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REPORT OF THE CHEMISTRY DIVISION
FOR THE MONTHS MARCH, APRIL, MAY, 1948

E. H. Taylor

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TABLE OF CONTENTS

Page No.

Abstract..... 4

1. REACTOR FUELS

Inorganic, Physical and Nuclear Chemistry

Hydrolytic Behavior of the Heavy Elements..... 8
Oxidation-Reduction Potentials of Plutonium Couples..... 8
Hydrolytic Behavior of Ce(IV)..... 8
Isolation of Americium from Plutonium Waste Solutions..... 18
Solvent Extraction of Protactinium from Fluoride Solutions..... 18

Process Chemistry

Chemical, Physical and Nuclear Properties of Heavy Isotopes..... 25
Process for Recovery of U^{233} from Thorium..... 25
The Recovery of Uranium from Enriched Piles..... 26

2. RADIOISOTOPES

A Method of Analyzing Radioactive Decay Curves..... 54

Xenon Cross Sections as a Function of Energy

Xe Retention Experiments..... 55
Calibration of Assay Equipment..... 59
Recovery of Cs^{135}..... 65

Research Relating to Radioisotope Production

The Removal of Alpha Emitters from Fission Products..... 70
Recovery of Ru^{106} from Metal Wastes..... 73
Recovery of Cs^{137} from Metal Wastes..... 75
Separation of Fission Rare Earths..... 76
C^{14} from Beryllium Nitride..... 78

Experimental Use of C^{14}

The Synthesis of Low Molecular Weight Intermediates Containing C^{14}..... 83
The Study of Reaction Mechanisms with C^{14}..... 85
Development of Analytical Procedures..... 88

3. SUPPORTING CHEMICAL RESEARCH

Inorganic, Physical and Radiochemistry

The Fundamental Chemistry of Ruthenium..... 89
Ion-Exchange Separations: Rare Earth Purification..... 94
General Radiochemistry: Heavy Rare Earth Radioisotopes..... 94
The Separation of Hafnium and Zirconium by Citrate Precipitation..... 96
Studies of Extractions with β-diketones..... 98

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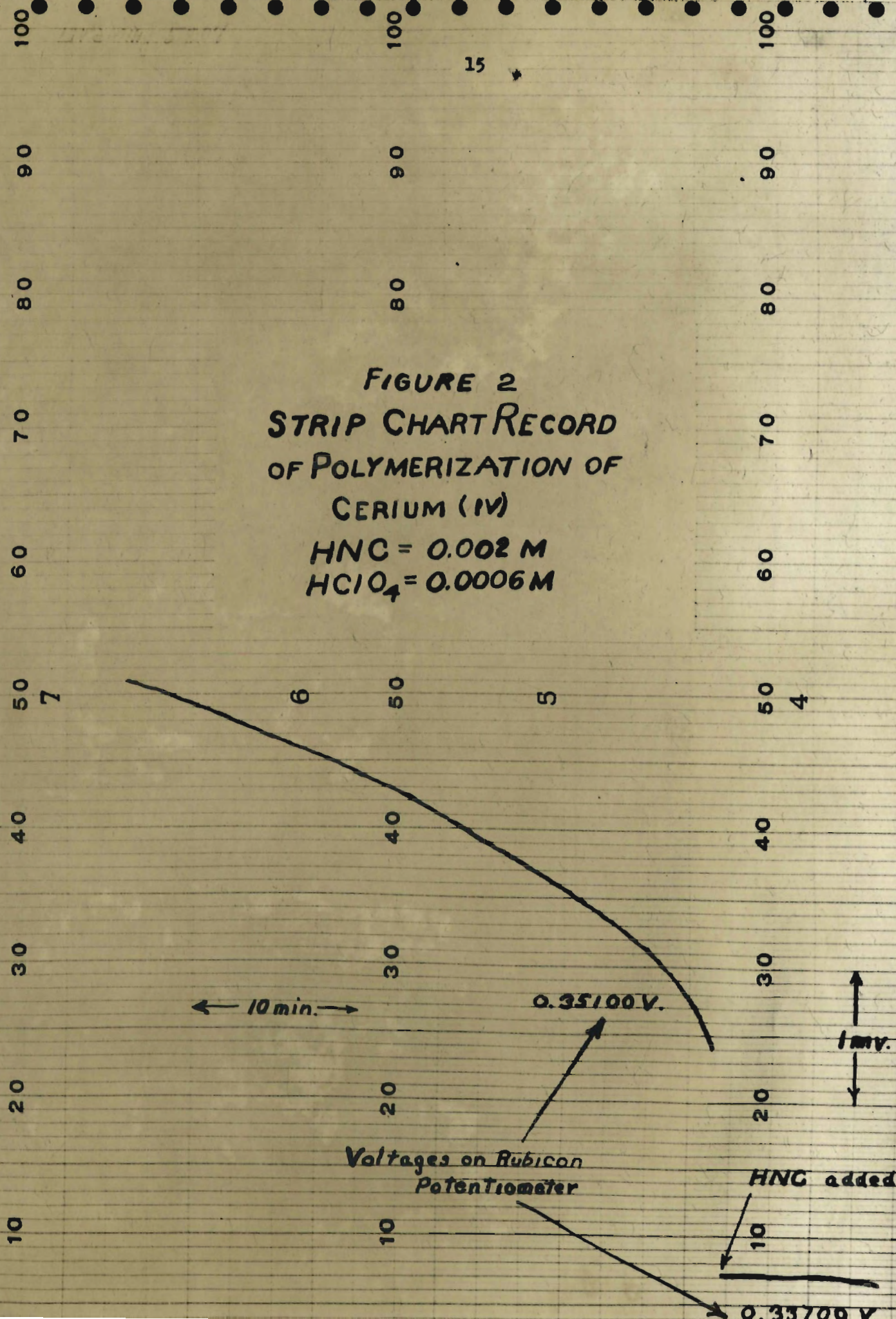
FIGURE 2
STRIP CHART RECORD
OF POLYMERIZATION OF
CERIUM (IV)
$HNC = 0.002\ M$
$HClO_4 = 0.0006\ M$



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Page No.

