 5 ml. of dilute sulfuric acid caused no further gas evolution. The barium carbonate recovered from the barium hydroxide traps weighed 0.401 g. (2.06 mmols). Thus, 2.94 mmols of carbon dioxide had reacted. The dilute sulfuric acid solution of the reaction product was made alkaline to phenolphthalein and evaporated carefully to dryness. Overheating at this point caused extensive

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conversion to oxalate. The dry residue was dissolved in water, and diluted to 100.00 ml. A 20.00 ml. aliquot required 16.8 ml. of 0.052 N potassium permanganate solution. This is equivalent to a total of 2.19 mmols of formic acid (75% on basis of carbon dioxide reacted). The residual formic acid solution was concentrated to 10 ml. volume and added to 10 ml. of water containing 2 g. of S-benzythiuronium chloride. On standing several days in the refrigerator, large flat prisms crystallized which melted at 150-152° (Lit[4]: 151°C.). The original formate solution failed to give a precipitate with calcium chloride, or with 4% alcoholic dimedon solution, showing the absence of oxalate and formaldehyde. It did give a precipitate when treated with a solution of mercuric chloride in dilute hydrochloric acid (test for formic acid).

Another 20.00 ml. aliquot of the formate solution was made acid to methyl red and boiled. The hot solution was then made exactly neutral to methyl red. After phenolphthalein and 25 ml. of glycerine were added, it then required 6.43 ml. of 0.1018 N sodium hydroxide for neutralization. This is equivalent to 3.27 mmols. of boric acid in the entire solution. The solution of barium hydroxide in the absorption traps, after removal of barium carbonate and precipitation of excess barium hydroxide with sulfuric acid, required 15.9 ml. of 0.1018 N sodium hydroxide to neutralize the boric acid present (1.62 mmols).

Reduction of Carbon Dioxide in the Presence of Methanol -- The preceding process was repeated, except that before the carbon dioxide was generated 5.25 ml. of 0.99 M solution of dry methanol in dry ether was added to the hydride solution (4.1 mmols of gas was evolved).

The process was also repeated in the presence of 10.1 mmols of methanol (15 mmols of gas evolved upon addition of the methanol to the hydride solution).

The results of these two runs are listed in Table I.

Reduction of Lithium Formate by Lithium Borohydride -- Pure lithium formate was prepared by the neutralization of 90% formic acid with C.P. lithium carbonate, and dried at 110°. One hundred and four milligrams of this was stirred with 3.85 ml. of 1.15 M borohydride solution and 20 ml. of dry ether for 6 hours at room temperature. Ether was then removed by warming, and the dry residue was hydrolyzed with dilute sulfuric acid. The solution was made alkaline to phenolphthalein, boiled to one-half volume to eliminate volatile organic matter, and then diluted accurately to 50.00 ml. A blank was prepared from 0.104 g. of lithium formate and 50.00 ml. of distilled water. A 10.00 ml. aliquot of the sample solution required 14.1 ml. of permanganate solution to oxidize the formic acid present; a similar aliquot of the blank required 14.7 ml. This difference is within the experimental error of the determination.

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(4) Donlevy, J. Am. Chem. Soc., 5 1004 (1938)

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Table I

Reduction of Carbon Dioxide

Conditions	mmols CO_2 charged	mmols CO_2 reacted	mmols $LiBH_4$	mmols HCOOH (% yield)	mmols B volatile	HCOOH in Rx solid	B in Rx solid	mmols Gas from Rx solid
Normal	5	2.94	4.50	2.19 (75%)	1.62	----	----	-
5 mmol CH_3OH added to BH_4	5	4.03	4.50	2.85 (71%)	2.24	----	----	-
1[illegible] mmol CH_3OH added to BH_4	5	2.20	4.50	0.91 (41%)	3.46	----	----	-
Solid Rx prod filtered off	5	3.84	4.50	----	1.59	3.04 (79%)	2.24	3

This process was repeated with the addition of 10 mmols of methanol to the slurry of lithium formate and lithium borohydride solution. Again there was no reduction of the lithium formate observable within experimental error.

Isolation and Analysis of the Reaction Solid -- The reduction of carbon dioxide to formic acid was carried out as above in a reaction vessel equipped with a sintered glass disk sealed in the bottom leading through a stopcock into a 50 ml. flask provided with an exit tube closed with a stopcock. The reaction vessel was surrounded with a sealed-on glass cup to contain the cooling bath. At the end of the reaction, the stopcocks were opened and the solution filtered into the lower vessel under slight nitrogen pressure. The solid remaining upon the filter disk was washed with two successive 10 ml. portions of dry ether (slight gas evolution owing to traces of water in the ether) and dried in a vigorous current of dry nitrogen. It was then hydrolyzed with dilute sulfuric caid. Three mmols of gas was evolved. The dilute acid solution of the solid was analyzed as above. The formic acid required 59.5 ml. of 0.1016 N permanganate solution, equivalent to 3.04 mmols of formic acid (3.84 mmols of carbon dioxide reacted with 4.5 mmols of borohydride), and the boric acid required 22.0 ml. of 0.1018 N alkali, equivalent to 2.24 mmols. The boric acid in the barium hydroxide absorbers was 1.59 mmols.

The filtrate from this reaction solid was also worked up in the same manner. It contained non-volatile organic matter equivalent to 0.48 mmols of formic acid, and 0.60 mmols of boric acid (some of the borohydride solution seeped into the space between the sintered disk and the first stopcock, which accounts for some of the boron in this solution. On other runs, the amount of boron was considerably less).

Methanol (W. J. Skraba)

Recently considerable difficulty has been experienced in the lithium aluminum hydride reduction of carbon dioxide to methanol. Yields have been in the range of 50% as compared to previous yields as high as 90%. In addition a low boiling contaminant has been found in recent preparations.

Consequently, all of the reagents and solvents used in the process have been purified and blanks have been run to determine the cause of the trouble. A low boiling impurity in the diethyl carbitol has been found which can be removed only by vacuum distillation of the carbitol through a Podbelniak column. Analysis of the commercial $LiAlH_4$ has shown the presence of a small amount of diethyl ether.

Using carefully purified solvents, the yield of pure methanol has been raised to 70%. Further work will be done with purified reducing agent.

Formaldehyde (W. J. Skraba)

The process for the preparation of C^{14}-labeled formaldehyde is being set up for routine production. The results from tracer scale runs are

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as yet incomplete, but indications are that the process is feasible for the routine production of formaldehyde in 60-65% yields.

Acetic Acid (D. N. Hess, O. K. Neville)

Work on the development of a method for the routine production of acetic acid of high specific activity has been naturally resolved into two parts (1) the carbonation of methyl magnesium bromide to produce acetic acid in high yield, and (2) the efficient recovery of anhydrous acetic acid of high purity. The present carbonation procedure is giving satisfactory results, since yields as high as 95% have been obtained. Recovery methods tried so far have not been very satisfactory, and work is continuing along this line.

Carbonation Procedures

Three carbonation methods have been studied. The first method, utilizing a vacuum apparatus, consisted of freezing the carbon dioxide into a pre-formed Grignard solution and allowing the reaction mixture to warm to -80°C. while it was stirred with a magnetic stirrer. Though the results were erratic, the method was fairly convenient. A second procedure which was studied was that of passing dry carbon dioxide over the surface of a Grignard solution contained in two successive flasks.

The present method consists of bubbling nitrogen-diluted carbon dioxide, which is generated by acidification of a weighed portion of barium carbonate and passed through drying traps, through a freshly prepared methyl magnesium bromide solution. The unreacted carbon dioxide is swept into two traps filled with barium hydroxide. The precipitated barium carbonate may be recovered, weighed, and reused.

The reaction vessel is equipped so that the successive manipulations, Grignard formation, carbonation and hydrolysis, can be carried out in the same flask. Upon hydrolysis, some additional carbon dioxide is released which is swept into the traps. The reaction vessel is cooled to -20°C. with an external bath while the carbonation is in progress. In the best run, 95.2% acetic acid was formed (determined by titration with standard base) based on unrecovered carbon dioxide. Usually 90-95% of the carbon dioxide formed is taken up in the reaction.

Recovery of Acetic Acid

The removal of water from acetic acid has proven to be a difficult task. It was decided, therefore, that if the hydrolysis of the carbonated Grignard were carried out with some other medium than water, the problem of preparing anhydrous acetic acid would be simpler. The first technique tried was as follows: (1) after the Grignard reagent was carbonated in diethyl ether, a solution of o-chlorobenzoic acid in diethyl carbitol was added (2) the ether was removed by distillation through a short column (3) the mixture was heated to 130° and swept out with helium to remove the acetic acid. The purpose of the o-chlorobenzoic acid was two-fold: (1) to hydro- [redacted]

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lyze the excess Grignard reagent present at the end of the reaction, and (2) to replace the acetic acid present as the bromomagnesium salt. This acid was chosen, since it is a stronger acid than acetic. This technique has failed to give either a high yield of acetic acid or a pure product, since a considerable amount of the higher boiling diethyl carbitol has always been swept over. Other acids tried under the same conditions have not given good results. These include stearic, lauric and oxalic. A number of similar exchange reactions carried out on sodium acetate have failed to give a satisfactory method of recovery.

Several methods have been studied for the recovery of small amounts of acetic acid from the water-acid hydrolyzed Grignard solution, in order to evaluate the various techniques used in carbonation. Straight distillation has failed if the volume of solution became low during distillation, since appreciable amounts of the hydrolyzing acid (phosphoric or sulfuric) were distilled over and interfered in the titration. Distillation with repeated additions of water was successful in this respect, but was tedious and time consuming; it also led to extreme dilution of the acetic acid.

Continuous extraction with ether failed to remove more than about 75% of the acetic acid from solution unless the solution was saturated with sodium bromide. Under these conditions HBr was extracted, again interfering with the titration of acetic acid.

A method has now been worked out which permits removal of the acetic acid from the hydrolysis mixture without any interfering substances, and without greater dilution of the acetic acid, thus permitting titration of the acetic acid, and consequent evaluation of the carbonation procedures.

The method used is as follows: after hydrolysis of the carbonated Grignard solution with water and phosphoric acid, the ether is removed by distillation through a short column. The reaction vessel is then connected to one arm of the equilibrium distillation apparatus shown in Figure 1. To the other arm is connected a flask containing a measured volume of standardized sodium hydroxide solution. Both flasks are immersed in an oil bath at 125°C. and are allowed to boil for several hours. The cold-finger condenser in the apparatus contains an off-center tip so that by turning the condenser in the ground glass joint the refluxing liquid may be returned to either flask. Ideally, it should be set so that each drop of distillate is divided equally between the two flasks. Since acetic acid and water are distilling from the acid solution and only water from the basic solution, the result is that the acetic acid is gradually distilled from the acid to the basic side of the apparatus. This basic solution may then be back-titrated with standard acid to determine the amount of acetic acid originally present in the hydrolyzed Grignard solution.

Experimental

The carbonation vessel consists of a three-necked 100 ml. flask, to the center joint of which is connected a mercury sealed stirrer. To one of the other joints is connected an inlet tube so constructed that, methyl bromide, nitrogen or carbon dioxide may be passed into the reaction solution.

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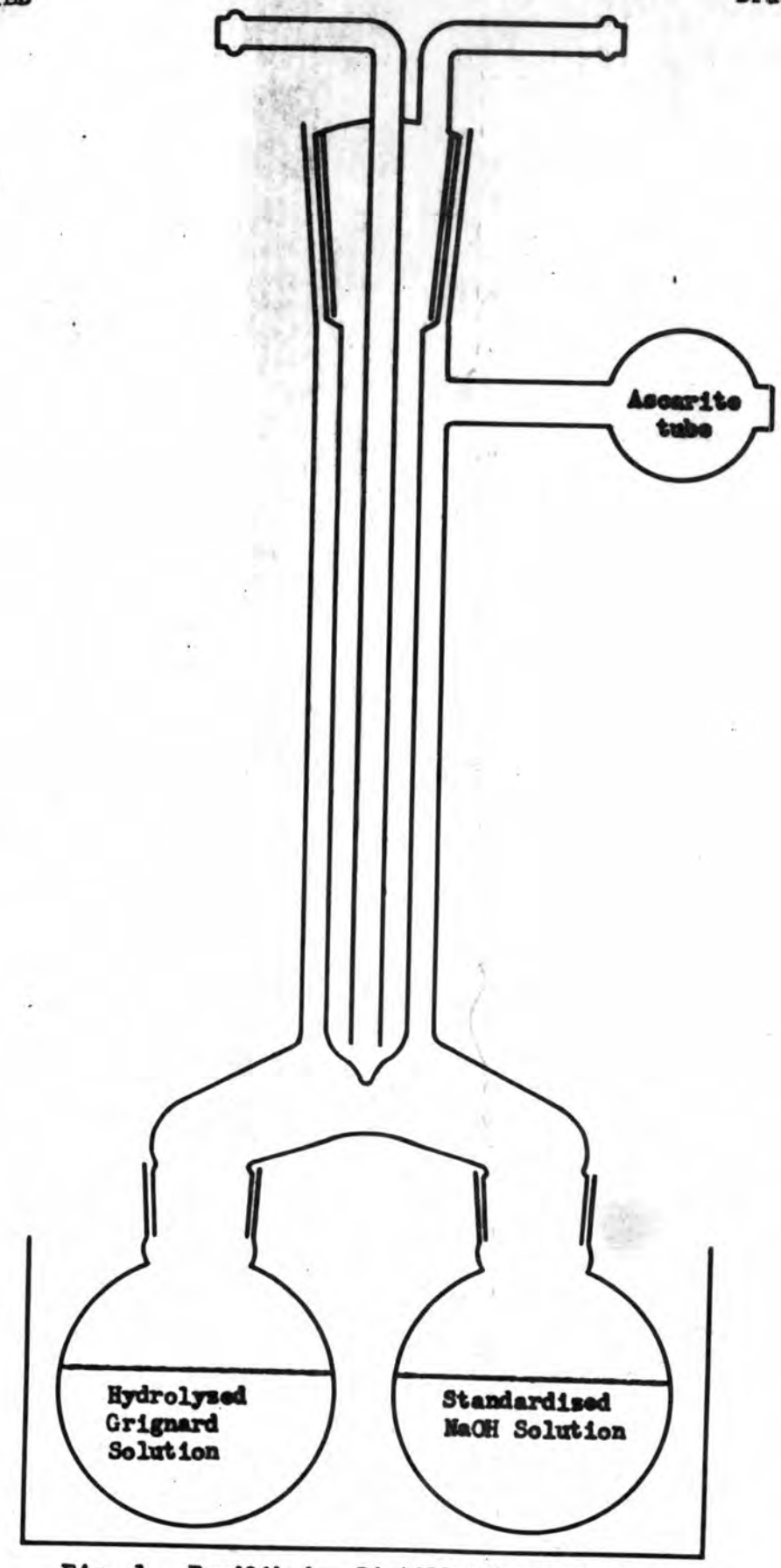

Fig. 1. Equilibrium Distillation Apparatus

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The third joint contains a Dry Ice condenser equipped with a gas outlet and an addition funnel.

The Grignard reagent is prepared by bubbling methyl bromide, from a cylinder into dry ether and magnesium contained in the reaction vessel. The Dry Ice condenser (equipped with a drying tube) is kept in position to condense the ether and methyl bromide.

After the Grignard reaction is complete the carbonation train is connected and the ether solution is cooled to -20°C. The carbon dioxide is generated by dropping 10% perchloric acid onto dry weighed $BaCO_3$. The escaping CO_2 is swept by nitrogen through two drying traps and the inlet tube into the well stirred Grignard solution. The unreacted CO_2 is swept by the nitrogen through the -80°C. condenser, through a -80°C. trap and then into two bubblers containing barium hydroxide where the CO_2 is removed. The slow introduction of CO_2 into the Grignard solution is allowed to proceed for about one hour. One-half hour is allowed to complete the reaction before hydrolysis is effected by passing in dilute phosphoric acid through the addition funnel. Any additional carbon dioxide released is swept into the barium hydroxide traps.

The reaction vessel is then disconnected, sufficient Ag_2CO_3 is added to precipitate the bromide, and the flask is connected to the equilibrium distillation apparatus.

In one experiment the following data were obtained:

15 millimoles .03 M Grignard solution

10.01 millimoles of barium carbonate

9.08 millimoles barium carbonate not recovered

30 millimoles H_3PO_4 in 30 ml. water used for hydrolysis

15 millimoles silver carbonate added to precipitate bromide

8.64 millimoles acetic acid recovered after equilibrium distillation for 14 hours

95.2% yield based on reacted CO_2

Acetylene, Malonic Acid (G. A. Ropp, H. E. Heller)

Equipment is being assembled and preliminary experiments are being carried out in the preparation of acetylene, malonic acid and related compounds.

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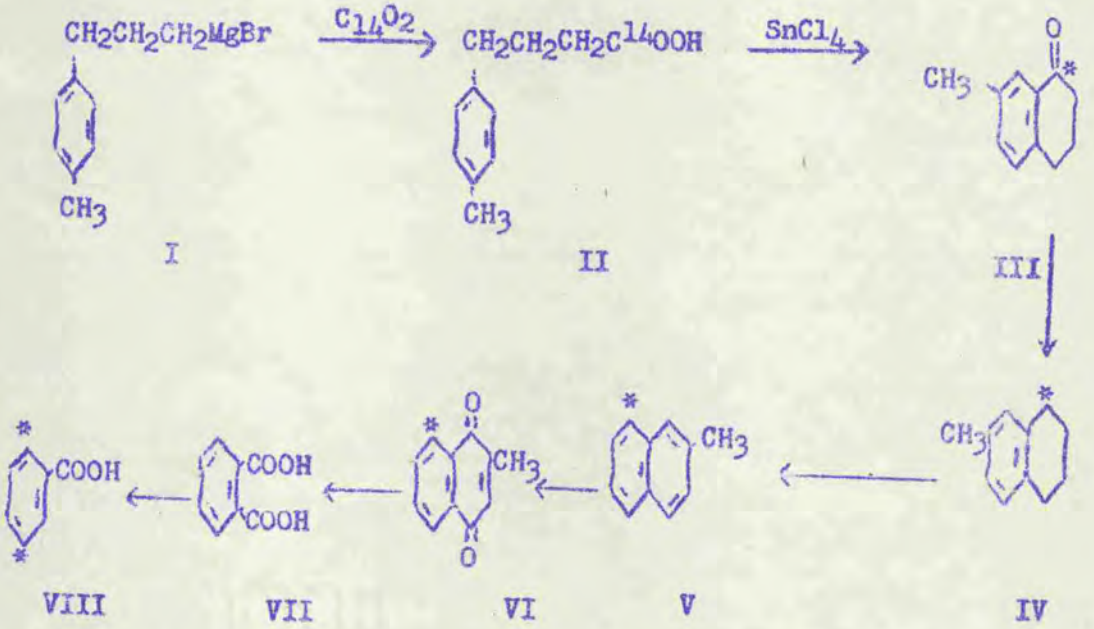
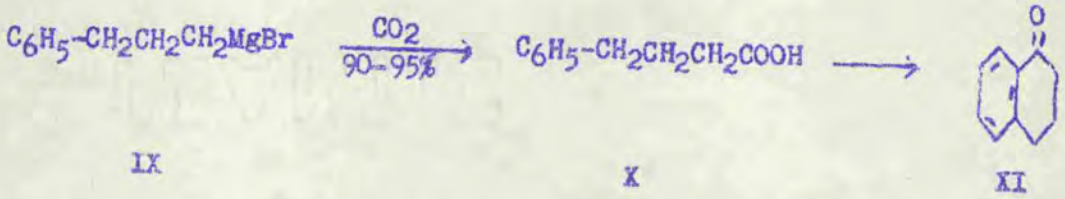
Synthesis of Higher Molecular Weight Compounds Containing C^{14}

"Ring-labeled" Benzoic Acid-C^{14} (C. J. Collins)

The synthesis proposed is as follows:



As a model experiment, the carbonation of γ-phenylpropylmagnesium bromide (IX) has been studied, and phenylbutyric acid (X) has been produced in yields of 90-95%:



The yield reported[5] for this carbonation is 58%. The ring closure of X to yield α-tetralone (XI) has been effected in yields of 85-90%.