Inorganic, Physical and Radiochemistry (Continued)

Hard Gamma Rays from Y^{88} 101
Solid Chemistry of Ruthenium 103
The Crystal Structure of $KRuO_4$ 103
Separation of the Long Lived Rare Earth Activities in Fission 105
Production and Measurement of K-Series X-Ray Spectrum of Element 61 115
Effects of Heavy Particles on Water and Aqueous Solutions 116
A Simplified Equation of State Applicable to Surface Films 132
A Comparison of Two Theories of Multilayer Adsorption 132
The System Uranyl Sulfate - Water 134
Cloud Chamber Studies 138
Calorimetry of Radioactivity 139

Analytical Chemistry

Electroseparation of Radiosilver from Palladium 141
Preparation of Silver-Free Palladium Metal 141
Studies of the Electrodeposition of Traces of Silver 141
Polarography with Solid Electrodes 142
Polarographic Analysis of Radioactive Cobalt Solutions 144
Determination of Tantalum with Alizarin 144
Colorimetric Determination of Ruthenium 144
Dissolving Gold and Silver Alloys by Electrolysis 147
Conductometric Titration of Aluminum with Solium Fluoride 147
Determination of 2-Hexylpyridine in Hexone 148
Colorimetric Determination of Nitrate 148
Volumetric Determination of Uranium in Alloys Using Ferric Sulfate as the Titrant 148
Remote Control Apparatus 149
The Decay Scheme of $Columbium^{95}$ 151
The Beta Spectra of $Strontium^{90}$ and $Yttrium^{90}$ 152
A Radiochemical Method for Plutonium 157

Diffraction and Microscopy

Electron and Photomicrographs of Powders 162
Corrosion Studies 162
Preparation of Evaporated Films 163
Crud 164
Nuleic Acid 164
K-25 Work 164
Miscellaneous Photography, Metallographic Polishing, Apparatus Design, Instrument Maintenance, etc 164
High-Temperature Vacuum Chamber for X-Ray Spectrometer 173
Crystal Structures of Beryllium Oxide 174
On the Possibility of a Cubic Structure of Ruthenium Dioxide Occurring in Calcined Barium Ruthenate 177
Miscellaneous X-Ray Diffraction Work 179

Instruments and Physical Measurements

Preliminary Experiments with Gas Tube Circuits 181
The Use of Proportional Counters in Coincidence Measurements 183
A Compact Beta Proportional Counter 184

4. ANALYTICAL SERVICE 185

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ABSTRACT OF QUARTERLY REPORT
CHEMISTRY DIVISION

1. REACTOR FUELS

In the current studies of the chemistry of the heavy elements in solution, work on the hydrolysis of Ce(IV), which is of interest in comparison with similar behavior of Pu, U, et al, has progressed to a point where qualitative conclusions may be drawn. In aqueous solutions Ce(IV) is hydrolyzed to $CeOH^{+++}$ as is the case with Pu(IV), but it does so in much more acid solutions than does Pu(IV) which is appreciably hydrolyzed only in solutions more alkaline than pH = 1.

The recovery of the sample of americium is proceeding satisfactorily, and the bulk of it is now in sulfuric acid solution ready for further separation by ion exchange.

One stage of the work on the solubility of thorium iodate has been completed and is being written up in a separate report.

The high temperature portion of the UO_2SO_4-H_2O system has been explored, and a region of two liquid phases partially mapped out.

The chemical work on the process for recovering uranium from enriched piles has been practically completed with the demonstration in the pilot plant of the adequacy of the present process. The additional work completed during this quarter has included further work on the extraction of Ru, on the use of organic amines to complex uranium and neptunium, and on the formation of solids in the present process.

The recovery of U^{233} by the chemistry division has been completed and about 9g. are available in about 160 ml. of solution. The special sample of U^{236} has been decontaminated and is awaiting transfer to Y-12 for the isotopic separation.

2. RADIOISOTOPES

Work on several phases of the Xenon problem has progressed during this quarter. The assay method appears to be in good shape after a number of studies to clear up doubtful points. The half-life of the short-lived isomer of Xe^{135} has been re-determined and found to be 15.3 minutes ± 2%. The fraction of the decay going by way of this isomer has been determined by coincidence counting methods to be about 20%. Other necessary studies have given figures for the loss of Xe to its expected during the PdI_2 precipitation.

The large scale separation of element 61 has yielded as by-products millicuries of 2-3 year Eu^{155} and 20 year (approximately) Sm.

Excellent photographs have been obtained at Y-12 of the K series X-ray lines of element 61, confirming the identity of the material.

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Abstract of Quarterly Report (Continued)

The ion exchange method for preparing radiochemically pure yttrium, which was described in the last quarterly report, has been adopted by the operations division.