The oxidation of β-methylnaphthalene (V) to β-methylnaphthoquinone (VI) and to phthalic acid (VII) has been studied. A considerable improvement in the method reported[6] for VI has been effected, and VI has been prepared by the chromic acid oxidation of V in 70-80% yields. Phthalic acid (VII) has apparently been produced by the permanganate oxidation of VI, and has been converted quantitatively to benzoic acid (VIII). The direct oxidation of V to phthalic acid has not been successful in this laboratory.

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(5) Rupe and Proske, Ber. 43, 1233 (1910)
(6) Rec. trav. chim. 59, 1027 (1930)

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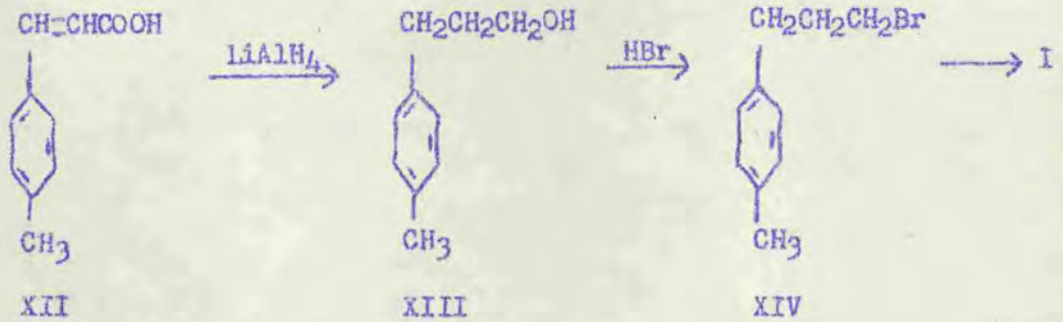
The preparation of p-methylphenylpropylmagnesium bromide (I) from p-methylcinnamic acid (XII) has not yet been effected. The lithium aluminum



hydride reduction of XII has produced an unsaturated alcohol, probably p-methylcinnamyl alcohol, which polymerizes readily on heating, or upon treatment with hydrobromic acid. This is surprising in view of the fact that cinnamic acid yields hydrocinnamyl alcohol on similar treatment[7].

Experimental

Phenylbutyric acid (X) -- To 5.0 cc. of γ-phenylpropylbromide and 0.90 grams magnesium turnings was added 25 cc. ether, and the mixture was warmed with vigorous stirring. The mixture immediately turned cloudy and then dark. After one hour the flask was surrounded with a dry-ice bath and 6.00 grams of barium carbonate was slowly decomposed with dilute perchloric acid, and the evolved CO_2 was swept through the Grignard solution with helium. The exhaust gases were led through a Dry-Ice trap and a barium hydroxide bubbler. Within 10 minutes the CO_2 evolution had stopped. The mixture was stirred and swept an additional 15 minutes, then, cautiously, 50 cc. of an aqueous solution containing 6.0 cc. of H_3PO_4 was added dropwise, continuing the sweep, and removing the dry-ice bath from the flask to prevent freezing out of the water. The ether-H_3PO_4 mixture was forced into a continuous extractor, and a continuous ether extraction was maintained for 5 hours. The ether solution was then concentrated, and to it was added 75 cc. of saturated $NaHCO_3$ solution. The mixture was stirred for 3 hours, then washed with two 5 cc. portions of ether, and added slowly to 25 cc. concentrated HCl in the continuous extractor. Continuous ether extraction and concentration and desiccations yielded 3.281 grams of crude phenylbutyric acid melting 44-47°. One crystallization from benzene-petroleum ether gave white crystals melting 49.6-51.0°.

From the barium hydroxide bubbler, 1.655 grams of barium carbonate was recovered. Yield of phenylbutyric acid, based on carbon dioxide used: 90-95%. Several runs of this type gave yields of 90-96%.

α-Tetralone (XI) -- To 3.00 grams of phenylbutyric acid (X), in 18 cc. dry benzene, was added 4.00 grams of PCl_5, and the mixture was allowed to stand 4 days. The mixture was then cooled in an ice-bath, and 3.20 cc. $SnCl_4$ in 7 cc. benzene was added. The color was yellow, and in 5-10 minutes

(7) Nystrom and Brown, J. Am. Chem. Soc., 69, 2548 (1947).

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a nearly white precipitate occurred. The mixture was stirred 1¼ hours, cooled, and to it was added 30 cc. of 6 N hydrochloric acid. The layers were separated, the benzene layer was concentrated, and to the concentrate was added 4.0 grams hydroxylamine hydrochloride, 15 cc. ethanol, and 15 cc. pyridine. Yield of oxime = 2.45 grams, or 83.5% of theory.

Lithium Aluminum Hydride Reduction of p-Methylcinnamic Acid (XII) -- Into an extraction thimble was weighed 10.0 grams p-methylcinnamic acid. An ether solution consisting of 400 cc. ether and 5.0 grams $LiAlH_4$ was warmed and allowed to reflux so that the ether flowed over the acid (XII) and back into the flask. After 45 minutes, 20 cc. of water was added cautiously, then 20 cc. of an aqueous solution containing 20 cc. H_2SO_4. The ether solution was separated, concentrated, washed with $NaHCO_3$ solution and water, then distilled under high vacuum, yielding 8.5 grams of product (85% of theory) melting at 28-31°. This material is believed to be p-methylcinnamyl alcohol, $CH_3C_6H_5CH = CHCH_2OH$, since considerable difficulty was experienced with polymerization. In addition a CCl_4 solution decolorized bromine in CCl_4, without apparent evolution of HBr.

2-Methyl-1,4-naphthoquinone (VI) -- The procedure of Sah[8] was followed with 5.00 grams of β-methylnaphthalene (V), except that continuous ether extraction was used in the isolation of the product after neutralization of the acetic acid with sodium bicarbonate solution. Yields of 65-75% were obtained.

(?) Phthalic Acid (VII) by Oxidation of 2-Methyl-1,4-Naphthoquinone -- To 1.31 grams of 2-methyl-1,4-naphthoquinone (VI) was added 20 cc. of water containing 1 gram sodium hydroxide. Next, 8.5 grams $KMnO_4$ in 75 cc. of water was added over a period of 15-20 minutes. During this addition the suspension was boiled and stirred vigorously. After boiling and stirring an additional 45 minutes the mixture was filtered through a talc pad, and the solid precipitate was suspended in dilute NaOH and filtered once more. The combined filtrates were acidified with concentrated HCl, and subjected to a continuous ether extraction for 3 hours. The ether was concentrated yielding a pink liquid possessing the odor of acetic acid. Desiccation yielded 1.28 grams of a solid, organic material. Purification and identification of this material are now in progress.

Benzoic Acid (VIII) from Phthalic Acid -- A sealed, evacuated tube containing 200 milligrams phthalic acid and 4.0 cc. distilled water was heated in a bomb containing water to 325° for 12 hours. The water white solution was concentrated and desiccated yielding a quantitative amount of benzoic acid melting 119-120°.[9]

Styrene (O. K. Neville, K. Wilzbach (on loan from Argonne National Laboratory))

Work has been directed toward the development of a method for the preparation of C^{14}-labeled styrene of fairly high specific activity. The immediate use of the styrene will be the preparation of polystyrene films to aid in the standardization of counting methods.

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(8) Sah, Rec. trav. chim. 59, 1027 (1930).
(9) Sultanov, J. Gen. Chem. (USSR) 16, 1835-44 (1946); c.a. 41, 6223-6224 (1947)

[redacted]

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Of several possible reaction schemes having CO_2 as the starting material, the sequence, as represented by the following equations, was first chosen for trial.

$$C_6H_5CH_2MgCl + \overset{*}{C}O_2 \xrightarrow{(H^+)} C_6H_5CH_2\overset{*}{C}OOH$$

$$C_6H_5CH_2\overset{*}{C}OOH + LiAlH_4 \longrightarrow C_6H_5CH_2\overset{*}{C}H_2OH$$

$$C_6H_5CH_2\overset{*}{C}H_2OH \xrightarrow{(OH^-)} C_6H_5CH{=}\overset{*}{C}H_2 + H_2O$$

Since it was recognized that the step likely to be most difficult was the first, involving the carbonation of a benzyl Grignard reagent, this reaction was studied first. A series of carbonations carried out at -80°C. demonstrated that Grignard addition to the acid was so rapid even at this low temperature that very low yields of acid and very high amounts of ketone and carbinol were formed. In no case was the yield of acid above fifty percent. Although other means of carrying out the carbonation might have been tried, it was felt that it was best to abandon this reaction at this time.

A second reaction scheme which has been considered is the following:

(1) $C_6H_5MgBr + CO_2 \xrightarrow{+(H^+} C_6H_5\overset{*}{C}OOH$

(2) $C_6H_5\overset{*}{C}OOH + ClCOCOCl \longrightarrow C_6H_5COCl + 2CO + HCl$

(3) $C_6H_5\overset{*}{C}OCl + H_2 \xrightarrow{Pd(BaSO_4)} C_6H_5\overset{*}{C}HO$

(4) $C_6H_5\overset{*}{C}HO + CH_2(COOH)_2 \longrightarrow C_6H_5\overset{*}{C}H{=}CHCOOH$

(5) $C_6H_5CH{=}CHCOOH \xrightarrow{\Delta, Quinoline} C_6H_5\overset{*}{C}H{=}CH_2$

The carbonation of the phenyl Grignard (equation 1) is considerably less difficult, and has already been carried out in 78% yield. This can probably be improved. The Rosenmund reduction (equation 3) of benzoyl chloride to benzaldehyde has been accomplished in 95% yield using commerical benzoyl chloride. The overall conversion of benzoic acid to benzaldehyde (steps 2,3) has not yet given desirable yields. The condensation of benzaldehyde with malonic acid (equation 4) (equation 5) and the decarboxylation have given excellent results.

Experimental

Rosenmund Reduction of Benzoyl Chloride -- Two and three-tenths grams of benzoyl chloride was placed in a 25 ml. flask having a ground glass joint. Ten ml. of dry xylene, 0.3 g. of Pd-$BaSO_4$ catalyst and 0.03 ml. of sulfur-quinoline inhibitor (made from synthetic quinoline) were added. Flask was equipped with a head containing an inlet tube and a condenser (with an outlet into a solution of NaOH) and was mounted on a shaker.

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Air in flask was displaced with hydrogen at a rate of 2 bubbles per second, contents heated to near boiling and shaking was started. HCl was evolved at such a rate that ca. 1 ml. of 0.1191 N NaOH was neutralized each minute ($2\frac{1}{2}$ hours total).

After being cooled the mixture was filtered and a solution of 4 g. $Na_2S_2O_5$ in 6 ml. H_2O was added to the filtrate. The mixture was shaken vigorously for a while and then filtered. The bisulfite addition compound dried in vac. at room temperature, weighed 3.4-3.6 g.

The bisulfite addition compound and the aqueous bisulfite solution from which it was precipitated were placed in 100 ml. 3 neck flask with stirrer, condenser, and dropping tube. Twenty-five ml. of H_2O was added and the mixture was heated to boiling. Seven ml. of concentrated H_2SO_4 was added dropwise with stirring and the mixture was refluxed for another 10 minutes. After cooling the ϕCHO was extracted with ether. The ether extract was washed with water, $NaHCO_3$ solution, water and then dried over K_2CO_3. The ether was distilled off leaving 1.6 g. ϕCHO.

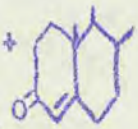
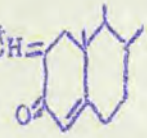
Cinnamic Acid -- To the benzaldehyde were added 4 ml. absolute ethanol, C_2H_5OH, 0.4 pyridine and 1.8 g. (10% excess) of malonic acid. The mixture was warmed with alkali to hydrolyze a little ethyl cinnamate that is formed, and the cinnamic acid was precipitated with HCl yield 1.8 g.

2-Hydroxymethylene-4,5-cholestenone (J. G. Burr)

Discussion

A projected use of labeled formic acid is the preparation of 2-hydroxymethylene-4,5-cholestenone-4 labeled at the hydroxymethylene carbon atom. This compound is of great interest to the National Cancer Institute, because it offers a tool by which to study the metabolism of colchicine and colchicine analogs which have shown great promise in the field of cancer therapy. The sequence of reactions proposed here is:

$$H\overset{*}{C}OONa + (C_2H_5)_2SO_4 \longrightarrow H\overset{*}{C}OOC_2H_5 + C_2H_5SO_4H$$

$H\overset{*}{C}OOC_2H_5$ +  ⟶ $HO\overset{*}{C}H=$ 

Experimental

The Preparation of 2-Hydroxymethylene-4,5-cholestenone-3 -- A solution of 1 g. of cholestenone (2 mmols, m.p. 80-81°) in 10 ml. of dry benzene was added to the dry sodium methoxide prepared from 0.5 g. sodium, and then a solution of 3 ml. of purified ethyl formate (b.p. 54-55°) in 10 ml. of benzene was added. The solution became deep red, and a gas was evolved. The solution was allowed to stand overnight in a nitrogen atmosphere. On addition of water to this solution, a heavy yellow precipitate formed, which was insoluble in benzene, water, or dilute sodium hydroxide. This is presumably

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the sodium salt of the enol. This solid was suspended in water and acidified with dilute hydrochloric acid. The gummy solid thus formed was extracted with ether, in which it was readily soluble. The ether solution was dried and evaporated. The residual deep orange gum could not be crystallized from a variety of solvents and solvent pairs. It was dissolved in dry benzene and absorbed on an alumina column. The results of eluation were: (1) benzene (yellowish crystals, small amount (upon crystallization this proved to be cholestenone)), (2) benzene-alcohol (2/1) (orange oil, small amount), (3) alcohol (yellow oil, trace), (4) glacial acetic acid (deep orange gum, largest fraction).

It was thought desirable to develop another condensing agent for this reaction. One of those tried was lithium aluminum hydride. The ketone selected for trial was 1-keto-1,2,3,4-tetrahydrophenanthrene, a sample of whose hydroxymethylene derivative was available. One g. of this was added to a suspension of lithium aluminum hydride in 25 ml. of benzene containing 3 ml. of ethyl formate. A vigorous reaction ensued, with heat evolution and foaming, and a turbid yellow solution resulted. Upon hydrolysis, after it had stood three hours, no alkali soluble matter was obtained; and from the neutral benzene-soluble material, a portion of unreacted ketone was isolated. Curiously enough, the water solutions obtained from the work-up of this reaction contained appreciable amounts of acetaldehyde, identified as the dimedon derivative, which melted at 143-144° unchanged by admixture with an authentic sample. No mechanism has been advanced to account for the formation of this substance.

The above reaction was repeated, using 0.5 g. of lithium hydride as the condensing agent. A small yield (circa 20%) of the desired enol was obtained.

The reaction was again repeated using sodium hydride as the condensing agent. This time a quantitative yield of the desired enol was obtained. This condensing agent has been employed in the condensation of ethyl formate with cholestenone with results which are as yet inconclusive but which appear excellent. Less than 10% of the cholestenone remains unreacted, and the enol has been isolated as the sodium salt in excellent yield.

New Equipment

Hershberg Hydrogenation Apparatus (A. R. Jones)

A modified Hershberg hydrogenation apparatus has been constructed. It consists of a manifold connecting three inverted mercury-filled burettes, a manometer and a standard taper joint for attaching the reaction flasks.

The compound to be hydrogenated, catalyst, solvent and a magnetic stirring bar are placed in an Erlenmeyer flask and the latter connected to the manifold. The system is then evacuated and filled with hydrogen several times. The appropriate burette is also filled and the system burette-manometer-reaction flask is equilibrated to atmospheric pressure and isolated. Stirring is begun and the rate and amount of hydrogen uptake is periodically determined.

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V. Applied Nuclear Chemistry

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Separation of Zirconium and Hafnium by Solvent Extraction Using TTA: (J.P. McBride, J.A. Swartout)

Introduction

A study of the separation of Zr and Hf by extraction into a benzene solution of TTA (thenoyltrifluoroacetone) has been resumed. Preliminary experiments are being conducted to determine the rate of extraction of the chelated metals and the effect of hydrolysis in the aqueous phase on the extraction phenomenon. In the extractions from 1 N acid using tracer concentrations of metals and 0.05 M TTA, reported below, extraction is more than 99% complete for both Zr and Hf within 30 minutes. However, equilibrium is not established until approximately 45 minutes to 1 hour in the case of Zr and 2 hours in the case of Hf.

Extraction of Zirconium

Zirconium tracer in 0.5% oxalic acid obtained from the isotope section was treated with $KMnO_4$ in HNO_3 and extracted with TTA into benzene. After the benzene solution of the chelate was washed twice with 0.5 M HCl to remove Cb, the chelated metal was stripped into 6 M HCl and fumed repeatedly with concentrated $HClO_4$. The final solution of the tracer was made ca. 10 M $HClO_4$. Before a series of extractions was made, the tracer solution was diluted 1 to 10 and aliquots were equilibrated for various times with equal volumes of 0.05 M TTA in benzene which had been previously equilibrated several hours with 0.1 M $HClO_4$. After equilibration the phases were analyzed for Zr by preparing counting samples in the usual manner and counting first through a 34.6 mg/cm^2 Al absorber and then through a 232 mg absorber, the difference in the counts being proportional to the total Zr. Table IA lists the results obtained for a series of extractions run immediately after dilution while Table IB lists extractions made from the same diluted tracer solution which had been allowed to stand for three days. In the final columns of each table after equilibrium has apparently been reached are listed equilibrium constants calculated for the reaction

$$Zr(OH)^{+3}_{aq} + 4\,\underset{B}{HT} \rightleftharpoons ZrT_{4_B} + 3H^+_{aq} + H_2O_{aq}$$

(Cf. Connick and McVey, UCRL-101), where HT refers to the enol form of the TTA and the subscripts refer to the phases in which the species appear.

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The constants calculated for the extractions run immediately after diluting the tracer are slightly higher than the $2x10^{-7}$ reported by Broido, MonN-311, ORNL-65, but are lower by a factor of ca. 20 than the value of $7.6x10^{8}$ calculated by Connick and McVey, UCRL-101. The discrepancy may be due to the fact that the tracer concentration in the aqueous phase was very low (100 c/m/ml) where the effects of counting errors and slight impurities would be extremely large. It is to be noted that the constants calculated for extractions made three days later are lower by a factor of 2 and are in even closer agreement with Broido's data. Additional experiments will be performed using concentrations such that constants and hydrolysis effects may be more accurately determined.

Extraction of Hafnium

Hf^{181} tracer was prepared by pile bombardment of high purity (99.8%) HfO_2, which was then dissolved in HNO_3-Hf, fumed five times with $HClO_4$ (twice to dryness), and finally made ca. 10 M in $HClO_4$. This solution was diluted to 0.97 M and several aliquots were agitated with equal volumes of 0.05 M TTA in benzene which had previously been equilibrated several hours with 0.1 M $HClO_4$. After equilibration, counting samples were prepared from each phase and counted without absorber in a standard beta chamber. The results are listed below in Table II. The last column lists equilibrium constants where equilibrium has apparently been established calculated assuming, as above, a third power acid and fourth power TTA dependence.

TABLE II

Extraction of Hafnium with TTA in Benzene

Conditions: 0.97 M $HClO_4$

0.05 M TTA in benzene

Time of Standing before mixing; in minutes	Equilibration Time; in minutes	D.R. $\frac{o}{a}$	$K_{Hf} \times 10^{-7}$
10	15	24.3	--
15	30	125	--
17	45	121	--
18	60	120	--
20	90	136	--
30	120	188	2.7
47	150	200	2.9
130	(18 hrs.)	191	2.8
130	(18 hrs.)	188	2.7

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[redacted]

TABLE IA

Extraction of Zirconium with TTA in Benzene

Conditions: 0.92 M $HClO_4$
0.05 M TTA in benzene

Time of Standing of Aqueous Solution before Mixing; in Minutes	Equilibration Time; in Minutes	D.R. $\frac{o}{a}$	$K_{Zr} x10^{-7}$
10	11	28.6	---
12	20	157	---
15	30	183	---
74	60	336	4.4
67	117	217	2.9
82	(19 hrs.)	278	3.7
82	(19 hrs.)	244	3.2

TABLE IB

Extraction of Zirconium with TTA in Benzene

Conditions: 0.92 M $HClO_4$
0.05 M TTA in benzene
Aqueous solution allowed to stand 3 days before extraction

Equilibration Time; in Minutes	D.R. $\frac{o}{a}$	$K_{Zr} x10^{-7}$
15	83	---
30	120	1.6
45	143	1.9
61	150	2.0
122	120	1.6
(67 hrs.)	88	1.2

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The equilibrium constants calculated for the above equilibria are higher by a factor of 4 than Broido's value of 7×10^6 (ORNL-65) but are in substantial agreement with the 3.3×10^7 calculated from the data of Huffman and Beaufait, UCRL-194, for the extraction of μg quantities of Hf from 2 M $HClO_4$, assuming a third power H^+ dependence. An equilibrium constant calculated assuming a second rather than fourth power TTA dependence (7×10^4) would be considerably higher than the 4.9×10^3 given in the September KAPL report in which a second power TTA dependence for Hf extraction from 1 M HNO_3 is postulated.