Rare earth fission products have now been satisfactorily separated from Pu and Am by the use of a more nearly completely sulfonated sample of the ion exchange resin, Dowex 50. Of the elements Y, Eu, 61, Nd, Pr, Ce, all were separated satisfactorily from Pu and all except 61 from Am, and all except Eu and Y were better than 99% free of each other.

In the course of the work on the beryllium nitride process for C^{14}, it has been found that the unirradiated Be_3N_2 contains about 0.15% carbon and that the reagents used in the H_2SO_4-CrO_3 recovery process introduce a negligible further amount. In the synthetic work with C^{14}, the principal results during this quarter have been the demonstration on a tracer scale of the reduction of $C^{14}O_2$ to methanol by lithium aluminum hydride, the preparation of ethanol by the reduction of acetoxy magnesium iodide with lithium aluminum hydride, and the obtaining of formaldehyde in yields of 65 to 70% by the pyrolysis of methyl triphenylmethyl ether.

A quantity of 104 millicuries of barium carbonate has been obtained by repurification. This material is intended for use as radioactive standards for C^{14}.

3. SUPPORTING CHEMICAL RESEARCH

A number of spectroscopically pure rare earths have now been prepared by ion exchange. Amounts varying from o.3 to 16 grams of the following are now available:

Tm_2O_3	Dy_2O_3
Er_2O_3	Tb_4O_7
Ho_2O_3	Sm_2O_3

Bothe's assignment of 34 day Yb to mass 169 has been confirmed by deuteron bombardment of purified Tm, a mono-isotopic element, followed by an ion exchange separation of Yb formed by the reaction d,2n on the Tm.

The 125-day Tm^{170} has been shown by β-ray spectrometer studies to be a pure beta emmitter with a maximum energy of 0.98 ± 0.0. Mev.

Experiments using commercial Zr (containing a few percent of hafnium) and tracer hafnium have shown that the separation by citrate precipitation is not sharp as had been reported from another laboratory.

Further studies have been completed of the distribution of various metal ions between water and benzene in the presence of TTA. The following equilibrium constants have been measured: Y 1.9×10^{-7}, La^{+++} 7.9×10^{-10}, Zr $\sim 2 \times 10^{7}$, hafnium $\sim 7 \times 10^{6}$. In the case of the latter two metals, it was found that both were slow in coming to equilibrium,

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Abstract of Quarterly Report (Continued)

with the hafnium being the slower of the two. The difference in the values for Zr and Hf is obviously not enough for a single stage separation but shows some possibility for a multi-stage process. However, a test with macro amounts showed that a precipitate was formed in 1 M HCl solution containing 10 mg/ml of Zr when TTA was added.

The most consistent results so far obtained for the decomposition of pure water in the pile have been obtained in silica ampoules with practically no free gas space. It has been demonstrated that the decomposition is entirely suppressed by a small addition of hydrogen. It has further been found that hydrogen peroxide leads to higher dissociation pressures by an inhibitory effect on the back reaction, although it is, of course, one of the reactants in the back reaction.

In solutions of HCl and KCl in water the steady state hydrogen pressure reached in the pile has been shown to increase with increased concentrations of both hydrogen and chloride ions.

Ampoules containing T_2O which have reached a steady state of pressure from the decomposition induced by the tritium betas show a drop in pressure when exposed to pile radiation.

The hope that pure sulfuric acid might, because of its resistance to radiation decomposition, be a suitable medium for a homogeneous pile has been dissipated by the demonstration that H_2SO_4 containing UO_2SO_4 decomposes with a greater gas evolution per fission than UO_2SO_4 in water. The excess gas produced includes SO_2.

The new phase of BeO reported previously has been studied further and has been shown not to be formed below 1900° C but to be formed above 2000° C. The impurity apparently responsible for its stabilization has not been determined. More lines have been found in its diffraction pattern through the use of samples richer in the new phase, indicating that it may possibly have a non-cubic structure.

A new form of RuO_2 which may be of cubic structure has been identified in calcined barium ruthenate.

A preliminary investigation has been made of the use of glow tubes in various circuits of interest such as scalers, multi-vibrators and coincidence circuits. These afford an economy in power and in number of other components over circuits using conventional high vacuum tubes, but have the disadvantage of being slower. The work on proportional beta counters has extended to the construction of one or two models for particular applications in the chemistry division.

The calorimetric work on tritium has shown that the average energy of the tritium beta is 5.6 Kv ± 3%.

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Abstract of Quarterly Report (Continued)

The analytical research work on polarography and electro-deposition is being written up in final form. Analytical methods have been developed for the colorimetric or polarographic determination of radioactive cobalt, tantalum and ruthenium as a means for the absolute assay of radioisotope samples of these elements. In the development of apparatus for conducting analytical work remotely, a method has been devised for measuring microliter volumes of solution by electrical capacity measurement. In connection with radiochemical analysis, decay schemes of Cb^{95}, Sr^{90} and Y^{90} have been studied with the β-ray spectrometer.

ANALYTICAL SERVICES

The number of analyses performed during this quarter was about 20% greater than in the last, due principally to increased demands from the programs of the technical division. About 34% of the analyses came from the 25 pilot plant, about 30% from laboratory and semi-works control, about 25% from the radioisotope program and the remainder (ca. 16%) from research and other functions of the laboratory.

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1. REACTOR FUELS

Inorganic, Physical and Nuclear Chemistry

Hydrolytic Behavior of the Heavy Elements
(C. F. Nelson, K. A. Kraus) (P. A. CX3-2)

Work on this problem has recently been summarized in reports CNL-19 (February 1948) and ORNL-23 (March 1948). Only a few supplementary experiments have been carried out which were not covered in these reports. Since these experiments did not change, the conclusions reached previously, they will not be reported here.

Oxidation-Reduction Potentials of Plutonium Couples
(G. E. Moore, K. A. Kraus) (CX3-2)

Work on this problem has continued since the previous quarterly report (CNL-37). The measurements have been extended to the Pu(V)/(VI) couple, and the Pu(IV)/(VI) couple as a function of acidity. Since the results were not sufficiently reproducible they will not be reported at this time.

Hydrolytic Behavior of Ce(IV)
(K. A. Kraus, R. W. Holmberg, F. Nelson) (P. A. CX3-2)

Since the previous quarterly report (CNL-37) where some work on this problem was reported, a considerable amount of additional information has been accumulated. Although the results are still primarily qualitative it appears desirable to summarize the work at this time, since a number of rather unique features have become apparent, not the least of these being an opportunity to study more advanced regions of hydrolysis which in most cases appear practically inaccessible to experimentation.

1) Introduction. During an investigation of the hydrolytic behavior of uranium (IV) and plutonium (IV), it was found [1] that their aquo-complexes, which exist in strongly acidic solutions in the absence of complexing agents, hydrolyze according to the equation:

$$X^{+4} + 2H_2O \longrightarrow XOH^{+3} + H_3O^+ \qquad (I)$$

The negative logarithms of the acid constants (pK values), were found to be 1.45 and 1.55 for U(IV) and Pu(IV), respectively, in 0.5M ClO_4^- solutions.

In addition it was found that U(IV) and Pu(IV) undergo polymeric reactions, which in the latter case occur with great rapidity at a pH where only approximately 50% of the aquo-complex has hydrolyzed according to equation 1.

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The polymers formed, though they closely approximate the formula of the hydroxide, are positively charged.

It is of interest to compare the hydrolytic behavior of cerium (IV) with that of these "actinides". If as a first approximation it is assumed that the hydrolytic reactions of these "rare-earth" ions of identical charge are primarily determined by the size of these ions one expects that Ce(IV) and Pu(IV) would behave very similarly since their crystal radii are almost identical. Actually very large differences in their behavior were found except for the approximate pH region where they undergo polymerization.

The primary difference between Ce(IV) and Pu(IV) lies in the acidity of their aquo-complexes. In the case of Pu(IV) the aquo-complex does not undergo appreciable hydrolysis until ca pH 1 is exceeded. In the case of Ce(IV) it is doubtful that, except perhaps in the most strongly acidic perchlorate solutions, any appreciable concentration of the non-hydrolyzed aquo-complex exists. It is interesting (and at first confusing) that Ce(IV) undergoes a hydrolytic reaction somewhere between pH 1 and 2 as Pu(IV) does; however, this is a reaction of a basic ion of Ce(IV) and not that of the non-hydrolized aquo-complex itself. On the other hand the pH regions, where reasonably rapid polymerization occurs, are about the same for Ce(IV) and Pu(IV).

2) Experimental Procedure. Two experimental methods of approach have been selected:

1) Spectrophotometry of solutions of ammonium hexanitratocerate (HNC) in perchloric acid solutions of varying acidity and usually of constant ionic strength ($\mu = 1$) and (2) measurements of the pH changes on dissolution of known amounts of HNC in perchloric acid solutions of known concentration and sufficiently high ionic strength to avoid significant changes in the activity coefficients of the ions involved.

All experiments were carried out in a thermostated room at 25 $\pm$ 1°C.

The spectrophotometric investigations were carried out with a Beckman quartz spectrophotometer which was carefully calibrated with respect to wave lengths using a mercury arc.

The pH measurements were carried out with a vibrating reed electrometer, coupled with a Rubicon type B high precision potentiometer and a Brown Electronic strip-chart recorder*. The full scale deflection on the recorder

* We are indebted to Mr. C. J. Borkowski and Mr. J. K. East for assistance in assembling and testing the equipment.

corresponded to 10 millivolts, yielding a reading accuracy of $\pm$ 0.01 millivolts. In general, it was attempted to balance out the potential changes with the Rubicon potentiometer.

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The pH measurements were carried out using a glass electrode-saturated KCl-calomel electrode assembly. The saturated KCl was separated from the test solution by an intermediate salt bridge of 1M sodium nitrate. The pH cell was enclosed in a shield constructed of 1/4" aluminum.

In general, the measurements of the pH changes were satisfactory although occasionally troubles (slow drifts of the potentials) were encountered probably due to changes in liquid junction potentials (λ). In favorable cases the measurements appeared to be reliable to $\pm$ 0.02 millivolts.

The experiments were carried out by dissolving small amounts of HNC in perchloric acid solutions of known acidity. The $HClO_4$ solutions of concentration less than 1M contained sufficient sodium perchlorate to keep the ionic strength at $\mu = 1$. If not otherwise noted all data were taken as a function of time, extrapolated to the time of mixing, and the resulting "zero"-time values then used.