A Study of the Electrolytic Behavior of Aqueous Hafnium and Zirconium Solutions: (J. C. Griess, J. A. Swartout)

This investigation has been completed and will be issued as a project report in the near future. The investigation consisted of a polarographic study of the individual metals in various solutions and an attempt at plating the metals on mercury and copper electrodes. While it was possible to obtain zirconium polarographic curves in chloride and perchlorate solutions, it was not possible to plate sizable amounts of the metal on either a mercury or copper cathode. Hafnium was not reduced at the dropping mercury electrode nor was it plated from aqueous solutions. In general the results, although of a negative nature, confirm the results reported in the literature.

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Recovery of Zirconium and Columbium from Separations Process Wastes: (W.H. Baldwin, R. Wacker and A.W. Smith)

Summary and Conclusions:

Tests were made to recover Zr-Cb from Redox process wastes by adsorption on silica gel and elution with 5% oxalic acid. Gross gamma counts indicate a separation but more tests are needed to establish the degree of separation of Zr-Cb from the other fission products.

Introduction:-

A need has been expressed for large quantities of radioactive materials (gamma emitters) with high specific activity, high degree of purity, and a half-life of the order of months. The fission products zirconium and columbium can fill the requirements and possess the additional advantage of being present in waste solutions from the processing of fissionable materials; i.e., no additional neutrons will be required to prepare zirconium and columbium.

Sources:-

The Redox process will have relatively large quantities of Zr-Cb as by-products. The plant dissolver solution may be considered one valuable source, that is the Zr-Cb might be removed from the dissolver solution before processing for Pu. The advantages that would result are control of the composition of the starting solution for the separation of Zr-Cb and additional decontamination that would lighten the burden on the Redox process itself.

An alternate source in the Redox plant is the waste stream from the solvent extraction of U and Pu. The composition of this solution will have been determined by the Redox process but the treatment of the solution will not be limited by the requirement for further processing after the Zr-Cb process.

Potential sources of Zr-Cb exist in other waste solutions. These include uranium containing wastes from the present plutonium process and waste solutions from the solvent extraction of enriched uranium from new piles.

The testing thus far has been limited to Redox plant waste solutions (Pilot Plant solution 1AW) of current composition that will be reported below. It is planned to test dissolver solutions later.

Redox Plant Waste Composition:-

The aqueous waste (rich in Zr-Cb) from the Redox process that is currently being tested has the composition; 0.8 M HNO_3, 0.74 M $Al(NO_3)_3$, 0.05 M $Na_2Cr_2O_7$, app. 0.001 M uranyl nitrate, 0.1% of the plutonium entering, most of the fission products, and is saturated with hexone[1].

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1 ANL SL-45, August 13, 1948.

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The pilot plant at X-10 is producing wastes of this composition and samples have been obtained for laboratory testing. The pilot plant operation and chemical development sections of the Technical Division expect that changes in the composition may take the following directions:

(a) less HNO_3 down to 0.2 M deficient (pH app. 2)
(b) higher $Al(NO_3)_3$ (1.5 M)
(c) another oxidizing agent (bromate)[2]

Methods Applicable to the Recovery of Zr-Cb:

Precipitation - The recovery of active Zr-Cb from solutions has been examined on the project for analytical estimation of these elements and for specific decontamination of various materials. Among the precipitates that have been studied are the phosphate[3], phenylarsonate[4], barium fluozirconate[5], ferric hydroxide[6] and manganese dioxide[7]. In addition the oxalate has been used to complex Zr and Cb in solution while precipitations were made to remove contaminating activities[4]. Zr-Cb and Ru activities have been removed (greater than 90%) from an $Al(NO_3)_3$ solution (0.1 to 0.5 M) at pH 2-3 by precipitation of 0.01% Fe as hydroxide and 0.01% Mn as dioxide[8].

Solvent Extraction - Carrier-free tracers have been prepared by the extraction into organic solvents, of organic complexes of the elements. Zr and Cb have been extracted into benzene as cupferrides[9]. Zr has been isolated by extraction of the TTA complex into benzene[10].

Ion Exchange and Adsorption - At the present time curie quantities of Zr-Cb tracer are prepared by the isotope production group (from dissolved slugs) using amberlite resin IR 100 H[11].

Kohn and Swartout[12] reported the adsorption of Zr-Cb from process plant wastes with charcoal. This method has been examined more completely since that time and is reported herein.

Experimental - Equilibrium studies (without agitation, Table I) were made using several materials that were thought to be potential adsorbers. Charcoal (cocoanut and Norit A) that adsorbed highly also caused reduction of dichromate with the formation of gas bubbles. Silica gel was comparable

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2 Personal communications from F.R. Bruce and D.G. Reid
3 PPR 9B 8.8.1
4 PPR 9B 8.8.2
5 PPR 9B 8.8.4
6 PPR 9B 8.8.8
7 PPR 9B 8.9.3 and PPR 9B 8.9.4
8 Personal communication R.E. Blanco
9 PPR 9B 8.8.9
10 ORNL-105
11 Private communication I.B. Whitney
12 ORNL-176, p. 23

[redacted]

[redacted]

to charcoal in absorption capacity but did not reduce dichromate and did not cause bubbles to form and was selected for further testing.

Samples of silica gel were agitated with a synthetic solution containing some process solution as spike at 26 ±. 5° C. Equilibrium was essentially reached after 20 hours (Table II). The silica gel was washed with water then equilibrated with various eluting agents to remove the gross gamma activity. The eluting agents tested (Table II) show 5% oxalic acid to be preferable. The effect of temperature has not been clearly shown and must be examined further.

Tests were made with a small column (1x8 cm.) packed with silica gel (20-60 mesh) to explore the feasibility of column operation (Table III). A large proportion of the gross gamma activity was adsorbed by the column, retained through washing and was eluted by hot 5% oxalic acid. Tests are being made to determine the distribution of Zr and Cb through these steps.

Program:

In addition to the testing of temperature effects and the distribution of Zr-Cb it is planned to test adsorption at lower acidities by neutralizing feed solutions of the present composition. Some thought will be given to the use of dissolver solutions directly since the Zr-Cb might well be removed before solvent extraction.

[redacted]

TABLE I

[redacted]

EQUILIBRATION STUDIES

Drawing # 6612

0.5 g adsorbent placed in 5 ml solution (0.8M HNO_3, 0.74M $Al(NO_3)_3$, 0.05M $Na_2Cr_2O_7$ spiked with
(1) Zr-Cb tracer
(2) 1AW from pilot plant run 4R

Allowed to stand at room temperature without agitation.

	Adsorbent	Gross Gamma Activity (%) Left in Solution — Exposure (Hours) 20(1)	20(2)	44(1)	92(1)	116(1)	140(1)	Remarks
1.	Bone Charcoal	93		84		87	86	Gas bubbles liberated on mixing
2.	Bone Charcoal	94		89		85	86	Gas bubbles liberated on mixing
3.	Animal Charcoal	94		87		88	91	Gas bubbles liberated on mixing
4.	Animal Charcoal	96		91		88	91	Gas bubbles liberated on mixing
5.	Cocoanut Charcoal	28		24		19	18	Reduced dichromate; Gas bubbles liberated on mixing
6.	Cocoanut Charcoal	22		11		8	9	Reduced dichromate; Gas bubbles liberated on mixing
7.	Cocoanut Charcoal		20					Reduced dichromate; Gas bubbles liberated on mixing
8.	Cocoanut Charcoal		19					Reduced dichromate; Gas bubbles liberated on mixing
9.	Norit A		7					Reduced dichromate; Gas bubbles liberated on mixing
10.	Norit A		7					Reduced dichromate; Gas bubbles liberated on mixing
11.	Alumina	42			27	12		
12.	Alumina	40			27	12		
13.	Alumina		57					
14.	Alumina		63					
15.	Silica gel		24					
16.	Silica gel		20					
17.	IR100H		34					
18.	IR100H		35					
19.	Dowex 50		85					

(1) Zr-Cb tracer used to spike synthetic feed
(2) Pilot plant waste 1AW run 4R used to spike synthetic feed

[redacted]

TABLE 2

Drawing # 6613

[redacted]

Equilibration Studies (Samples Agitated at 26° C.)

10 ml. solution, wt. of silica gel as indicated

Silica gel g.	Aqueous Solution	Gross Gamma Activity (%) in Solution — Exposure (Hours) 1	3	4	5	7	16	22	37	48
0.542	Synthetic Feed* Spiked with 1AW Run 4R	63		43		37	28			23
0.576	Synthetic Feed* Spiked with 1AW Run 4R	62		42		36	27			23
0.570	Synthetic Feed* Spiked with 1AW Run 4R									22
0.636	Synthetic Feed* Spiked with 1AW Run 4R									21
0.505	Synthetic Feed* Spiked with 1AW Run 4R									22
0.508	Synthetic Feed* Spiked with 1AW Run 4R									22
0.524	Synthetic Feed* Spiked with 1AW Run 4R						29	26		24
1.116	Synthetic Feed* Spiked with 1AW Run 4R						22	21		19
	Activity on Silica Gel was Eluted									
0.542	20% HCl						34	34	35	35
0.576	20% HCl						32	32	33	33
0.570	1% $(NH_4)_2SiF_6$						41			
0.626	1% $(NH_4)_2SiF_6$						43	43		
0.505	5% Oxalic at 70°C.		82	93						
0.508	5% Oxalic at 70°C.				96					
0.524	5% $(NH_4)_2SiF_6$						49	49		
1.116	5% $(NH_4)_2SiF_6$						42	42		
0.563	5% Oxalic							92		92
0.716	5% Oxalic							90		91

* 0.8M HNO_3, 0.74M $Al(NO_3)_3$ 0.05M $Na_2Cr_2O_7$

[redacted]

TABLE 3

[redacted]

Column Studies

Drawing # 6614

Column: 11 mm i.e., packed 80 mm.

Feed solutions: (A) and (B) were synthetic solutions (0.8M HNO_3, 0.74M $Al(NO_3)_3$, 0.05M $Na_2Cr_2O_4$) spiked with 1AW from run 4R (Pilot Plant), (C) 1AW from run 4R (Pilot Plant)

Silica gel: 69% retained on No. 20 screen, 19% on No. 30, 8% on No. 40, and 4% on No. 60

	Column packing	Feed	Percent (of total Gamma Count Added) found in the effluent — ml Effluent employed: 5	10	15	20	25	30	35	40	Aqueous Wash Comp.	Vol. ml.	Activity (%)	Stripping Solution Comp.	Vol. ml.	Act. %	
12	Cocoanut charcoal	A	0.8	3.3	8.2	11	14.6				H_2O	29	30.8	0.5% oxalic	22	6.9	
	Total						37.9						68.7			75.6	
14	Silica Gel	B	1.8	4.6	6.6	7.8	8.2				3% H_2SO_3	50	30.4	0.5% oxalic	65	25.5	
	Total						29.0						59.4			84.9	
16	Silica Gel	B					14.9				3% H_2SO_3	27	23.3	1M K oxalate	24	23	
	Total						14.9						38.2	Heated 0.3M K oxalate, 3M HCl	26	36	
19	Silica Gel (from 16)	C					45%				H_2O	24	11.5			97.2	
	Total						45						56.5	5% oxalic (70°C)	50	43	Silica retained 0.3%
20	Silica Gel (from 19) Adsorbed at 70°C	B	0.23	1.0	1.6	1.7	1.8	1.9	2.4		H_2O	29	4.7			99.5	
	Total								10.6				15.3	5% oxalic (70°C)	26	91	
21	Silica Gel (from 20)	B	0.4	1.3	1.6	1.9	2.1	2.0	2.0	1.9	H_2O	57	4.8			106.3	
	Total									13.3			18.1	5% oxalic (70°C)	28	86.9	
																105	

[redacted]

[redacted]

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

I. Introduction and Summary:

The development of a process for the separation of the fission rare earths (Y, Eu and Sm) by ion exchange (ORNL-176) has been continued. Techniques have been developed whereby distribution data can be readily reproduced within 10%. Data are presented herein for the distribution of Eu between resin and buffer at 26° C. It is planned to expand this data to include Eu, Sm and Y over a wide range of temperatures and pH's.

II. Ion Exchange

A. Distribution data

Distribution coefficients for Eu were run at 26° C using unscreened Dowex 50 resin and 5% citrate. Tests were made which showed that distribution coefficients were the same using oven dried or air dried resin. A second set of distribution tests was made to determine if results could be reproduced. Results of the first test are shown in Table I and Figure I. Results of the second test are shown in Table II and Figure I.

To prevent great change in pH of the buffer upon equilibration with resin, the resin was pretreated as follows: cations were removed with 3 M HCl, HCl and resin fines removed by back washing with H_2O, resin converted to ammonium form with NH_4Cl, excess NH_4Cl washed out and resin equilibrated with pH 3.03 citrate (0.238M), excess citrate washed out with water, and resin air dried 60 hrs. at 25° C. Resin dried at 107° C for 20 hrs. was also used in distribution tests.

The equilibrium tests were run as follows: in a 25 ml. mixing cylinder were placed a weighed amount of resin (dried at 107° C for 20 hrs.) and 15 ml. 0.238 M citrate containing Eu tracer. The cylinder was placed on the mixing apparatus and equilibrated at a temperature of 26 ± 0.5° C for 16 to 64 hrs. After equilibration 2 ml. of buffer were used to measure pH and activity. The remaining 13 ml. were used for a second equilibration. The resin was stripped to obtain a material balance by adding a known amount of NH_4OH to obtain a pH of 7 to 8 and equilibrating the mixture 16 hrs.

The beta activity was measured by plating aliquots on platinum plates, flaming to destroy citrate, and counting at 10% geometry.

B. Particle size determination

In order to determine the resin particle diameter of the Dowex 50 used, photographs were taken of air dried and oven dried resin. The dry particles were measured and the size distribution is shown in Figures II and III.

[redacted]

[redacted]

TABLE I

Distribution Coefficients* 26° C

Solution: 15.1 ml .236 M citrate, $2x10^{-7}$ M Eu**, pH as tabulated, NH_4OH used to adjust pH;
Resin : Dowex 50, ammonium form, 10-75 microns, oven dried

pH=	2.95		3.00		3.08		3.22		2.87		2.98	
	1	2	1	2	1	2	1	2	1	2	1	2
Wt. resin (grams)	0.514	0.562	0.363	0.410	0.896	0.944	3.115	3.295	0.176	0.204	0.474	0.485
Original buffer pH	3.05	3.05	3.05	3.05	-	-	3.35	3.35	2.90	2.90	3.00	3.00
pH after 1st Equil.	2.96	2.95	3.00	3.00	3.08	3.08	3.22	3.24	2.87	2.87	2.98	2.98
pH after 2nd Equil.	2.96	2.96	3.00	3.00	3.08	3.08	3.22	3.22	2.86	2.87	2.96	2.98
Eu K_D-1st Equil.	45.7	41.9	31.6	33.3	16.7	16.3	2.36	2.35	70.0	74.2	28.9	32.0
Eu K_D-2nd Equil.	41.2	44.4	34.2	31.6	17.2	15.6	2.33	2.27	75.3	75.2	33.1	31.5
Eu K_D-Resin strip	39.8	47.2	34.6	33.8	17.3	15.8	3.05	3.16	67.3	61.0	29.2	29.0
Ave.=	42.2	44.4	33.5	32.9	17.1	15.9	2.6	2.6	70.9	70.1	30.4	30.8
% Mat'l. Balance	99.3	107	101	103	100	100	110	113	95	90.5	94.2	96.2
Ave. Eu K_D	43.3		33.2		16.5		2.6		70.5		30.6	

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

** Beta activity in buffer (original) = 79000 c/m/ml - 10% geometry - no absorber

[redacted]

[redacted]

TABLE II

Distribution Coefficients* 26° C

Solution: 15 ml. 0.238M Citrate, $2x10^{-7}$ M Eu**, pH as tabulated, NH_4OH used to adjust pH
Resin : Dowex 50, ammonium form, 10-75 microns, oven dried

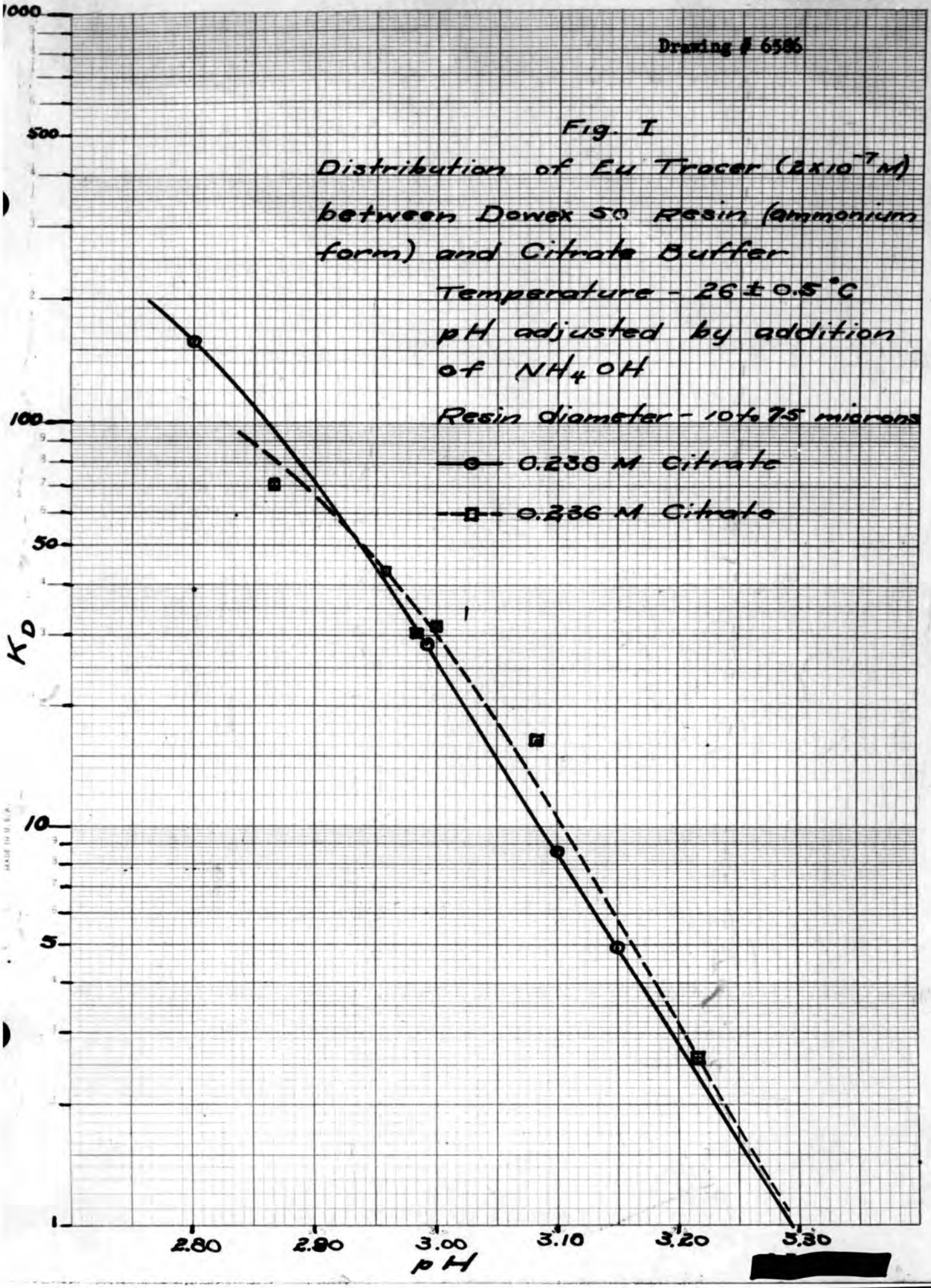
pH	2.80		2.99		3.10		3.15	
	1	2	1	2	1	2	1	2
Wt. resin	0.156	0.145	0.499	0.306	0.696	0.769	4.770	5.060
Original Buffer pH	2.82	2.82	3.04	3.04	3.17	3.17	3.29	3.29
pH after 1st Equil.	2.82	2.80	2.99	3.00	3.10	3.10	3.17	3.15
pH after 2nd Equil.	2.78	2.80	2.97	3.00	3.08	3.10	3.14	3.14
Eu K_D - 1st Equilibration	162	169	31.4	29.2	9.3	7.9	4.3	4.6
Eu K_D - 2nd Equilibration	157	143	27.2	25.4	7.3	8.3	4.1	4.1
Eu K_D - Resin Strip	166	154	30.9	26.1	9.0	10.2	6.3	6.0
Ave. -	162	155	29.8	26.9	8.5	8.8	4.9	4.9
% Material Balance	103	105	106	101	106	107	127	131
Ave. Eu K_D	158		28.4		8.65		4.9	