The HNC was of high purity as shown by gravimetric and spectrographic analysis. Analysis for free acid in the material was carried out by dissolving a suitable quantity in a weakly acidic solution of sodium iodide and measuring the pH change after reduction appeared to be complete. Since Ce(III) is only weakly acidic, this method for detecting free acid in the HNC is quite sensitive. It was found that the material contained a maximum of 0.005 moles H_3O^+ per mole of cerium. It is possible that a considerable fraction of even this small amount of acid found was due to a residual small fraction (0.1%) of the Ce(IV) in the form of its polymer, which could have been formed simultaneously with the reduction of Ce(IV) and which once formed would probably reduce only slowly.

A study of nitrate free Ce(IV) solutions has only recently been attempted since it was feared that the Ce(IV), especially in perchlorate solutions, might undergo slow changes in species (e.g. polymerization) thus complicating the picture considerably. Although there is now good evidence that such polymeric reactions occur at low acidity, it is doubtful that complicating reactions occur at very high acidity and a corresponding study of perchlorate solutions was started and some of the results have been included. The nitrate-free perchlorate solutions were prepared by a modification of the method of Sherrill and co-workers[2] and assayed by titration with ferrous ammonium sulfate.

3) Results. Only little work appears to be available in the literature from which the ionic species existing in Ce(IV) solutions could be deduced and in addition the available data are contradictory. Thus, Noyes and Garner[3] concluded from potential measurements of the Ce(III)/(IV) couple in nitric acid solutions that Ce(IV) is neither (partially) hydrolyzed nor complexed by nitrate ions. Sherrill, King and Spooner[2], on the other hand, concluded from their potential measurements of the Ce(III)/(IV) couple in perchlorate solutions that Ce(IV) is extensively hydrolyzed even in 2.4M $HClO_4$, in apparent contradiction to the work of

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Hoyes and Garner. In their work on the sulfate complexes of Ce(IV) Moore and Anderson[4] did not consider partial hydrolysis of Ce(IV) in perchloric acid solutions. Similarly G. F. Smith[5] did not consider partial hydrolysis, and instead postulated that a hexaperchlorate complex exists in strong $HClO_4$ solutions. It is interesting that recently Miss Evans[6] concluded from the small difference in the entropy of Ce(III) and Ce(IV) that Ce(IV) is partially hydrolyzed in 0.5 M $HClO_4$.

Our data, to date, confirm in essence the conclusions of Sherrill et al., and of Evans, namely that Ce(IV) is partially hydrolyzed even in rather concentrated perchloric acid solutions. We have found that the hydrolytic reactions of Ce(IV) in the acid range studied (ca 0.01 to 10 M $HClO_4$) are very complex and the various reactions have not yet been completely elucidated. The description of the results which follows, if thus essentially qualitative, and should only be considered preliminary.

It was hoped that accurate measurement of the pH changes occuring on addition of HNC to weakly acidic perchloric acid solution would permit estimation of the average composition of any basic ions formed, i.e., estimation of the average number of moles hydroxide ions per mole of Ce (to be referred to as "hydroxyl number" n) in the average formula $Ce(OH)_n^{+4-n}$. In this connection it was of particular interest to see if there is a pH range where the hydroxyl number is two, as would be expected, if a ceryl ion, exists, as has been proposed.

With the extremely sensitive pH equipment which had been assembled it became feasible to determine the amount of acid liberated on dissolution of comparatively small amounts of HNC even in reasonably acidic solutions. The procedure was to measure the voltage change of the cell previously described when small amounts of HNC were added to the perchlorate solutions of accurately known acidity (m_{h_1}).

From the pH measurements the final acidity (m_{h_2}) was obtained and hence the average hydroxyl number "n" from the relationship

$$n = \frac{m_{h_2} - m_{h_1}}{m_{Ce}} \qquad \text{(II)}$$

where m_{Ce} is the concentration of Ce(IV).

If the change in liquid junction potential ($\Delta \lambda$) and the change in the activity coefficients of the oxonium ions (γ) are known (or negligible) the final acidity m_{h_2} can be obtained from the change in cell potential ΔE through the equation

$$-\log \frac{m_{h_2}}{m_{h_1}} = \frac{\Delta E}{R} - e \qquad \text{(III)}$$

$$\text{where } e = \frac{\Delta \lambda}{R} - \log \frac{\gamma_{h_2}}{\gamma_{h_1}} \qquad \text{(IV)}$$

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and where R is a constant at any acidity and would be expected to be ca 0.059 volts. Actually, it was found, be measuring the voltage of the cell over a considerable concentration range of acid, that R generally is less than 0.059 volts though approaching this value at low acidities. The considerable deviation of R from 0.059 is somewhat surprising since all solutions contained enough $NaClO_4$ to keep the ionic strength $\mu = 1$ throughout. It is not clear to what extent this change in R is due to changes in liquid junction potentials and to what extent to changes in the activity coefficients of the oxonium ions at constant μ.

The correction term "e" (equation 3) would depend on the composition of the solutions. It would be expected to be very small for the dilute solutions studied. It is however, not completely negligible for the more concentrated HNC solutions, since, assuming e = o, calculation of the average hydroxyl number, though for large ΔE values showing a decrease with increasing acidity, showed a pronounced increase when ΔE became small. When e = ca. 0.5 millivolts is used for 0.01 M HNC solutions (and proportionally smaller values of e for the more dilute HNC solutions) n is found to decrease continuously with increasing acidity m_{h_2}.

This general magnitude of the value of "e" was substantiated since ΔE = ca 0.4 millivolts was observed on making a 0.5M $HClO_4$ solution 0.01 M in thorium nitrate and 0.02 M in NH_4NO_3. Since Th(IV) would not be appreciably hydrolyzed in 0.5 M HCl , ΔE in this case would be expected to be almost identical with "e".