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

** Beta activity in buffer (original) = 18,200 c/m/ml at 10% Geom.-no absorber.

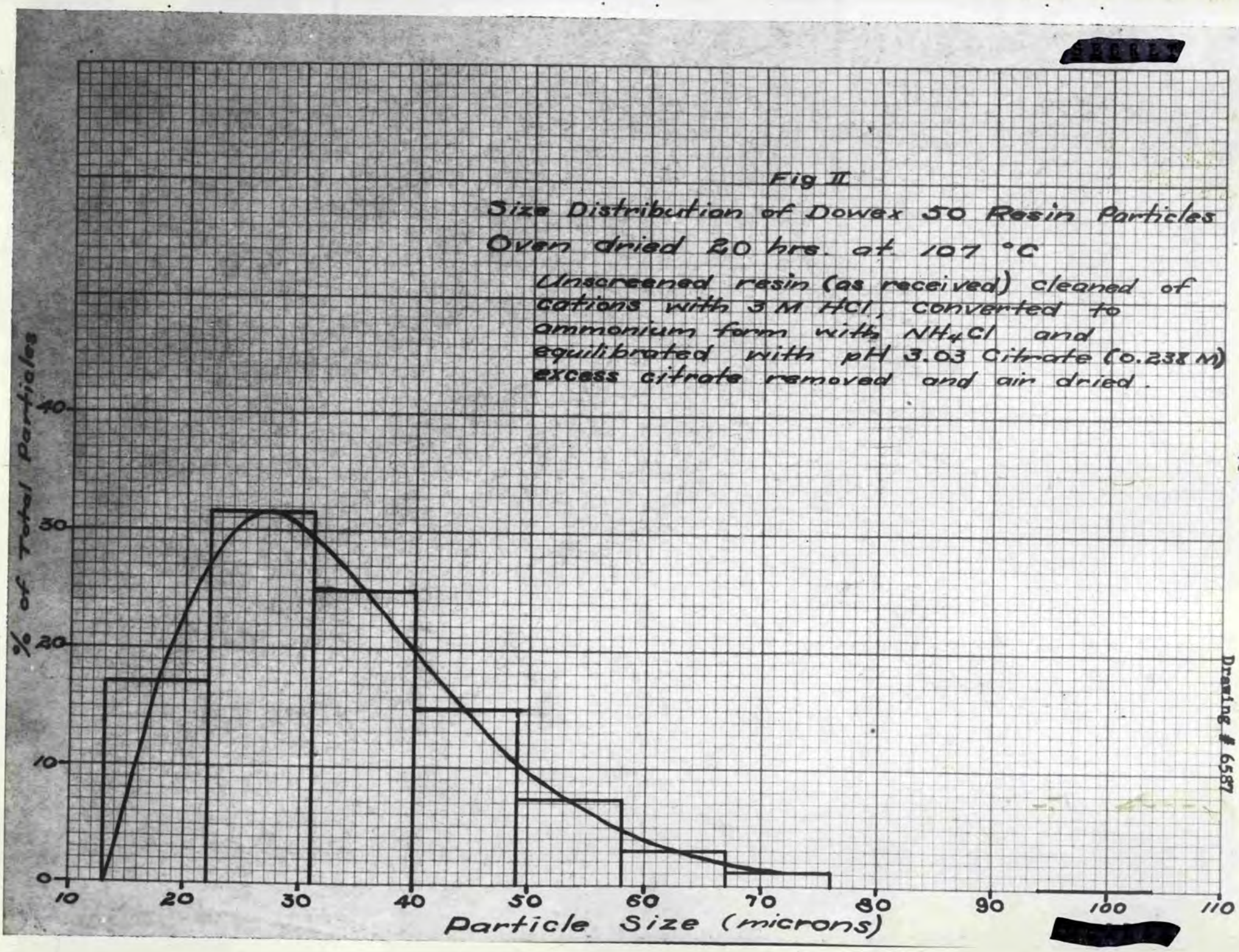
[redacted]

[redacted]



[redacted]

[redacted]



[redacted]

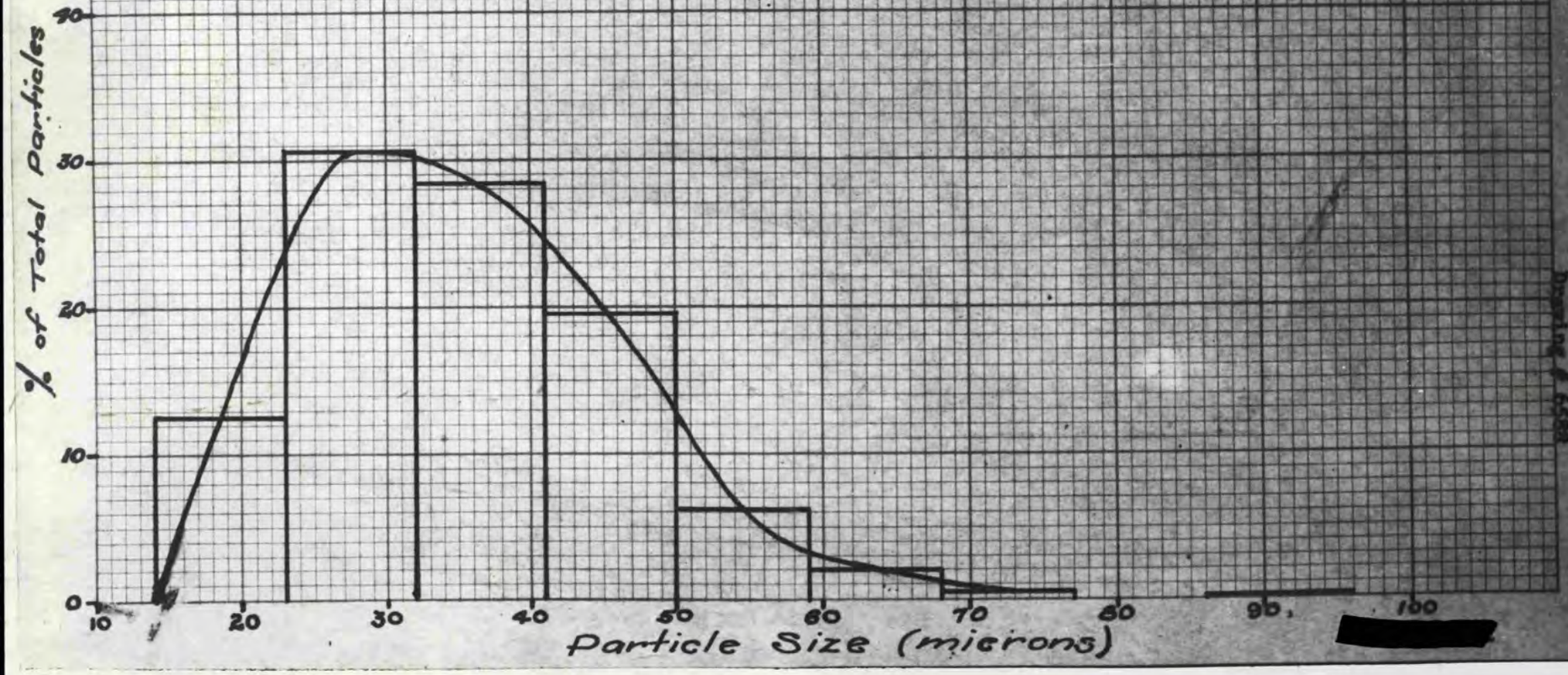
Drawing # 6587

[redacted]

Fig III

Size Distribution of Dowex 50 Resin Particles
Air Dried Resin

Unscreened resin (as received) cleaned of cations with 3 M HCl, converted to ammonium form with NH_4Cl and equilibrated with pH 3.03 Citrate (0.232 M) excess citrate removed, resin air dried 60 hrs. at @ 25 °C



[redacted]

-71-

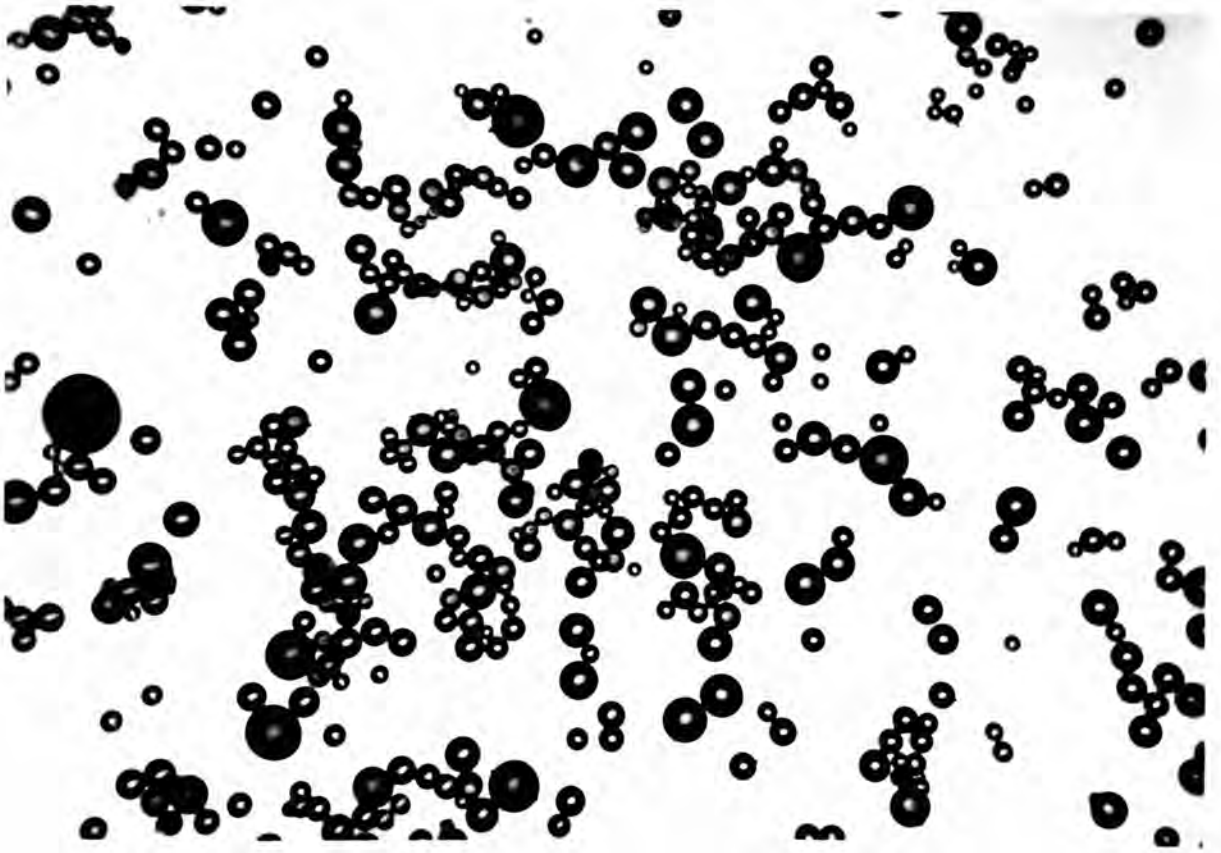
Drawing # 6589

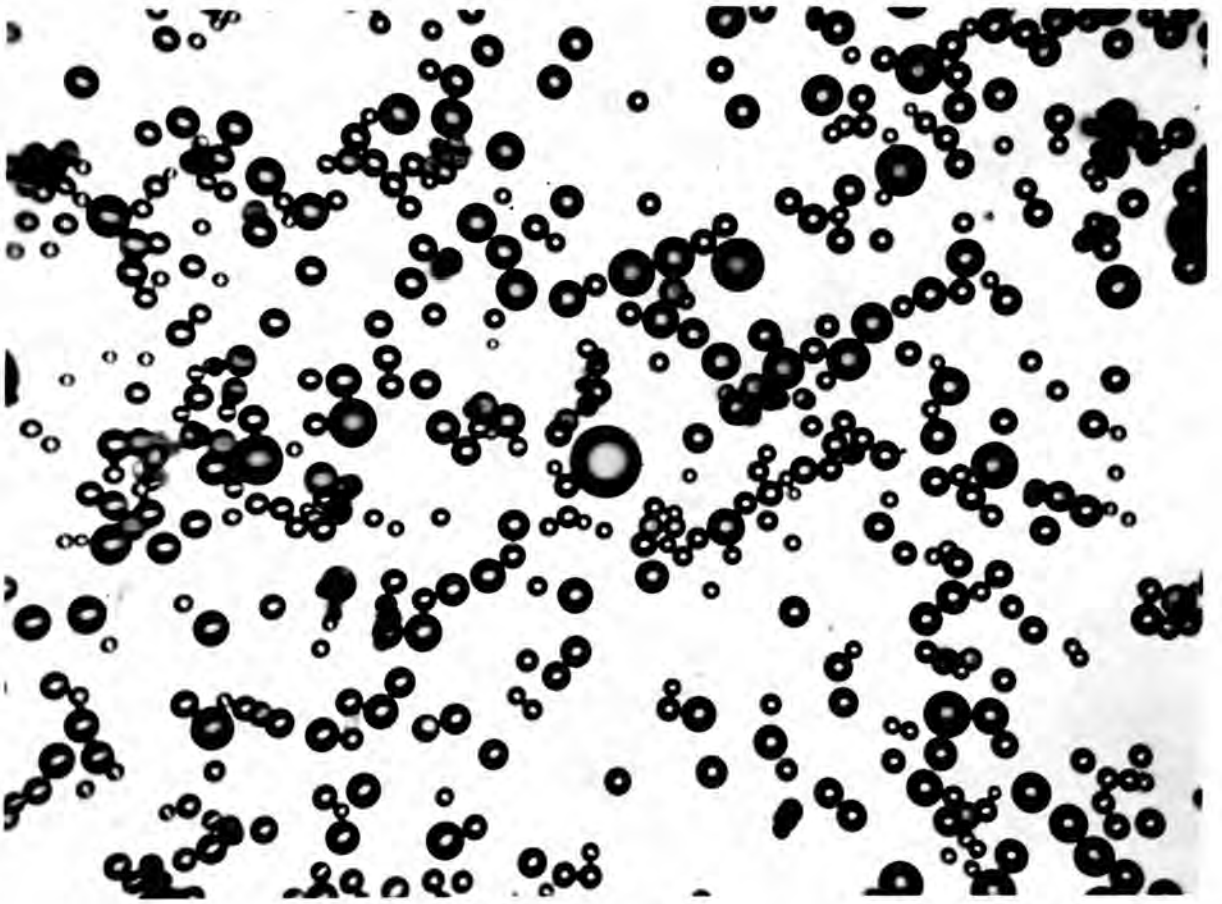
[redacted]

M-278-5 Dowex 50 resin oven dried
20 hrs. at 107° C.
Photographed dry
100 times actual size

M-277-5 Dowex 50 resin air dried
60 hrs. at 25° C.
Photographed dry
100 times actual size

[redacted]



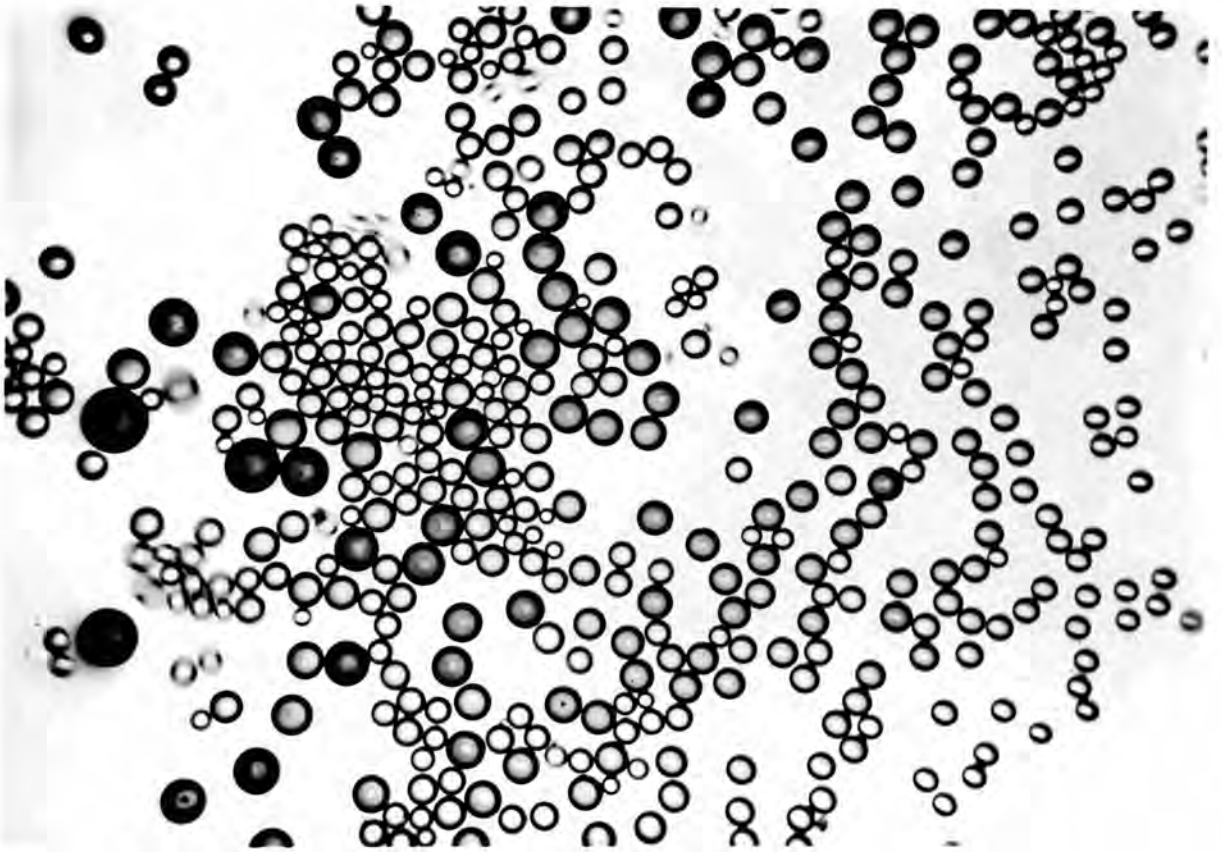


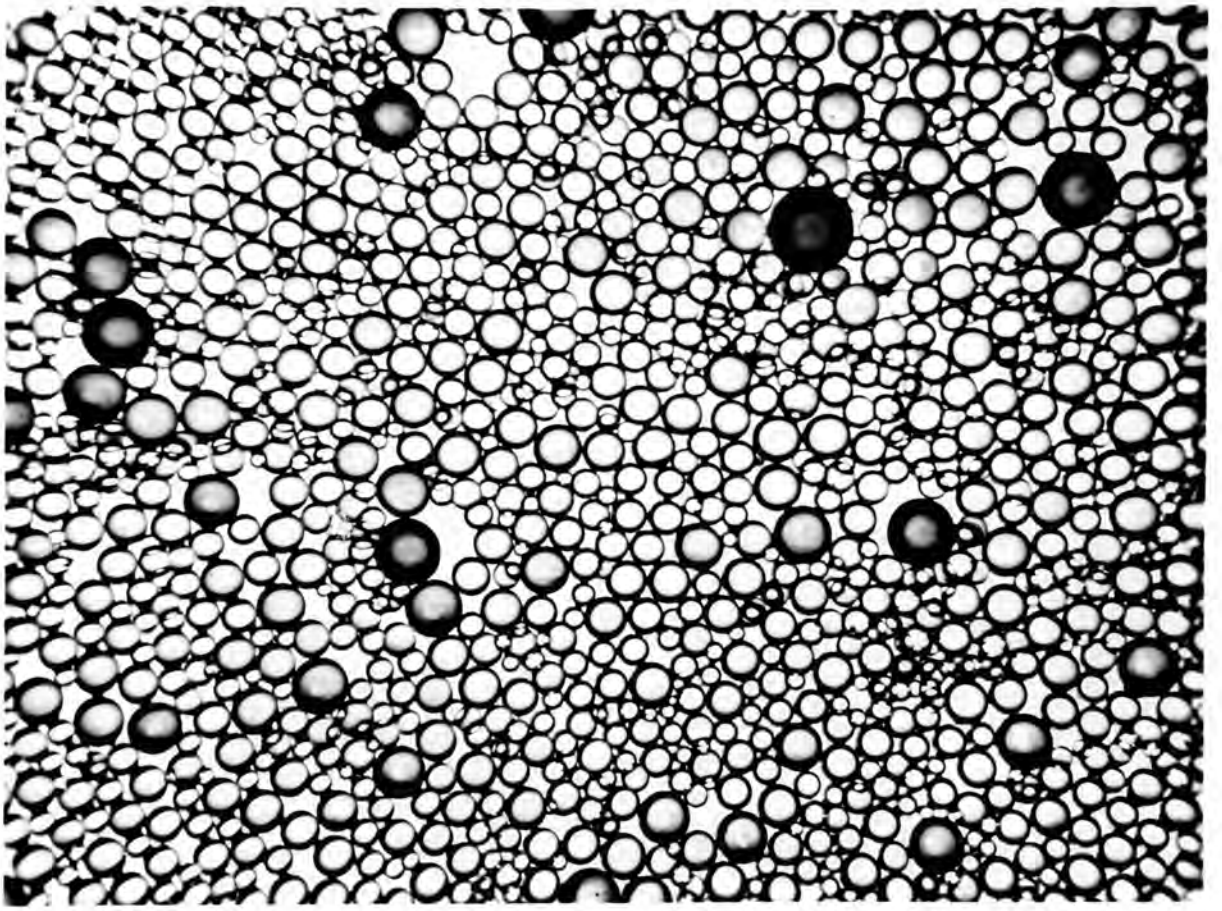
[redacted]

M-275-5 Dowex 50 resin oven dried
20 hrs. at 107° C.
Photographed wet - 100 x
Wetting agent (aerosol in ethyl alcohol) was used to spread particles better and give better lighting.

M-279-5 Dowex 50 resin air dried
60 hrs. at 25° C.
Photographed wet - 100 times actual size
Wetting agent (aerosol in ethyl alcohol) was used to spread particles better and give better lighting.

[redacted]





[redacted]

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

During the past quarter the continued use of the techniques of exchange chromatography, fractional crystallization and amalgam reduction have led to the production of additional quantities of a number of spectrochemically pure rare earths. In fact, the objective in this work (see ORNL-176, p. 38) which has been to separate and purify one gram quantities of the ultra-pure oxides has almost been achieved: presently, varying quantities of all of the earths, with the exception of europium (and 61) are available. The following inventory summarizes these labors:

Pr_6O_{11}	0.150 g.	Y_2O_3	8.118 g.
Nd_2O_3	0.150	Ho_2O_3	1.276
Sm_2O_3	16.279	Er_2O_3	6.353
Eu_2O_3	------	Tm_2O_3	1.916
Gd_2O_3	6.774	Yb_2O_3	0.519
Tb_4O_7	0.335	Lu_2O_3	0.627
Dy_2O_3	2.323	Sc_2O_3	-----

Currently efforts are being made to produce pure Eu. A samarium-europium concentrate weighing 63.68 g. (sesquioxide) estimated to contain 10% Eu as an upper limit has been made ready for a direct isolation of europium.

It is to be understood that the foregoing listed quantities of earths are, in actuality, comprised of a series of separate samples some of which are believed to be of great purity. Independent confirmation of this in the case of our dysprosium sample has been afforded recently by the mass spectrometric study of Hess and Inghram [Phys. Rev. 74, 1724(1947)] in which a new naturally occurring isotope, Dy^{156}, was discovered. We quote: "A final sample of much higher purity prepared by the ion exchange process was obtained from D. H. Harris of Oak Ridge. No rare earth ions other than the known dysprosiums and the new peak at mass 156 were detectable to greater than one part in seventy thousand. Again with this sample the ion current appeared initially at 0.05 per cent and did not change detectably with time or temperature. It was possible with this sample to observe the $Dy^{156}O^{16}$ position free of impurities. The abundance was again about 0.05 per cent of the total dysprosium isotopes. We therefore conclude that dysprosium has a previously unknown isotope of mass 156 which is present to about 0.05 per cent of the total. A future publication will give more accurate data on the abundance of this rare isotope, and new values for the abundances of the remaining isotopes."

Some of the other uses to which our research preparations are being put may be of interest:

Praseodymium

This pure sample originated from the cerium earth separation NPC-1. Fractions 12-17 from this separation [see Figure 9, D. H. Harris and E. R.

[redacted]

[redacted]

Tompkins, J. Am. Chem. Soc., 69, 2792 (1947)] are being irradiated to prepare the 19.3 h Pr^{142} for beta ray spectrometer measurements by the Indiana group under A. C. G. Mitchell.

Neodymium

This sample resulted from a special separation designed to determine if the neodymium isotopes are fractionated in the course of passage through an ion-exchange column. Since as many as 1000 theoretical plates are observed with 100 cm beds, ratio analyses accurate to 0.1% should allow the detection of separation factors as small as 1.00002. Selected fractions from the leading and tail portions of the "elution peak" containing Nd have been submitted to the Argonne mass spectrometry group under Professor Dempster and Dr. Inghram.

Erbium

Aliquots from this preparation have been examined in the neutron crystal spectrometer by Messrs. Stanford and Stephenson [See ORNL 159, p. 9] who report a possible strong resonance at 0.5 ev. Presently 200 mg. aliquots of Ho_2O_3 and Yb_2O_3 are being studied.

Additional disbursements have been:

a) To Y-12 for spectrochemical studies - ca. 50 mg. quantities of Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Sm, Nd, Y.

b) To Dr. M. Bredig for X-ray crystal studies of the oxides - ca. 50 mg. of same preparations as in a).

c) To Mr. B. H. Ketelle - 10 mg. Dy_2O_3 and 50 mg. Lu_2O_3 for nuclear chemical studies (vide infra).

d) To Drs. Mateosian and Goldhaber for nuclear studies - 10 mg. of Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Sm and Nd.

[redacted]

[redacted]

VI. Physical Chemistry and Chemical Physics

Experiments with Molecular Beams: (E. H. Taylor)

Preliminary experiments are under way in a study of certain problems in chemical kinetics using the method of molecular beams. Advantages of this approach are that experiments are freed of the ambiguities of secondary reactions, and that energetic and geometric factors are more accessible to direct and independent study. The principal difficulty is that of detection and measurement of small numbers of atoms and molecules; the present plan is to study reactions of substances containing atoms of relatively high neutron capture cross-section and measure the substances by pile-induced radioactivity.

The work now in progress includes design and construction of apparatus and development of suitable techniques for sample irradiation and measurement. Specific experiments will be chosen after the development of the technique indicates which substances of kinetic interest are feasible to use.

Cloud Chamber Studies: (R. Livingston)

In order to correct the troublesome sweep field effect noted in ORNL-176, the chamber was returned to the laboratory and work started to coat the top fluorothene window with a transparent, conducting film.

Thin test evaporated films of platinum and nickel were placed on samples of fluorothene and one each placed in a fluorine atmosphere for about one week. The nickel film showed very little change in transparency and electrical conductivity. The platinum film became much more transparent and the conductivity went to essentially zero. A thin evaporated nickel film will be used on the chamber window.

The cloud chamber work was stopped temporarily while undertaking work on the particle problem.

[redacted]

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VII. Physical Measurements and Instrumentation

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

(1) Particle Problem

Over half of the time of the group has been spent on several phases of the particle problem, which will not be discussed here since it is being written up as part of a separate report (ORNL 197).

(2) K-25 Work

Work for K-25 occupied about 10 to 15% of the time.

(3) Beryllium

A number of photomicrographs have been taken for the technical division in connection with the work on machinability and corrosion of beryllium. Further work is contemplated with one of the samples presented.

(4) Exchange Resins

The study of the size, size distribution, shape, and other microscopically observable characteristics of available exchange resins has continued in co-operation with G. E. Boyd and other members of the chemistry division. The results will be made available in a separate report.

(5) Miscellaneous

More than the normal amount of time has been spent on (1)evaporation of thin films of various materials, and (2) photographic slides, prints, micrographs, etc.

[redacted]

[redacted]

X-Ray Diffraction
(M. A. Bredig)

1) Crystal Structures of Refractory Beryllium Compounds (Oxide, Nitride, Carbide)

a) The new, optically biaxial, crystal phase in beryllium oxide:

Efforts to find the foreign substance forming a solid solution in BeO with an optically biaxial structure slightly different from the common hexagonal one have been continued, with W. W. Galbreath Jr., formerly of the Power Pile Division, now with Argonne National Laboratory, and the Electrotechnical Laboratories of the U. S. Bureau of Mines at Norris, Tennessee, collaborating.

Three samples, (XR-376, 377, 378), consisting of pure BeO (Brush G. C.), and of BeO containing 10 and 30 percent beryllium carbide Be_2C (kindly supplied by Dr. O'Leary of the Nepa project) were briefly heated in the Norris electric furnace to fusion (approximately 10 minutes at 2450°C). Instead of the expected solid solution phase of BeO, practically no BeO was found left in the graphite crucibles. Rather, cubic Be_2C was found to have formed by reaction of the oxide with the graphite of the crucible, and in addition, in amounts approximately equal to those of Be_2C, a second phase, which has been characterized in a previous report (ORNL-176, page 83) by the spacings 2.415, 2.209, 1.732 and 1.435 Å when it was found in the reaction zone between berylliacrucible and graphite. It will be shown further below, that this phase most probably is a new crystal modification of beryllium nitride, which must have formed in these experiments by the reaction: $3\ BeO + 3C + N_2 = Be_3N_2 + 3CO$.

In another series of tests, three similar compositions (XR-412, 413, 414) were heated under similar conditions, with beryllia crucibles substituted for the graphite. While a small amount of the solid phase was found in the specimen containing 10 percent Be_2C, besides the common hexagonal BeO phase and some cubic Be_2C, no trace of the optically biaxial crystals was found in x-ray patterns of the pure BeO sample. This result might again have been taken to demonstrate a decisive influence of beryllium carbide upon the formation of the new phase. However, the small concentration of the new phase, i.e., the failure to obtain reaction throughout the whole pellet with all of the beryllium carbide added, is very difficult to understand under the circumstances. In view of this and previous failures to obtain larger concentrations of the new phase by the addition of carbide, it seems that another explanation may have to be sought.

From recent observations, referred to in the following paragraph, it appears that nitrogen, rather than carbon, may be the active ingredient in the formation of the solid solution phase.

[redacted]

[redacted]

b) Polymorphism of Beryllium Nitride.

In a preliminary attempt to test the possibility of nitrogen producing, the new phase in beryllium oxide, a small piece of beryllium nitride was heated intensely with an acetylene-oxygen torch for approximately one minute. A pure white layer of oxide which turned out to be in the hexagonal form, was removed from the surface as effectively as possible. The remaining core, after pulverizing, gave a powder x-ray pattern of a mixture of the well known normal cubic form of the nitride, of a quantity of the oxide, and of a large amount of a third phase which showed almost exactly the same spacings as those found in the product of high-temperature reaction between the beryllia crucibles and graphite, mentioned in a) (spacings 2.415 etc). In the table in which reflections from BeO, Be_2C and graphite, also appearing in the patterns, have been omitted, it is shown that these spacings can be explained well by the assumption of a hexagonal structure of the (anti-) lanthanum sesquioxide type, that is with one molecule Be_3N_2 contained in a unit cell of the approximate dimensions a = 2.870 and c = 4.850 A (c/a = 1.69). The specific gravity calculated from the lattice constants would be approximately 2.65, very similar to that of the cubic nitride (2.70).

One line of medium intensity (spacing 1.532 Å) remained unexplained. Whether it is due to an impurity or to a possible third modification ("B-form", see below) of the nitride is not clear as yet. Before a sample of higher purity of the new nitride phase can be examined, the interpretation of the x-ray pattern must be considered tentative.

If it is correct, the atomic positions of beryllium and nitrogen ions would be quite similar to those proposed by L. Pauling in 1928 (Strukturbericht I, 785) for oxygens and lanthanum ions in O_3La_2 respectively, namely 000 and $\pm$ 1/3 2/3 v for Be and $\pm$ 1/3 2/3 u for N^{3-}. (Another atomic arrangement proposed for lanthanum oxide by W. H. Zachariasen in 1926 has seemed to be less probable). The numerical values of v and u remain to be determined from the x-ray intensities of preparations higher in concentration of the new nitride phase. In the figures of the table, they were very roughly taken as v = 2/3 and u = 1/4. In accordance with the anti-isomorphism with La_2O_3 seven beryllium ions would be surrounding a nitrogen ion in the structure, as compared with 6 in the cubic structure. As far as the relationship of the two crystal modifications to each other is concerned, the polymorphism of beryllium nitride may be related to that of samarium sesquioxide, O_3Sm_2, which was reported in 1925 by V. M. Goldschmidt (Geochem. Verteilungsgesetze, Oslo) to occur at 2000°C with the simple hexagonal structure of the so-called A-form of the rare earth oxides namely of lanthanum, cerium, praseodymium and neodymium. At temperatures below 700°C samarium sesquioxide is known in the more complex, cubic, lowest-temperature form of the Yttrium group oxides (c). A third form, B, thought by Goldschmidt to be stable in samarium oxide in the intermediate temperature range, may remain to

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Table

X-Ray Patterns (Spectrometer) of Hexagonal Phase of Beryllium Nitride

Structure (F_o) and Multiplicity (M) Factors		Be_3N_2 heated (XR-422d) (C-635)			Nitride Phase in BeO + C(+N_2) (12.6%N) (C - 630)		
Indices Hexag.	$\|F_o\|^2M$	Intensity	exp. Å	calc. Å	Intensity	exp. Å	calc. Å
00.1	0	-	-	4.814	-	-	4.856
10.0	55	C	(2.486)	2.482	C	C	2.490
00.2	100	100	2.403	2.407	100	2.428	2.428
10.1	25	C(25)	2.212	2.210	15	2.217	2.215
10.2	70	C	(1.735)	1.730	10	1.735	1.738
00.3	25	C	(1.608)	1.605	C	(1.613)	1.619
-	-	25	(1.532)	?	?C	?C	?
11.0	450	45	1.433	1.436	32	1.438	1.438
11.1	0	0	-	1.378	C	(1.377)	1.379
10.3	25	C	(1.356)	1.350	C	(1.356)	1.355
20.0	20	C	1.240	1.241	C25	(1.235)	{1.245
11.2	150	C	(1.234)	1.233			1.236
20.1	40	C	(1.209)	{1.205	2	1.210	{1.206
00.4	25			1.204}			1.214}

C means: Coincidence with lines of cubic Be_2C, or cubic Be_3N_2, or BeO.

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be found in beryllium nitride.*)

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*) It is not clear on what experimental evidence A. T. Wells based the statement in his book 'Structural Inorganic Chemistry'(1945), page 314, that lanthanum and neodymium oxides have the cubic structure at elevated temperatures. This would be in disagreement with the earlier study by Goldschmidt on the morphotropism of the rare earth oxides.

Further tests, with exclusion of oxide, are required to determine whether partial oxidation of the nitride which occurred in the present experiment, was actually needed in producing, or at least stabilizing, at room temperature, the new structure of the nitride. Only then will it also be possible to state more definitively what is now assumed to have a high degree of probability, namely that the occurrence of the hexagonal phase in beryllium nitride in the test described was due to the formation of a solid solution with the oxide, and that generally speaking nitride and oxide can form solid solutions at least at elevated temperatures. An extension of this assumption leads at once to the possibility that the new phase in beryllium oxide may also be produced by just such a solid solution, of a small amount of nitride, in oxide, and this is being tested in new experiments. A quantitative determination of nitrogen in sample XR-178 which had shown a particularly large amount, of 50 or more weight percent of the new oxide phase, gave 1.8% N (or 3.5% Be_3N_2), which would be entirely sufficient - it is believed - to explain the formation of a large amount of a new oxide phase by solid solution. A study of the nitrogen content of various samples of heat treated beryllium oxide, nitride, and carbide, is underway, and possible important consequences of the existence of solid solubility in these refractory beryllium compounds in connection with their physical and chemical technology will be examined. An investigation of the fundamental crystal-chemical aspects of solid solubility of oxides, nitrides and carbides of light elements in general, about which little or nothing appears to be known, also seems attractive.

2) Study of Pile-Irradiated Metals

The examination of the effect of pile radiation upon the width of the (111) reflection in 2% beryllium-copper alloys submitted by D. S. Billington and R. H. Kernohan was continued during this quarter, The table contains all results obtained thus far, using copper K_α x-ray radiation in the Norelco diffraction spectrometer.

It may be noted that the large effect observed in the samples X-1 and X-15 (XR-298 and 297, respectively) of the first series was not reproduced in new specimens X-48 and X-49 (XR-369 and 370) which had received similar treatment as X-1. No explanation can be given in the case of X-1, nor for a third major deviation from a regular behavior, the abnormally large line width of the unirradiated sample X-78, except that they must be due to irregularities in the

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Table [redacted]

Effect of X-10 Pile Irradiation on Crystal Lattice of Copper-Beryllium Alloys

XR-No Before Irradiation	XR-No After Irradiation	D. S.*) Billington No. Before	D. S.*) Billington No. After	Aging*) Time Minutes	Hardness*) Before 3 weeks of irradiation in X-10 Pile	Hardness*) After 3 weeks of irradiation in X-10 Pile	Hardness*) Change %	X-Ray Diffraction - Phase CuBe	X-Ray Diffraction (111) reflection halfwidth Before	X-Ray Diffraction (111) reflection halfwidth After	X-Ray Diffraction (111) reflection halfwidth Change %
1a) α-quench; no cold work; no aging:											
295	294	X-L	X-7	0	13.8	43.7	+210	-	0.35	0.35	0
b) same, second series:											
	371		X-32	0	51.7	49.6±.4		-		0.41	0?
	372		X-34	0	52.0±.2	49.5±4		-		0.41	0?
2a) α-quench, cold work (50% reduction of area); no aging:											
299	298	W	X-1	0	87.0	86.7	-0.4	-	0.58	0.80	+38
b) same, second series											
	369		X-48	0	84.2±0	87.9±.3		-		0.55	0?
	370		X-49	0	84.3±.2	86.9±.3		-		0.53	0?
3a) α-quench; cold work(50% red); aged at approximately 300°C(?):											
296	297	X-16	X-15	16	102.4	101.8	-0.6	+	0.50	0.80	+60
-	306	X-12	X-11	30	"	100.4	-2.0	+	Sample not available	0 47	?
318	300	X-14	X-13	60	96.0	95.3	-0.7	+	0.39	0.48	+23
319	301	X-10	X-9	180	93.9	93.3	-0.6	+	0.42	0.45	+7
b) same (second series)											
400	392	X-72	X-70	5	93.7±1.1	95.2±0.4	+1.6		0.47±.01	0.48±.02	0
401	393	X-75	X-73	15	98.2±1.8	99.2±0.5	+1		0.51±.01	0.55±.01	+8
402	394	X-78	X-76	30	99.8±1.5	101.0±0.5	+2		0.75±.00	0.64±.02	(-15
403	395	X-81	X-79	60	100.6±0.7	101.4±0.2	+1		0.90±.01	0.97±.03	+8
c) same, without cold work; (second series)											
396	388	X-59	X-57	5	69.8±3.6	86.5±0.9	+22		0.38±.03	0.44±.02	+15
397	389	X-62	X-60	15	89.0±3.8	90.1±0.4	+1		0.43±.03	0.45±.03	+4
398	390	X-65	X-63	30	93.1±0.6	95.1±0.2	+2		0.43±.03	0.57±.01	+33
399	391	X-68	X-66	60	97.6±0.8	981.±0.2	+0.5		1.06±.04	1.18±.05	+11
4a) α-quench; cold work (50% red.); overaged at 500°C											
	305	X-17	X-18	55	65.1	67.5	+3.5	+	sample not avail.	0.43	0?
317	315	X-22	X-19	600	54.5	70.7	+30	+	0.35	0.50	+43
b) α-quench; no cold work; overaged at 500°C:											
304	314	X-M	X-A	600	57	(70.9)	(+25)	+	0.37	0.35	0

* Data in columns marked by asterisk were supplied by D. S. Billington and R. H. Kernohan.