The results of the pH measurements have been summarized in Figure 1, where the average hydroxyl number "n" has been plotted as a function of the final acidity m_{h_2}.

Several series of measurement have been carried out over the concentration range 3×10^{-4} to 1×10^{-2} M, the concentration in each series being kept constant. For most of the solutions spectrophotometric data were also collected in the wave length region 400 - 450 mμ . The extinction coefficients observed at 430 mμ have been included in Figure 1.

Depending on the cerium concentration and the initial acidity the observed potential changes ΔE were between 0.5 and 50 millivolts.

It may be noticed from Figure 1 that at cerium concentrations less than ca. 2×10^{-3} M, the average hydroxyl number is practically independent of Ce(IV) concentration and only dependent on the acidity of the solutions. At higher Ce(IV) concentration "n" appears to be concentration dependent. The spectral data on the other hand show considerable concentration dependence even at the lowest concentrations studied indicating that different species (probably of different degree of condensation) are present at different concentrations even when their average formula is the same.

As was to be expected "n" was found in general to increase with decreasing acidity. At low acidities and low concentration of Ce(IV) "n" appears to be ca. 2.35 over a considerable range of acidities. This

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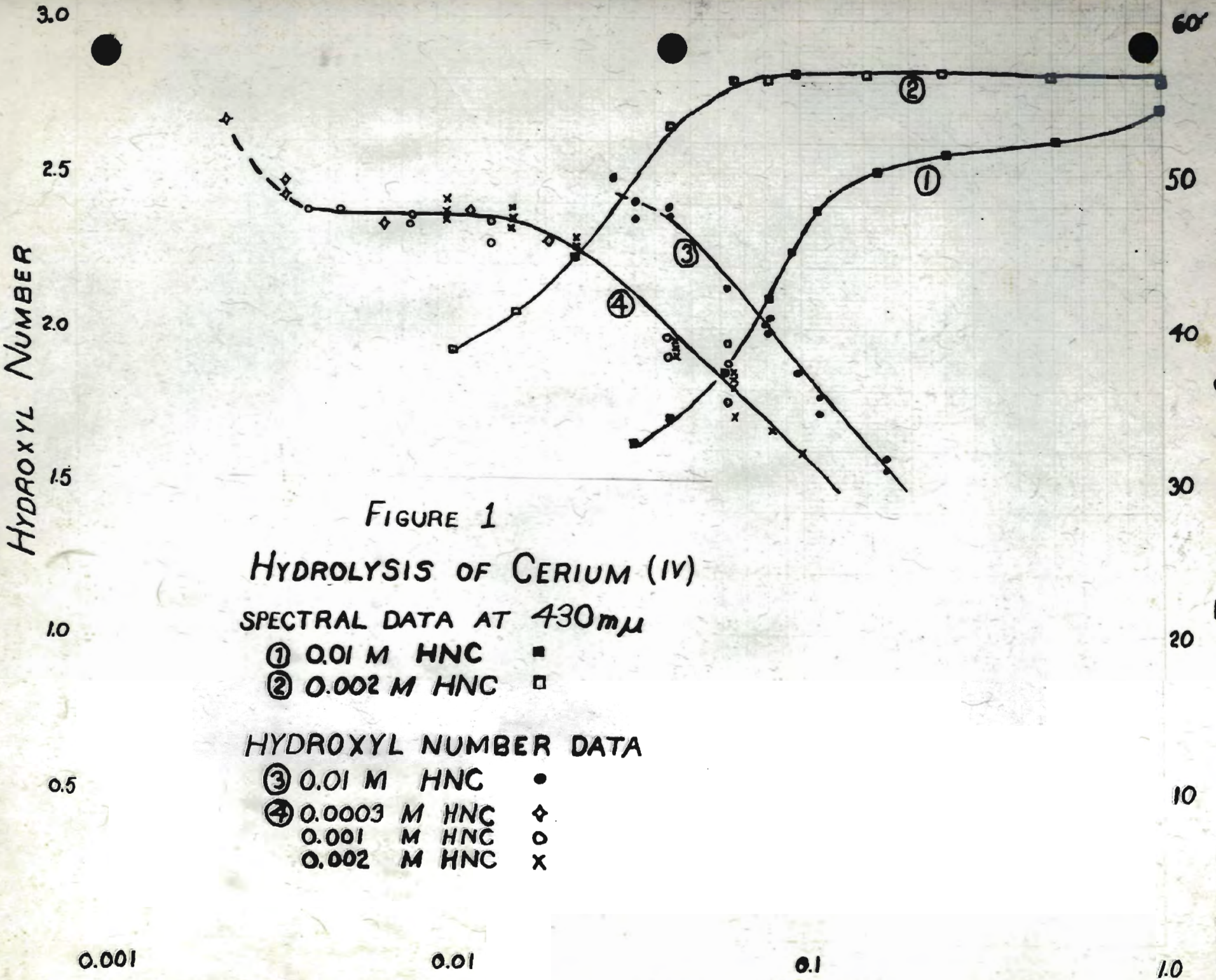

FIGURE 1

HYDROLYSIS OF CERIUM (IV)

SPECTRAL DATA AT 430mμ

① 0.01 M HNC ■
② 0.002 M HNC □

HYDROXYL NUMBER DATA

③ 0.01 M HNC ●
④ 0.0003 M HNC ◇
0.001 M HNC ○
0.002 M HNC X

Drawing # 5806

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suggests that a particular aggregate (e.g., a trimer) and/or some of its condensation products have somewhat higher stability than other hydrolysis products. In connection with the question of the existence of a ceryl ion it might be pointed out that the measurements do not support assumption of such a species. The curve of "n" vs. acidity does not show any plateau at n = 2, but rather at n = 2.35, the difference being considered to be outside the experimental error.