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preparation of the samples rather than in the x-ray measurements. The second series of samples does seem, however, to show, with all the reservations that are imposed by the occurrence of the irregularities just cited, that a small radiation effect did occur in this alloy. There was a rather consistent increase in the line width of irradiated samples, compared with that before irradiation, ranging from 0 to 33 percent for aging periods, of 5, 15, 30 and 60 minutes. Because of the irregularity in sample X-78 which eliminates it as a control sample for X-76, it cannot be stated with any certainty whether a maximum in the relative line broadening was actually reached after 30 minutes of aging, as the specimen X-63 seems to indicate. All that, in the opinion of the writer, can be said at this stage of the investigation is that line broadening of an order of magnitude just exceeding the average deviation of the measurements (which is largely determined by variations in the specimens) did occur in those specimens that had reached the higher hardness values as a consequence of aging.

A comparison of the pair X-70/72 with the pair X-63/65 showing approximately equal hardness (Rockwell G:95), but different degrees of line-broadening seems to indicate that it is not so much absolute hardness that determines the degree of line-broadening in a given composition of matter on exposure to nuclear reactor radiation as the capacity left in the material for more hardening through lattice deformation. Line-broadening under the influence of radiation seems the stronger the smaller this capacity is, as in X-63 which is nearer than X-70 to the maximum hardness, attainable in each of these materials (98 as against 101.4, in this hardness range a significant difference). This is also in line with the observation that the line width as a function of hardening rises sharply at the higher hardness values.

In this way the particularly high degree of line broadening of 60%, in specimen X-15, might even appear reasonable though it will certainly have to be checked. In it the highest value of age-hardening (Rockwell G - 102.4) had been reached. (That this occurred after 16 minutes of aging, while longer aging periods led to softer materials, must according to D. S. Billington, be ascribed to irregularities of the furnace operation (temperature control) in this series.) The lower absolute values of the line width in this case may also be due to a higher aging temperature. However, it is certain that many more data will have to be examined before final conclusions can be drawn. The study is being continued.

3) <u>X-Ray Diffraction Work in Connection With The Radioactive Particle Hazard at X-10</u>.

Various phases of this work are being reported in a special report of the Chemistry and Physics Divisions. The significant results are the following:

a) UO_2 and U_3O_8 have been found in highly radioactive particles collected by the Health Physics Division at different locations.

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b) Oxides produced in laboratory experiments (conducted by L. T. Newman) were UO_2, when obtained at low temperature, and U_3O_8, when rapid oxidation caused the temperature to rise to a red heat.

c) Besides the lines of common constituents of the soil such as α-quartz, limestone and mica, 3 x-ray spacings that match those given in the literature for sodium stearate were obtained in an x-ray pattern of a deposit from pile stack gases on a CWF #6 filter. The use of stearic acid in certain pile operations (canning of calcium nitrate)suggest it as the possible source for a stearate dust, that may or may not have been responsible for the x-ray lines observed and the clogging of the filters.

d) A grey brittle substance formed at the interface of a uranium slug and its aluminum can was identified as the intermetallic compound $U\,Al_3$. Its formation may be a contributing factor in slug failures.

4) Uranium Metal Single Crystals (with T. A. Read, and F. A. Sherrill, of the Physics Division).

A large number of Laue patterns of uranium metal rods showed that they did not consist of single crystals but of polycrystalline metal of a varying degree of preferred orientation. In one such rod a somewhat larger grain of the order of 1 mm^2 was found and a good single crystal Laue pattern obtained. Attempts are being made to isolate and use such larger grains in x-ray diffraction studies of lattic distortions by fission recoil and neutron impact.

5) Thorium Carbide and Other Substances for Neutron Diffraction Studies

An x-ray pattern obtained with a sample of thorium carbide, to be used in neutron diffraction studies by C. G. Schull, and submitted by the latter, revealed a splitting of x-ray reflections which indicates that this compound does not have the tetragonal structure ascribed to it by M. von Stackelberg (Strukturber. I, 1932), but must be of lower symmetry, and only pseudotetragonal. It has been learned that R. E. Rundle, of Iowa State College, has made the same observation and is in progress of determining the real structure of this substance, so that it seems inappropriate to pursue this subject further in this laboratory.

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Instrument Research and Development

An Improved Differential Discriminator Circuit For The Alpha Range Analyzer
E. Fairstein

A series of improvements for the Alpha Range Analyzer* was described

*Mon C-416

in the last quarterly report. Minor changes only were made in the differential discriminator. Since then, this portion of the circuit has been completely rebuilt with very gratifying results.

The operation of the circuit is as follows: -

There are two gate circuits separated in operating level by a voltage increment continuously adjustable between zero and one volt. This increment is set by the slit-width control. Pulses greater in magnitude than either gate level will trip the associated univibrator.

It is the purpose of the discriminator to accept pulses whose heights lie only between the two operating levels, i.e., within the slit-width increment. For pulses above these levels, the anti-coincidence circuit prevents transmission of the signal from the univibrator associated with the lower gate.

The lower-gate univibrator produces an eight microsecond pulse. This pulse is differentiated and fed into the half of the anti-coincidence tube which is normally held at cutoff. (See the associated oscillogram). Unless a pulse is also fed into the other half of the tube from the upper-gate univibrator, the positive portion of the differentiated pulse is transmitted to a third univibrator, where it undergoes amplification and lengthening.

If the upper gate is also tripped, a sixteen microsecond pulse is fed into the "on" half of the anti-coincidence tube. This keeps the other half cut off until the differentiated pulse produced by tripping the lower gate dies out. The remainder of the circuit is a conventional rate meter circuit.*

* LA-1002, Chapter 4.

The gate circuits have a gain of about thirty. This gain results in a region of unsure operation considerably shorter than can be obtained by using the univibrators alone as the gate circuits.

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The "Solite" capacitors in the integrating circuit of the rate-meter are manufactured by the Solar Manufacturing Company. These were chosen because they are the only low-priced commercially available units (other than polystyrene capacitors) with a dielectric hysteresis effect comparable to that of polystyrene capacitors. However, they are subject to occasional short circuits, even when not overloaded. This undesirable feature is at least improved by providing a momentary-make switch to connect them to the filament supply, (the "capacitor blowout" switch on the diagram) and so far has proved effective in removing the short circuit.

The circuitry associated with the pulse height selector potentiometer (gate-level potentiometer) has not been shown. It will be quite similar to the older circuit but with more steps available.

The advantages of this circuit over the older one are as follows: -

1) The stability is better by a factor of at least ten, permitting stable operation at slit-widths of one-tenth volt.

2) The dead time of the circuit has been reduced from 1500 microseconds to approximately thirty microseconds, permitting samples of much higher counting rate to be used.

3) The time-constant is inversly proportional to the setting on the counting-rate switch, resulting in better spectrograms.

4) Continuously adjustable slit-width, counting rate, recorder zero controls, and a variable time constant control have been provided.

With these, it is possible to get good spectrograms in the activity range of ten counts per minute to 100,000 with a minimum of effort.

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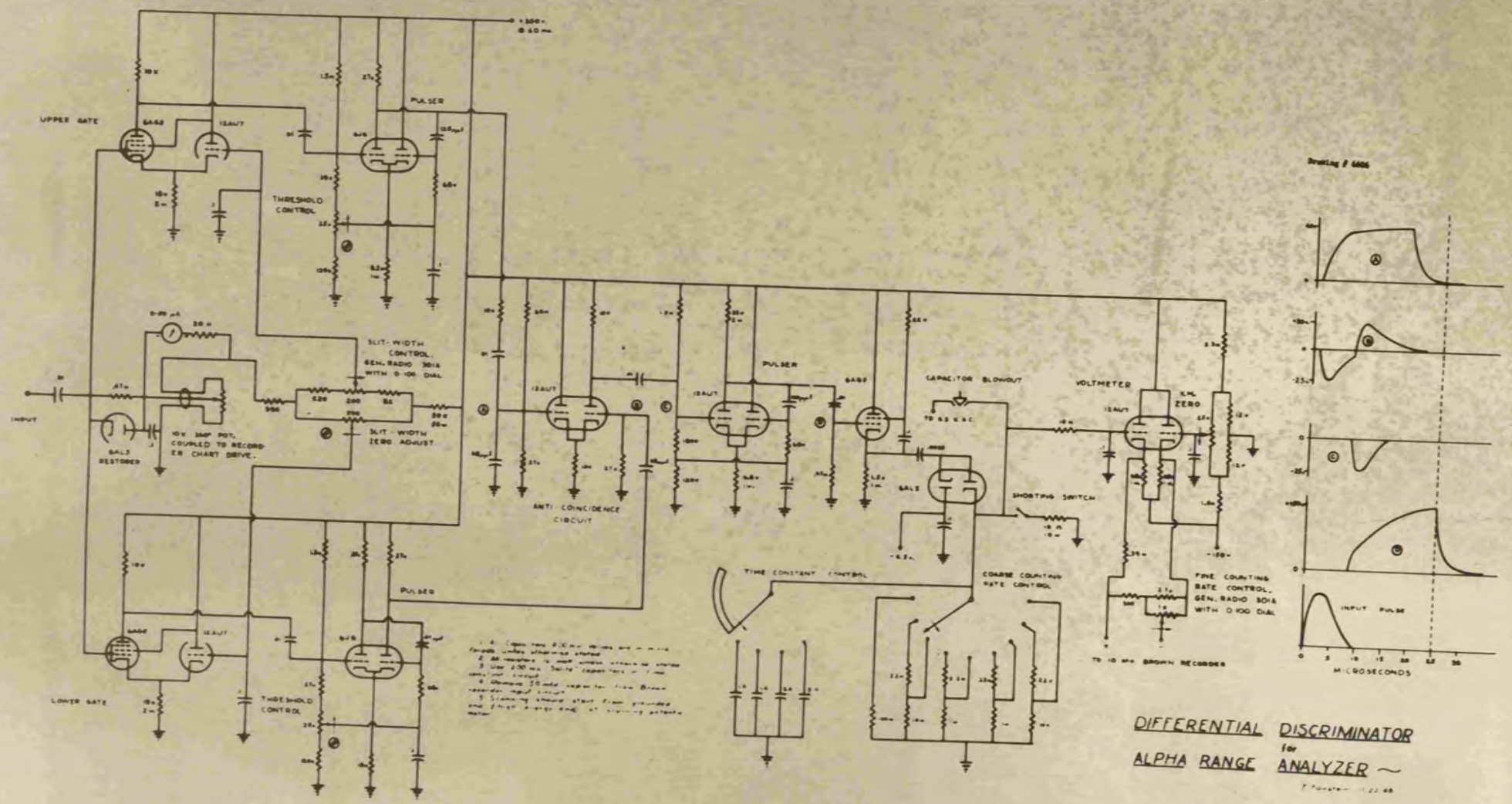

DIFFERENTIAL DISCRIMINATOR for ALPHA RANGE ANALYZER ~

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VIII. Analytical Chemistry

Ionic Analyses - Research and Development

Micro Determination of Nitric Acid in Redox Process Solutions: (P. F. Thomason)

The Hanford oxalate method[1] for the determination of nitric acid has been successfully scaled down to a micro titration with the collaboration of Mr. D. F. Shepard of Hanford Engineering Works. The oxalate procedure heretofore has been used for relatively inactive samples which permitted the titration of several milliliters. As the samples submitted by the pilot plant are quite radioactive (2 r. per ml. at contact) submilliliter samples must be analyzed. By using micro equipment 10 λ samples of a redox feed solution which is 0.3 N HNO_3 and 2 M UNH can be easily titrated. Scrub solutions that are 1.3 M $Al(NO_3)_3$ and deficient in acid can be determined using a 10 λ aliquot and spiking with a known amount of nitric acid. Waste samples 0.8 M $Al(NO_3)_3$, 0.06 M $K_2Cr_2O_7$ and 0.001 M UNH can also be titrated after precipitating the chromium with $Pb(NO_3)_2$ and correcting for the acid liberated by this reaction.

The stirring equipment consists of an electric stirring motor with a gear reduction such that the 1/4" shaft turns at 125 rpm. As the titration is carried out at 0 - 4° C., an ice bath was made of a plastic 50 ml. graduate cut-off at the 12 ml. mark and fitted with a plastic cap made from 1/8" sheet plastic. The cap was drilled with a 5/8" bit which permitted the bottom of the platinum dish used as the titration vessel to come into contact with the ice water in the plastic graduate. The platinum dishes are the same as used for the fluorimetric determination of uranium and are 3/4" in diameter, with a capacity of 200 λ. By drilling a 1/4" hole in the bottom of the graduate it fits snugly on the shaft of the motor which rotates the entire assembly around the stationary electrodes and thereby effects adequate mixing.

The potentiometric titration is carried out as outlined in the procedure utilizing the Beckman 290X1 glass electrode and a regular 270 calomel electrode which is fitted with a KCl salt bridge made from 6 mm. diameter tubing drawn to approximately 2 mm. at the tip. An asbestos wick is sealed into the tip to prevent excess flow of KCl. The titration is performed with a Kirk micro burette containing standardized 0.3 N NaOH. The NaOH is added slowly in 1 cm. increments, reading the pH meter after each addition. The maximum inflection of approximately 0.5 pH unit is easily seen on a Beckman Model H pH meter. As each cm. of the burette scale is equivalent to 1.5 λ, delivery of approximately 7 cm. of 0.3 N NaOH is required for a 10 λ sample of 0.3 N acid.

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(1) Hanford Engineering Works Laboratory Manual RNA-1c.

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The results of synthetic samples are as follows:

Sample No.	Present	Found
1 Feed	2 M UNH 0.40 N HNO_3	0.37 N HNO_3
2 Feed	2 M UNH 0.25 N HNO_3	0.26 N HNO_3
3 Feed	2 M UNH 0.1 M $K_2Cr_2O_7$ 0.10 N HNO_3	0.12 N HNO_3
No. 1AW	0.75 M $Al(NO_3)_3$ 0.001 M UNH 0.006 M $K_2Cr_2O_7$ 0.91 N HNO_3	0.89 N HNO_3
No. 1AW	0.75 M $Al(NO_3)_3$ 0.001 M UNH 0.06 M $K_2Cr_2O_7$ 0.66 N HNO_3	0.67 N HNO_3

The Separation of Thorium from Aluminum for Analytical Purposes (W. H. Davenport P. F. Thomason)

As a routine control method was needed for the determination of aluminum in the presence of thorium, several colorimetric methods were tested. It was found that thorium interferred in the hematoxylin, alizarin S, and the aluminon method(1) when present in the expected concentration of 1.0 molar $Th(NO_3)_4$ to 0.3 molar $Al(NO_3)_3$. Therefore it was decided to separate the thorium from the aluminum by a simple method if possible.

It was found that the thorium in 25 λ samples of a solution containing 0.3 M $Al(NO_3)_3$ and 1.0 M $Th(NO_3)_4$ could be extracted with a 1% thenoyltrifluoracetone (TTA) solution in carbon tetrachloride. The following procedure has been found satisfactory for the extraction.

A 25 λ sample is pipetted into a 50 ml. separatory funnel and diluted to approximately 15 ml. with distilled water. The pH is adjusted to 2 $\pm$ .05 with dilute HCl. The aqueous solution is extracted twice by shaking 3 minutes with 15 ml. of a 1% TTA solution in carbon tetrachloride, discarding the organic layer each time. The aqueous solution is made to 50 ml. volume and aliquots are taken for the estimation of aluminum by the conventional aluminon (1) colorimetric method.

Several synthetic samples containing 400 micrograms of aluminum and 11 milligrams of thorium in the 15 ml. volume were extracted in this manner. The thorium remaining in the aqueous solution was less than 55 micrograms (approximately 0.5%) as determined by the thoron(2) colorimetric method. The aluminum found was

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(1) Colorimetric Determination of Traces of Metals, p. 117, E. B. Sandell Interscience Publishers, Inc., N.Y. 1944.

(2) P. F. Thomason, M. A. Perry, and W. M. Byerly, A Colorimetric Method for the Determination of Microgram Amounts of Thorium, ORNL-90.

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388 micrograms (97% recovery).

Determination of Methyl Isobutyl Carbinol in Hexone (E. K. Hanig, P. F. Thomason)

Impurities in methyl isobutyl ketone (hexone) greatly affect the decontamination factor obtained in the Redox extraction process. Therefore, limits of impurities have been specified[1]. Mesityl oxide in hexone has been satisfactorily determined by its absorption at 2450 Å in a Beckman spectrophotometer. However, methyl isobutyl carbinol (MIBC)[1] has been determined by an indirect method involving the colorimetric estimation of the chromic ion obtained by the reduction of $K_2Cr_2O_7$ by the MIBC. As this method is empirical and depends pon the exact control of a number of variables such as acidity and the degree of mixing of the $K_2Cr_2O_7$ and hexone, accurate results could not be obtained on synthetic samples.

The volumetric method[2] for the determination of the hydroxyl group based on the esterification of the alcohol by phthalic anhydride in anhydrous pyridine has proved to be satisfactory for the estimation of MIBC in hexone in the range of 0.02 to 0.10% by volume. As water will hydrolyze the phthalic anhydride, the hexone must be dry as possible. It was found that the azeotrope of hexone and water could be distilled at 88° C. When the distillation temperature reached 114° C., approximately 5 milliliters were distilled. Then the fractioning column was stopped and aliquots of the remaining hexone were taken for esterification. Pyridine was also distilled to remove the water.

The esterification of the MIBC is accomplished by refluxing 25 - 50 ml. of hexone with 25 ml. of freshly prepared 10% solution of phthalic anhydride in anhydrous pyridine. The mixture after refluxing for an hour is hydrolyzed with 50 ml. of distilled water. The solution is made homogeneous with 25 ml. of methyl alcohol, and the acid is titrated with 1 N standardized NaOH to a phenolphthalein end point. The MIBC is calculated from the amount of phthalic anhydride consumed by the esterification, which is the difference between the acidity of the blank (25 ml. of 10% solution of phthalic anhydride without sample) and the refluxed sample. Correction was made for the volume change in the water removal step assuming that no MIBC is lost. Several spiked hexone samples were run to check the possible loss of a MIBC azeotrope in the water removal step. Fifty milliliters of water saturated hexone were spiked with 813 mg. of MIBC (approximately 1.5% by weight) and analyzed. The recovery was 841 mg. of MIBC, 3% high which is sufficiently accurate. The 25 ml. blank of 10% phthalic anhydride in pyridine after hydrolysis requires approximately 32.5 ml. of 1 N NaOH to titrate to a phenolphthalein end point. As a difference of 0.1 ml. of 1 N NaOH for a 50 ml. sample is equivalent to approximately 0.02% MIBC in hexone, the titration should be carefully controlled.

Polarographic Determination of Uranium (W. H. Davenport, P. F. Thomason)

The routine analytical groups have been using the colorimetric thiocyanate[3] method for determining uranium in the range of 200 to 1000 micrograms, and the fluorimetric[4] method in the range of 0.01 to 1.0 micrograms. There has been a need for a method between these two ranges for the

(1) Hexone Specifications Memo Dr. J. Marsden to Dr. O. H. Greagor, H.E.W. July 15, 1948.
(2) Elving, P. J., and Warshowsky, B., Ind. and Eng. Chem., Anal. Ed., 1006, (1947).
(3) Currah, J. E., and Beamish, F. E., Colorimetric Detn. of Uranium with Thiocyanate, Anal. Chem. 19, 609, 1947.
(4) Sadowski, G. S., et al, The Fluorimetric Detn. of Uranium, Part I, CNL-23.

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Redox process solutions. Recent work has shown the solutions may be analyzed polarographically in the range of 10 to 200 micrograms of uranium per milliliter. The procedure is to determine the wave height at -0.20 volts vs. the saturated calomel electrode in a supporting electrolyte of 0.1 N HCl as recommended by Tishkoff[1].