Furthermore, even these aggregates are not of very great stability, since in the same pH range where they appear to occur, the properties of the solutions change continuously with time. The data in Figure 1, as was previously stated, only refer to the species existing in the solutions at, or close to the time of mixing.

Both the spectrophotometric and the pH measurements reflect these time dependent changes. Thus the extinction coefficients in the 400 mμ range decrease on standing and the acidity of the solutions (i.e., the average hydroxyl number) increases. The average composition of the species appears to approach that of the hydroxide. The increase in acidity of the solutions is illustrated in Figure 2, the data for which were obtained under conditions where the changes with time are reasonably rapid. The rate of reaction increases with decreasing acidity of the solutions and with increasing concentration of Ce(IV). Although no molecular weight determinations have been carried out, it is most probably that the time dependent changes are due to a polymerization reaction and the product finally formed is probably similar to the "colloidal" cerium (IV) hydroxides whose occurrence is well known.

In view of the magnitude (and uncertainty) of the term "e" in equation 3 it was not possible to determine the change of the average hydroxyl number n with sufficient precision at acidities larger than 0.1M. The only certain statement which can be made is that at higher acidity "n" for a 0.01 M Ce(IV) solution must be less than ca. 1.5.

Only the spectral changes thus permit calculation of the average formula at acidities larger than 0.1 M. Not sufficient data have been accumulated as yet to permit calculation of equilibrium constants. However, it has been found that some spectral changes occur throughout the acidity range 0.1 to 10M $HClO_4$. Of these, some of the spectral changes above 1M $HClO_4$ have been discussed in the previous report (CML-37) and, it may suffice here to say that these spectral changes are dependent on acid, Ce(IV) and NO_3^- concentration. No dependence of the data on ClO_4^- (i.e., $NaClO_4$) concentration was found, making it unlikely that a perchlorato-complex, as suggested by G. F. Smith[5] is formed.

It can be seen from Figure 1 as well as from the data in CML-37 that the spectral data are practically acid independent (though concentration dependent) between ca 0.1 and ca 1M $HClO_4$. However, further investigation of this acid range (using either HNC in $HClO_4$, or "pure" Ce(IV) - perchlorate solutions) in the ultraviolet (210-350 mμ) showed pronounced spectral changes as shown in Figure 3. Thus the acid range where any spectral

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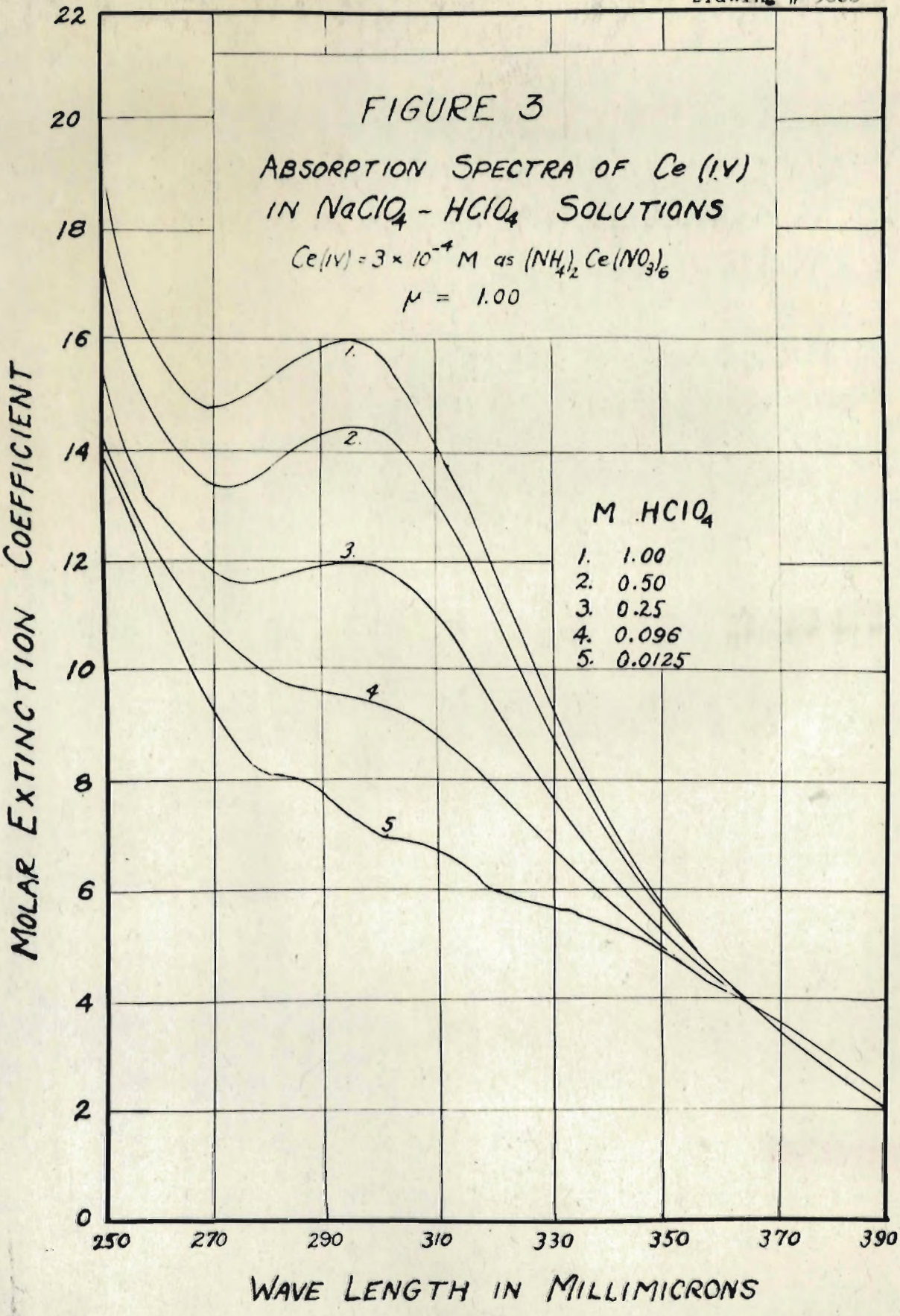
Drawing # 5808