As some of the Redox solutions contain $Al(NO_3)_3$ and $K_2Cr_2O_7$, interference from these ions was investigated. Aluminum nitrate in amounts 0.65 molar did not cause appreciable errors. However 0.1 M $K_2Cr_2O_7$, as expected, overlapped the uranyl wave. It was found that as much as 0.02 molar $K_2Cr_2O_7$ could be tolerated if the chromium was reduced to the chromic ion with hydrazine. The diffusion current became less pronounced when the chromium exceeded 0.02 molar to 0.001 molar uranium, probably due to oxidation products of hydrazine.

A calibration curve for uranium was made by running polarograms of various concentrations of UNH in 0.1 N HCl with a Model XX Sargent polarograph. The dropping mercury electrode with a falling time of 2.9 seconds was used versus the saturated calomel electrode. Five milliliters of solutions containing 10, 20, 50, 100, and 200 micrograms of uranium per milliliter were placed in the cell degassed with nitrogen and their polarograms recorded. The calibration curve appears in Figure 1. The micrograms of uranium per milliliter were plotted versus microamperes rather than molar concentration as the routine analytical group makes it a practice to report other analyses as micrograms of uranium per milliliter.

Hexone solutions of uranium can not be analyzed for U directly using the polarographic method. An aqueous solution of U containing as little as 1% hexone gave a peculiar wave.

It was found that a hexone solution containing 100γ U/ml. could be stripped with an equal volume of 0.1 N HCl. If the aqueous solution is heated to boiling to remove dissolved hexone, the solution may then be analyzed by the polarographic method described above.

The polarographic method should prove to be a valuable supplement to the other methods. Dr. M. T. Kelley has designed a simple polarograph for the routine group and it is being constructed by the instrument group.

Synthesis of Thoron (benzene-2-arsonic (1-azo-1) 2 hydroxynaphthalene 3-6, disulfonic acid) (F. J. Miller, P. F. Thomason)

Several grams of thoron which is used for the colorimetric determination of thorium were synthesized without difficulty according to the directions given by Kuznetsov[2]. The temperature must be carefully controlled to 0° - 4° C. during the diazotation steps otherwise the synthesis is straightforward. A comprehensive step by step report[3] on this synthesis has been issued by Iowa State College.

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

Report completed and issued as ORNL-161.

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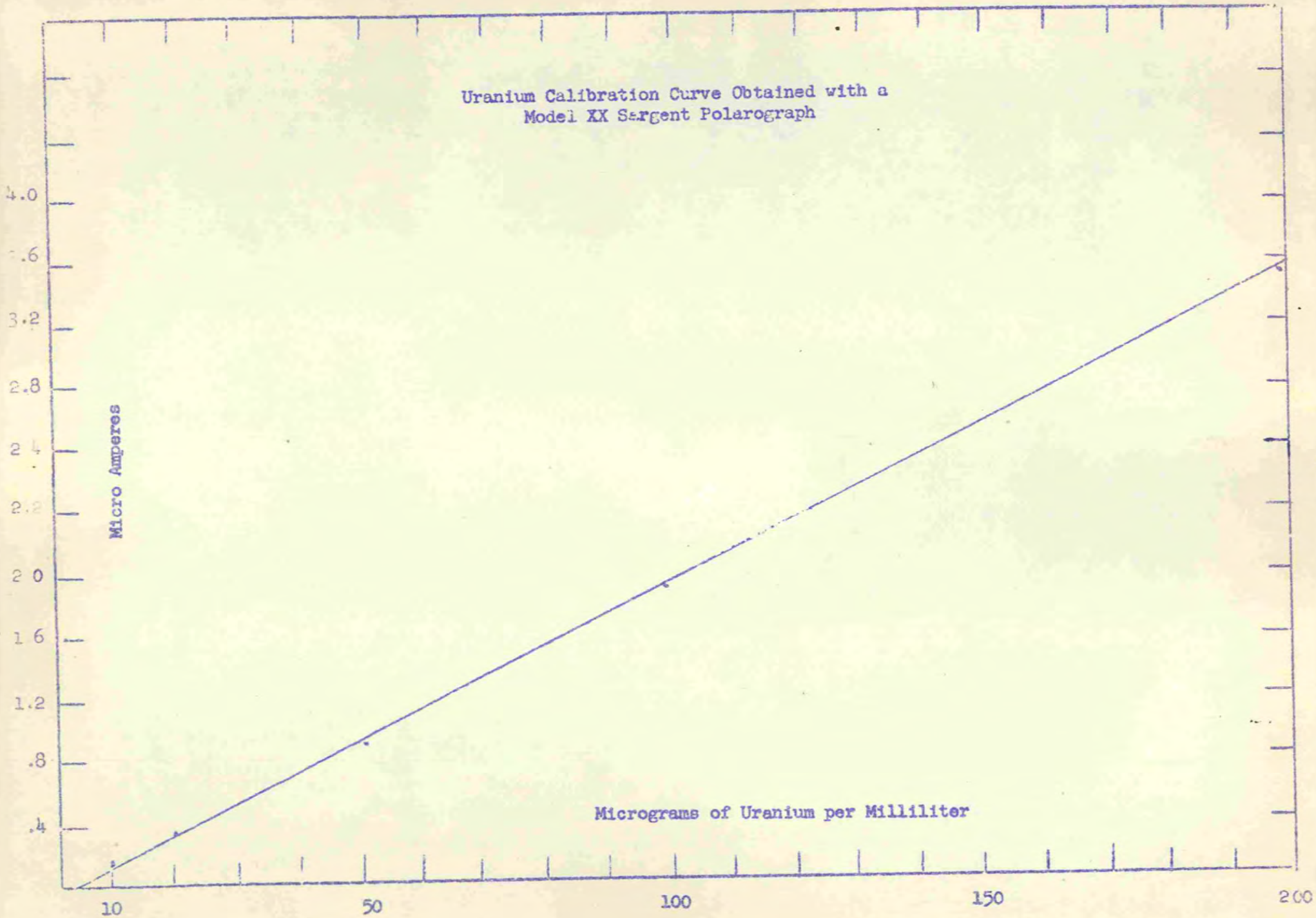
(1) Tishkoff, G. H., Polarographic Analysis of Uranium AECD-2005.
(2) Kuznetsov, V. I., J. Gen. Chem. (U.S.S.R.) 14 914-19 (1944).
(3) Reed, S. A., Byrd, C. H., and Banks, C. V., Preparation of the Di Sodium Salt of 1(O-arsonophenylazo0-2-naphthol-3,6-disulfonic acid (Thoron) ISC-26.

[redacted]


Uranium Calibration Curve Obtained with a
Model XX Sargent Polarograph
Micro Amperes
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
.8
.4
Micrograms of Uranium per Milliliter
10
50
100
150
200

[redacted]

Fluorophotometry (H. L. Hemphill, P. F. Thomason)

The new fluorophotometer model 475, serial no. 101 was calibrated and uranium glass standards were made for a reference for future adjustment of the instrument. This instrument was sent to the A. E. C. for comparative studies with other project fluorimeters.

Several changes in the optical system of this instrument by Dr. M. T. Kelley resulted in a more stable fluorimeter. The major change was installing a reflector of shorter focal length in order to focus the ultra-violet source more sharply upon the sample dish. This permitted removal of the Fresnel lens used on the older models which diffused the ultra-violet light rather than focussing it. The filter change of 5874 to 5860 removed more of the reflected visible spectrum of the AH-4 mercury arc ultra-violet source. The increased efficiency in this optical system resulting from these changes permitted a reduction in the gain required of the multiplier tubes and a consequent increase in stability. The sodium fluoride flux blanks now read approximately 10 microamperes as compared to 30 microamperes on the former instrument. This 10 microamperes is equivalent to approximately 0.4 milli-gamma of uranium.

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Radiochemical Analyses - Research and Development

Summary

Work has been done on the decay schemes of I^{131}, Ag^{110}, and Cl^{36}. Low-thickness plastic absorbers have been made, and standards for routine counting are being prepared. Comparison of NBS and ORNL beta geometry standards has been made. Methods of determining total Pu, and Pu valence states by TTA extraction have been developed, and a method for determining Am in Pu samples is being investigated. Work on activation-analysis methods has begun, and development of a new radiozirconium analysis has continued.

I. Decay Scheme of Ag^{110} (W. S. Lyon)

Betas of 2.82 and 0.52 Mev, and several gammas have been found. The observation of M. Deutsch (1) that over 50% of the "beta rays" are absorbed by 2 mg. absorber has been verified, but the soft radiation seems to be conversion electrons. Coincidence counting will be used in an attempt to devise a decay scheme from the observed data.

II. Decay Scheme of Cl^{36} (S. A. Reynolds)

Absorption curves on purified Cl^{36}, using ordinary end-window counters, and the proportional beta counter (2), indicate a 0.7 Mev beta, no X-ray (from K-capture or internal conversion of gamma), and no gamma. Approximately 26 microcuries of Cl^{36} gave a reading on the gamma ionization chamber equivalent to 1.4×10^{-3} rd Co^{60}. This is equivalent to annihilation radiation from 0.04 μc of a positron emitter. Thus the fraction of Cl^{36} decaying by positron emission must be at most 0.2%. If a gamma ray of ordinary strength (e.g., 1 Mev) were present, its maximum percentage would be 0.3%. A very weak gamma would be detected less efficiently, but no such radiation was found in the absorption curves. It is probably safe to conclude that at least 99% of Cl^{36} decay is simple beta emission. On this basis, an approximate calculation of the half-life was made, using the equation

$$\lambda = \frac{A\,M}{6.02 \times 10^{23}(nvt)\sigma}$$

$$T\,1/2 = \frac{0.693}{\lambda}$$

A = Specific activity of bombarded chlorine
= $0.16\ mc/g = 6 \times 10^{6}\ ds^{-1}g^{-1}$
M = Atomic weight
nvt = $3.5 \times 10^{20}\ cm^{-2}$, max.
σ = 32.3 barns (3)

The half-life is found to be 7×10^{5} years, in fair agreement with Overman's value (3), 10^{6} years.

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(1) M. Deutsch, Phys. Rev. 72, 527.
(2) G. W. Leddicotte, unpublished work.
(3) R. T. Overman, MDDC-857

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III. Decay Scheme of I^{131} (W. S. Lyon)

The decay scheme (two betas, four gammas) given in unpublished data of Deutsch (4) has been verified except for the weaker beta, which is masked on the spectrometer curves by conversion electrons. An attempt to find this beta by coincidence-absorption methods gave indeterminate results. Further work is awaiting installation of a coincidence device on the spectrometer.

IV. Coincidence Corrections for High Counting Rates (W. A. Brooksbank)

A plate, consisting of two samples of Co^{60}, has been made up according to the directions of T. P. Kohman (5). It will be used to determine the coincidence correction for counting rates in the range 25,000 - 100,000 cts./min. with a G-M tube of the usual type connected to a scale of 1024.

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

U_3O_8 beta standards and radium gamma standards are being made. The brass plates for the beta standards are still in the shop, but several "experimental" gamma standards have been fabricated. Full growth of radon and daughter activities is awaited in order to determine the sample size of Ra solution to give 5000 - 7000 gamma counts per minute (second shelf) in the finished standards. Both beta and gamma standards will be calibrated by counting them on ten or more G - M counters with tubes set at the usual distance from the second shelf. The results will be averaged, and the averages used as calibrated values for the standards which are to be used as normalizing standards for slight variations in tube efficiency, etc. After calibration, the standards will be distributed to all analytical groups using G-M counters.

Six standards of Co^{60} for gamma counting and six of C^{14} for beta were requested by Butenhoff of A.E.C. These were prepared. The counting rate of C^{14} was determined on the proportional beta counter, and that of Co^{60} on a regular G-M counter through the gamma sandwich.

VI. Thin Plastic Absorbers (W. S. Lyon)

Absorbers of thicknesses ranging from 40 micrograms per square centimeter to 3 mg/cm^2 have been prepared. Formvar is dissolved in ethylene dichloride to make solutions of various strengths. To prepare a film, some solution is evaporated on a glass slide; the resulting film is stripped off under water, dried; the area is measured and the weight found to determine mg/cm^2. Absorption curves were taken on the C^{14} standard (Borkowski's) so that in the future new absorbers can be calibrated simply by counting.

VII. Activation Analysis (G. C. Bell, S. A. Reynolds)

A. Hf in Zr.

Two samples were run. In each case it was known from spectrographic analysis that sufficient impurities were not present to interfere with gamma measurements on activated Zr and Hf (cross sections 0.4 and 10 barns). Weighed samples of pure ZrO_2, pure HfO_2 and unknown were wrapped in thin aluminum foil, bombarded sixty-four hours, and the samples were allowed to

(5) T. P. Kohman, MDDC-905.

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decay for a week to remove 17-hour Zr. Readings were then taken on the gamma chamber. The gamma radiation due to a definite amount of Zr was found from the ZrO_2 sample. The percentage of Zr in the unknown (from spectrographic results) was used to compute the radiation due to Zr in the unknown. (Since the % Hf in the unknown was known to be low, the weight of Zr could have been taken to be equal to that of the unknown, to a good approximation.) The difference between the total radiation of the unknown and its radiation due to Zr was the radiation due to Hf. This figure, compared with the radiation from the HfO_2, gave the amount of Hf in the unknown.

Sample	Spectrographic	Activation
1	0.31 % Hf	0.29% Hf $^{+}_{-}$0.03
2	1.9%	2.0% $^{+}_{-}$0.2

B. Na in Al.

Two aluminum samples were submitted by Reynolds Metals Company. They were run spectrographically by M. Murray, and colorimetrically by E. Hanig. In the first activation analysis, samples of metal and weighed samples of C. P. Na_2CO_3 for standards were bombarded 64 hours in the pile. It was known that Al yields Na^{24} by the reaction Al^{27} (n, α) Na^{24}, in addition to the Na^{24} produced by capture of neutrons by the Na impurity. To correct for this, samples of metal and Na_2CO_3 were surrounded by cadmium foil during the bombardment. Thus only neutrons of energy above the Cd "cut-off" were effective in this case. It was assumed that the yield of Na^{24} from the n, α reaction would be the same in the unshielded and in the Cd-shielded samples, so that by subtracting the amount of Na activity found in the shielded sample from the total in the unshielded sample, the amount of Na activity due to neutron capture could be found. In the first experiment no chemical separations were made. It was believed that by making measurements on the gamma chamber and taking a decay study, the Na^{24} could be differentiated from the other gamma activities. Apparently the activity from copper (as suggested by Dr. G. E. Boyd) interfered, however, because results obviously too high were obtained. In the second run the aluminum samples were dissolved in HCl, Na and Cu carriers were added, and H_2S and NH_4OH precipitations were made. The supernatant liquid, containing at least 80% of the Na^{24} (by experiment) was read in the gamma chamber against Na_2CO_3 standards. The samples decayed with half-lives of 14.5 - 15 hours. The results are believed to be within 25%, but an additional run will be made using beta-counting technique rather than gamma measurements.

Na in Al

Sample	"Fusion-Leach" (6)	Spectrographic	Colorimetric	Activation
Foil	0.0012%	0.003%	0.0045%	0.001% $\pm$ 0.0003
Ingot	0.0002%	0.003%	0.0030%	0.001%

C. Radioisotope Target Materials

Eight samples of target materials have been received from J. A. Cox

(6) A. E. Rising, letter to J. A. Cox.

[redacted]

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for determination of yield of product in a month's bombardment, as well as identities and quantities of by-products. Spectrographic analyses are being run on them.

VIII. Total Pu by TTA Extraction (F. L. Moore)

The method given by Moore and Hudgens (7) for determination of total Pu by TTA extraction has been tested on solutions containing high concentrations of $Al(NO_3)_3$ (up to 1.6 M), and on solutions containing much Pu (VI). Recoveries of 98 - 100% have been obtained. It has been shown that no aluminum extracts under the conditions of analysis. Methods involving the use of La carrier appear not to work in $Al(NO_3)_3$ solutions. Fluoride precipitation gives coprecipitation of AlF_3, and $La(OH)_3$ precipitation, with the Al being converted to aluminate by excess NaOH, gives only about 80% recovery. The reason for this is not known at present.

IX. Valence States of Pu

A. TTA Extraction (F. L. Moore)

In order to use the TTA method for determination of valence states, by virtue of the extractibility of Pu(IV) under conditions giving no extraction of Pu(III) or Pu(VI), several facts had to be established. It was found that essentially no reduction of Pu(VI) took place during four ten minute extractions of a Pu solution containing 0.02 N $NaBrO_3$ as holding oxidant. The tracer contained 47.7% Pu(IV), 52.3% Pu(VI).

Extraction	% Pu Extracted
1st	47.8
2nd	0.2
3rd	0.1
4th	0.05

The effect of $Al(NO_3)_3$, up to 1.6 M, in causing increased extractibility of Pu(VI) has been investigated. Little, if any, effect was noted. A tracer solution containing about 9% Pu(IV), 91% Pu(VI), with 0.02 N $NaBrO_3$ was used.

$Al(NO_3)_3$ Conc.	% Pu Extracted
1 M	9.2
1.6 M	10.9

Using the same tracer as above, the effect of 0.25 M $NaNO_2$ on Pu(VI) extractibility was tested. Two runs gave 8.8% and 9.2% Pu extracted. The effect on Pu(IV) of destroying polymer by heating with conc. HNO_3 was tested. A Pu(IV) tracer solution was used. After HNO_3 treatment, 100% recovery of Pu(IV) was achieved.

It has been demonstrated that depolymerization of process Pu solutions will almost always be necessary. A typical example is afforded

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by a solution which, untreated, gave 5,000 c/m/ml by the TTA method; heated with conc. HNO_3, 144,000 c/m/ml. This solution was 1.2 M in $Al(NO_3)_3$ and had remained for a week at pH 2.

Since depolymerization is necessary before TTA extraction, it is obvious that solutions containing considerable quantities of oxidizing agents cannot be run by this method since the valence state of the Pu would be changed by treatment with an oxidizing agent in the presence of hot HNO_3. The maximum tolerable amounts of such materials as $NaBrO_3$ and $K_2Cr_2O_7$ have not been determined, but they are probably quite low.

If a solution contains no polymer, the TTA method gives good results for "reduced" plutonium (Pu(r) = Pu(III, IV)). The results for "oxidized" Pu (Pu(O) = Pu(VI)) are unsatisfactory, but this figure can be obtained by subtracting Pu(r) from total Pu. (The latter figure is almost always required.)

Procedure

Add sample. Adjust acidity to 1 M HNO_3. Make the solution 0.2 M in $NaNO_3$. Perform two ten minute extractions with half-volume portions of 0.5 M TTA-benzene solution. Evaporate a portion of the organic phase, or strip as in method for total Pu (7).

B. Precipitation (J. D. Gile)

The Berkeley method, using $K_2Cr_2O_7$ as holding oxidant, has proven satisfactory for use in aluminum-free solutions. Using 0.02 N $NaBrO_3$, about 30% of the Pu(VI) is reduced. Higher concentrations of $NaBrO_3$ have not been tested. Methods of analysis in the presence of high concentrations of $Al(NO_3)_3$ have not been investigated.

X. Am in the Presence of Pu (S. A. Reynolds)

Samples of pure Am^{241} and Pu^{239} were obtained. The Pu was re-purified by oxidation with $KMnO_4$, precipitation of LaF_3 carrying any Am present, and reduction of the Pu, followed by precipitation with LaF_3. The precipitate was dissolved with nitric and boric acids, and the solution diluted to serve as tracer.

The method investigated thus far has been given in its essentials (8). It depends on the fact that Pu is rather readily oxidized to the hexavalent state while Am remains in the trivalent state in aqueous solution (9). The hexavalent state of Pu will not carry on LaF_3; hence, after vigorous oxidation it should be possible to precipitate Am on LaF_3, free of Pu. This method appears satisfactory in the absence of $Al(NO_3)_3$. After one oxidation with 5% $KMnO_4$ at 50° less than 1% of the Pu remains to be precipitated on LaF_3. After dissolving the LaF_3 and re-oxidizing, less than 0.01% of the Pu remains. A minor difficulty is that MnO_2 has precipitated with the LaF_3 giving too much self-absorption for accurate alpha counting. This may be avoided by use of

(7) F. L. Moore, J. E. Hudgens, ORNL-153.
(8) S. A. Reynolds, Special Radioisotope Methods.
(9) K. A. Kraus, informal communication.

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another oxidizing agent, or the MnO_2 may be dissolved by use of an acid-reducing-agent wash. 5% $Na_2Cr_2O_7$ has been tested but gave only about 60% oxidation in an hour at 50°.

If $Al(NO_3)_3$ is present, the Al must be removed in some way. Use of a $La(OH)_3$ precipitation with the aluminum "complexed" as aluminate gave only 85 - 95% recovery of Am. This problem will be investigated further.

XI. New Radiozirconium Analysis (R. H. Powell)

The investigation of the colorimetric method for determining Zr carrier yield has continued along the lines described in the previous quarterly report (10).

Since it is planned to use TTA extraction for purification of Zr, with stripping of the organic phase with dilute hydrofluoric acid, a means of decomposing the $ZrF_6^{=}$ complex has been sought. It has been noted (11) that boric acid - up to 0.1 M - does not form complexes with Zr. A large excess of H_3BO_3 has been added in alcohol solution to complex fluoride. No effect of H_3BO_3 on color formation has been noted in solutions free of fluoride. With fluoride present, no color is noted with boric acid absent. With boric acid and HF, a transmittance curve is obtained which is different from that obtained in fluoride-free solutions. Different materials have been tested as solvent for the boric acid and dispersion medium for the Zr lake. Although H_3BO_3 is most soluble in methanol, results using this alcohol are poor. Ethyl, n-propyl, isopropyl, n-butyl, isobutyl, and tert-butyl alcohol, glycerin, and acetone have been tested. Isopropyl alcohol gave the best results thus far. Unfortunately, it appears that boric acid is slowly esterified by the isopropyl alcohol solvent. At least, the boric acid solutions become less effective in complexing fluoride after standing a week or more. If the "esterified" solution is allowed to stand in contact with HCl, the H_3BO_3 becomes "available" again.

XII. Manuals and Reports.

J. D. Gile's report, "Literature Search on the Rare Gases", will be issued soon.

"Special Radioisotope Methods", a manual by S. A. Reynolds has been issued.

(10) ORNL-176, p. 76.
(11) URCL-101, p. 53.

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4. ANALYTICAL SERVICE

Summary of Analytical Work for Quarter
August 15 to November 15, 1948
In Man Hours

	Radiochem. Dev.	Ionic Dev.	Spectro-chem. Group	General Radiochem. Group	General Ionic Group	Water Analysis	Lab. and Semi-Works Control	Pilot Plant Control	Production Control	Totals
Personnel Tech.	7	5	4	10	2	1	2	4	4	39
Non-Tech.	2	2	-	13	2	3	8	22	16	68
Biology	Development only		1							1
Physics			6	14	11					31
Chemistry			104	204	7					315
Technical			11	3416	361	1488	9920	12150		27346
Metallurgy					3					3
Operating Div.			53	1487		193			5269	7002
Health-Physics				552						552
K-25		100	1	76						177
NEPA			4							4
		100	180	5749	382	1681	9920	12150	5269	35331

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IX. Radioactive Particle Problem

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Determination of Particulate Radioactivity in Air

C. J. Borkowski, P. Chastagner

To determine particulate activity in air it was decided to use an Air-Way Sanitizor vacuum cleaner which is well suited for this purpose, is commercially available and can be used without making any additional changes.

Air is sucked through a disposable paper filter bag in the cleaner at a rate of 27 cu. ft. per minute. Particles of 1 micron and larger are collected in the bag with over 95% efficiency. The filter paper bag has a surface density of 12 milligrams per sq. cm. After a suitable collection period the paper bag is removed, the top cardboard ring cut off with scissors and the open ends of the bag scotch-taped. The bag can then be handled without danger of losing any of its contents. If desired the total activity in the bag can be measured by rolling the bag into a form of a cylinder and sliding it into a piece of tubing 3 inches in diameter and 12 inches long. The tubing is placed around an Eck-Krebs type G-M counter 12 inches long which is supported at one end. The counter is thus along the axis of the tube and filter bag.

For a one hour collection period of uncontaminated air the counting rate immediately after collection is of the order of 300 c/m at 5% geometry. After 24 hours the counting rate decays to background. This activity is primarily the decay products of radon and thoron everpresent in air. Alpha activity in air can be detected with the Air-Way vacuum cleaner by cutting the bag open after a suitable collection period and exposing the inside of the bag to a flat type air alpha proportional counter.

The vacuum cleaner bag was radioautographed with 10" x 12" Eastman no-screen x-ray film in order to detect particulate activity. The flat bag was placed on a 10" x 12" piece of 1/4" plywood and a sheet of film in its yellow paper wrapper was placed on the film and the resulting sandwich was taped together and sealed light tight with scotch photographic tape. This operation was performed in a photographic dark room under a Wratten series 2 safelight.

A 24 hour radioautograph exposure was made and the film developed in DuPont x-ray developer to a slightly higher contrast than recommended for normal x-ray work. To attain the maximum sensitivity it is necessary to place the film directly into the folded flat bag so that the film is in intimate contact with the dust or active particles which usually become imbedded in the paper bag. This is the preferred procedure and will reveal many more small particles than the previously described procedure.

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Eastman no-screen x-ray film was used because Cobb and Solomon (R.S.I. 19, 441 (1948)) had found this type of film to be the most sensitive for autoradiography.

Preliminary air sampling with the first Air-Way cleaner indicated that radio-active particles down to one micron size could be collected and radio-autographed.

The number of active particles collected varied from 0 to 75 per 1000 cu. ft. of air collected. The higher values were collected near the base of the Pile stack and in the 105 building. The beta disintegration rate of the particles varied from 20 d/m to 10,000 d/m. Fig. 1 shows a photograph of the Air-Way vacuum cleaner and the disposable filter bag before and after cutting off the cardboard top.

It was also of interest to determine particulate activity on various indoor and outdoor surfaces. For this purpose the 10" x 12" Eastman no-screen x-ray film was placed in intimate contact with the surface. In order to make a light tight, low surface density, and reasonably weather resistant package for the film, two .001 inch layers of aluminum foil were used.

The film was packaged in the following manner: sheets of .001 inch aluminum foil 26 inches long were cut from a roll 12 inches wide; a sheet of foil was folded in the middle to form a 12" x 13" folder and a sheet of film inserted so that there was an inch of foil on all sides. The folder was then sealed by making two successive half-inch flat folds on each side and the open end. The envelope thus formed was then wrapped in another sheet of foil in the same manner. The wrapping of the film was done in a photographic darkroom using a Wratten series 2 safelight.

The films thus wrapped were laid on the surfaces to be radioautographed and covered with 1/4 inch plywood. Twenty-four hour exposures were usually made.

The results of the direct autoradiographs indicated:

1) The area around the base of the 105 stack was covered with radio-active particles varying from a few to several thousand particles per square foot. Fig. 2 shows a typical radioautograph of a flat concrete surface taken at the base of the stack.

2) The number of active particles per square foot diminished both in number, size, and activity with distance from the pile stack.

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3) The interior of the 105 building was badly contaminated with particulate activity which was loose and could become airborne. Fig. 3 shows a radioautograph of a surface taken near the control desk of the Pile building. Fig. 4 shows an air sample taken inside of the 105 building and indicates about 75 particles per 1000 cu. ft. of air. The particles vary in disintegration rate from 10 d/m to several thousand d/m. This sample represented an 80 hour collection period with the Air-Way cleaner. More active particles were collected in air samples taken in this building than in any other location tested.

After it was shown that the Air-Way cleaners were satisfactory air samplers for particulate activity, ten additional cleaners were purchased for the Health Physics Division use.

Determination of Particulate Radioactivity in Pile Exhaust: (R.L. Livingston)

A completion report, ORNL-197, is now in preparation. A summary of the material worked on includes cyclone sampling of the exit gases from the pile over the period September 23 to November 7, 1948; filter tests after the cyclone separator; multiple filter and charged wire experiments in a separate flow system to demonstrate the presence and amounts of fission gases present in the pile gas stream; and a continuous monitor for the fission gases using a moving electrically charged wire.

The sampling systems were originally installed to find out the quantity and nature of solid matter present in the pile air stream and to correlate this with pile operating conditions, pile instrumentation, health physics ground and air sampling, etc. The samples collected were studied by many members of the Chemistry Division.

In the course of the sampling work, short-lived fission gases were found in the air stream. Studies (with H. A. Levy) of these gases were made in a separate sampling flow system, and finally a continuous monitor was built to record the concentration of these gases in the air stream at all times while the pile is operating. This monitor in effect measures the amount of exposed fissionable material in the pile lattice, or the "cleanliness" of the pile. The monitor is quite specific for just short-lived fission gases. A preliminary report of the monitor will appear in ORNL-197, and a final report will be issued separately at a later date.

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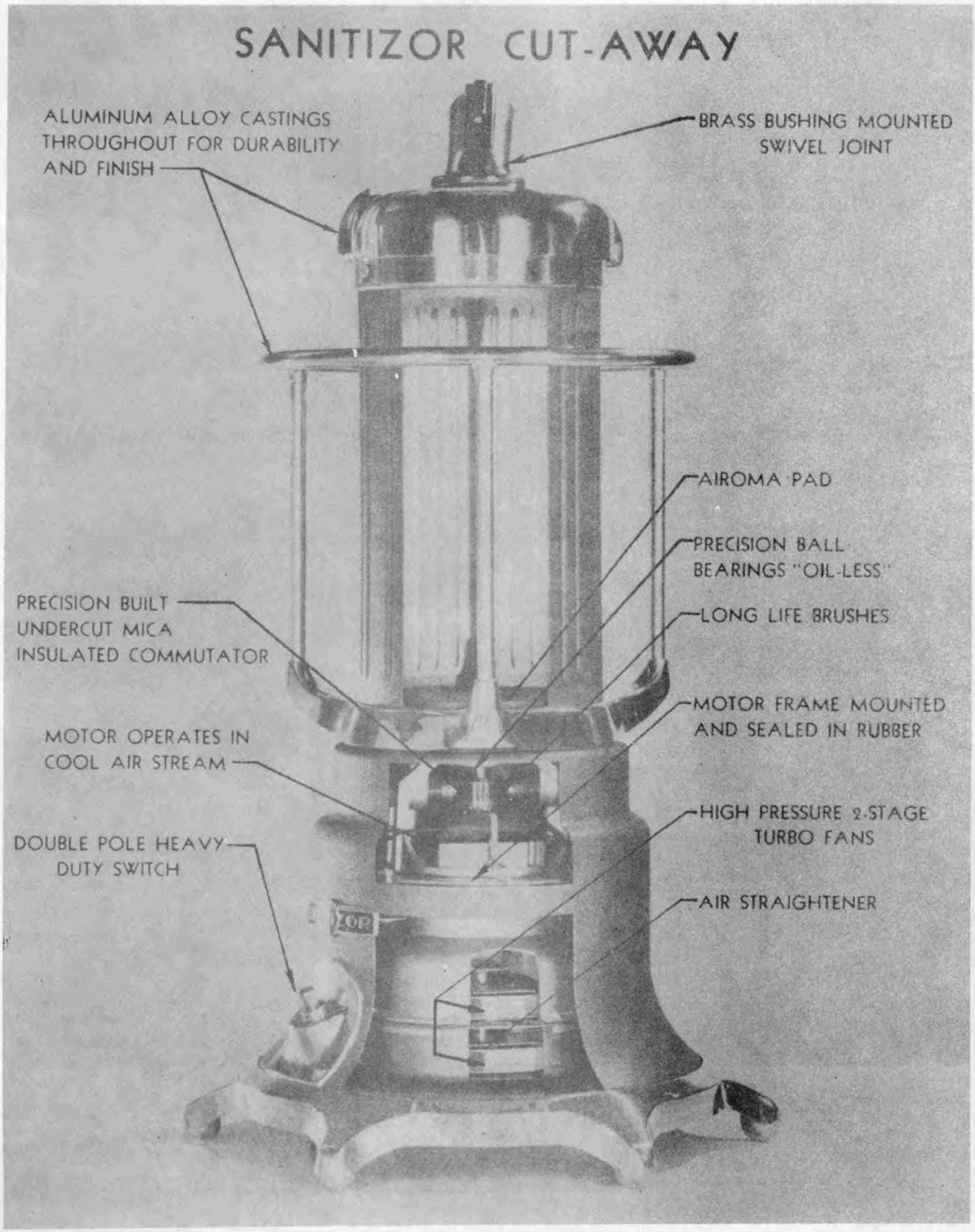
SANITIZOR CUT-AWAY
ALUMINUM ALLOY CASTINGS THROUGHOUT FOR DURABILITY AND FINISH
BRASS BUSHING MOUNTED SWIVEL JOINT
AIROMA PAD
PRECISION BALL BEARINGS "OIL-LESS"
LONG LIFE BRUSHES
PRECISION BUILT UNDERCUT MICA INSULATED COMMUTATOR
MOTOR FRAME MOUNTED AND SEALED IN RUBBER
MOTOR OPERATES IN COOL AIR STREAM
HIGH PRESSURE 2-STAGE TURBO FANS
DOUBLE POLE HEAVY DUTY SWITCH
AIR STRAIGHTENER

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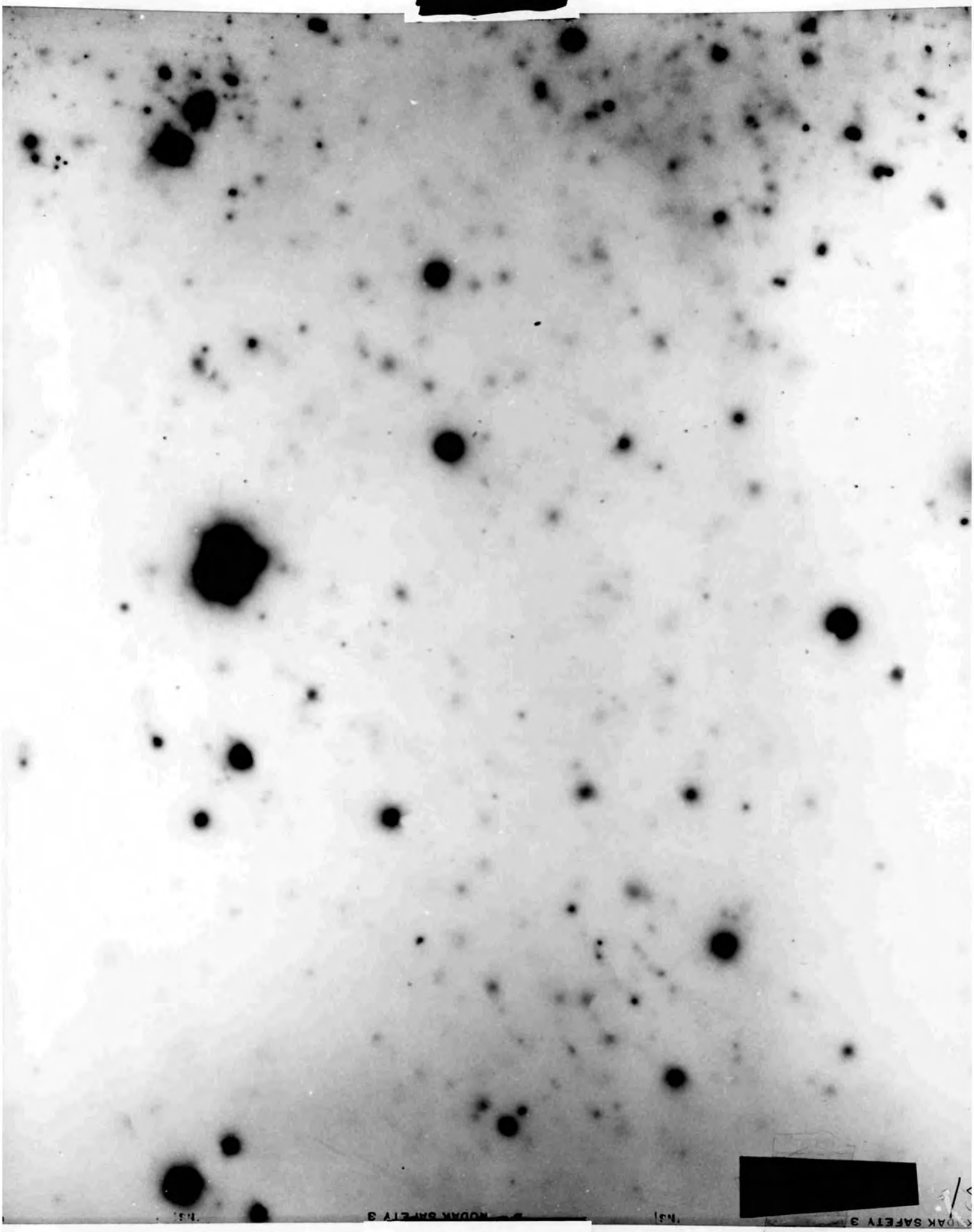

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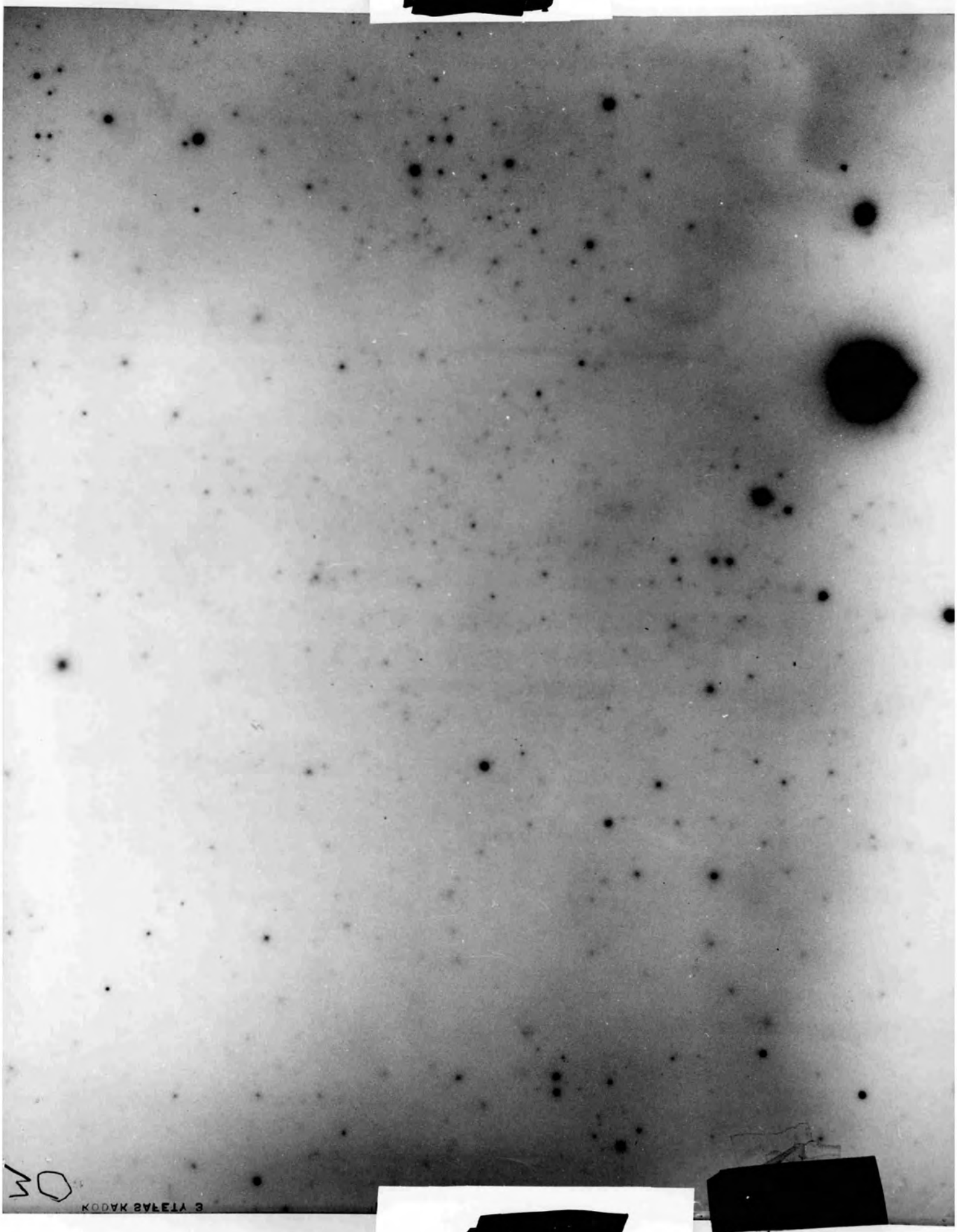

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