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changes can be found extends all the way from the polymerization region to concentrated $HClO_4$, showing that some changes of species occur throughout this range. It is hoped that a more thorough analysis of the spectral data will permit identification of some of the equilibria involved. At the present time one can express the data in terms of average hydroxyl numbers "n" which at lower acidity than 0.1M are as described above and above this acidity n is less than ca 1.5 though apparently still larger than zero in 10 M $HClO_4$. Furthermore, it is evident that the complex equilibria involved mostly involve species which are at least dimeric, if not of higher degree of aggregation.

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(6) M. W. Evans, CN-3138, August 1945.

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

During the last quarter the isolation procedure described in the previous quarterly report (CNL-37) was tested further and the main body of the fluoride slurry was worked up using extensive fuming with sulfuric acid to remove fluorides. The bulk of the Am (and plutonium) is now available in the form of a sulfuric acid solution ready for the adsorption process.

During the sulfuric acid treatment considerable amounts of calcium sulfate separate. It was found, both in preliminary experiments and with the main body of the material, that considerable amounts of (5-20%) of alpha activity are retained by the precipitate. This activity is due to both Pu and Am, the latter being somewhat enriched. Experiments have been under way to develop methods for the extraction of the activity from the calcium sulfate though as yet no very satisfactory method has been found.

Solvent Extraction of Protactinium from Fluoride Solutions
(K. A. Kraus, A. Garen) (P. A. CX3-2)

1) Introduction: In the previous quarterly report[1] a few experiments on the extraction of protactinium from fluoride solution were described using di-isopropyl carbinol as solvent. It was found that, although fluoride ions markedly inhibit the extraction of Pa, addition of aluminum ions (to complex fluoride ions) is effective in again increasing this extractability.

It appeared of interest to further study the extractability of protactinium from such fluoride buffer solutions, where the fluoride concentration would be controlled by the stability constants of various metal-fluoride complexes. From such a study one might obtain:

1) information on the practicability of isolation procedures for Pa from fluoride systems, without previous removal of fluoride ions by other means (such as fuming or precipitation);

2) information regarding Pa-fluoride complexes, such as number of fluoride ions attached and stability constants; and

3) information on the stability constants of other metal-fluoride complexes, using protactinium (e.g., Pa^{233}) and its extractability as an analytical tool.

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The success of such studies appeared to depend mainly on the reproducibility of the results and the ease with which equilibrium could be attained. It was surprising that no such difficulties were encountered in view of the fact that the hydrolytic behavior of protactinium generally is considered rather unfavorable. It is true that in the Al-F-Pa system which was studied in some detail, ca. two hours of stirring were necessary to attain equilibrium. The aluminum-fluoride system itself, at low fluoride concentrations, has been reported[2] to slowly attain equilibrium, thus qualitatively at least accounting for the observed slowness of the reaction.

2) Experimental Procedure: Experiments have been carried out using aluminum and thorium to complex the fluorides.

1 ml samples of HCl solutions of Pa^{233} tracer containing $AlCl_3$ (or $Th(NO_3)_4$) and varying concentrations of HF were equilibrated for three hours with one ml samples of di-isopropyl carbinol using closed lusteroid vessels and magnetic stirring. In some cases equilibration was carried out for longer periods of time without signigicant changes in the results. Each set of experiments was carried out at constant Cl^-, H_3O^+, and metal concentration* (3.1 M HCl, 0.82 M $AlCl_3$ and 2.77 M HCl, 0.78 M $Th(NO_3)_4$).

*We are indebted to D. Lavalle and P. Thompson of the Analytical Section for analysis of the Al and Th solutions.

The Pa^{233} tracer was of high purity as shown by its decay curve.

The distribution coefficients

$$D_o = \frac{P_{aq}}{P_s} \qquad \text{(I)}$$

where P_{aq} and P_s represent the concentrations of Pa in the aqueous and solvent phases respectively, were determined by radio-assay for Pa^{233}. In most cases only one phase (the solvent phase, except for small values of D_o) was assayed, although in a number of cases both phases were assayed to establish the reliability of the results.

3) Results and Discussion:

The results of the experiments are given in Figure 1, where the observed distribution coefficients D_o have been plotted as a function of the ratio

$$R = \frac{F_o}{A_o - F_o} \qquad \text{(II)}$$

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Drawing # 5809

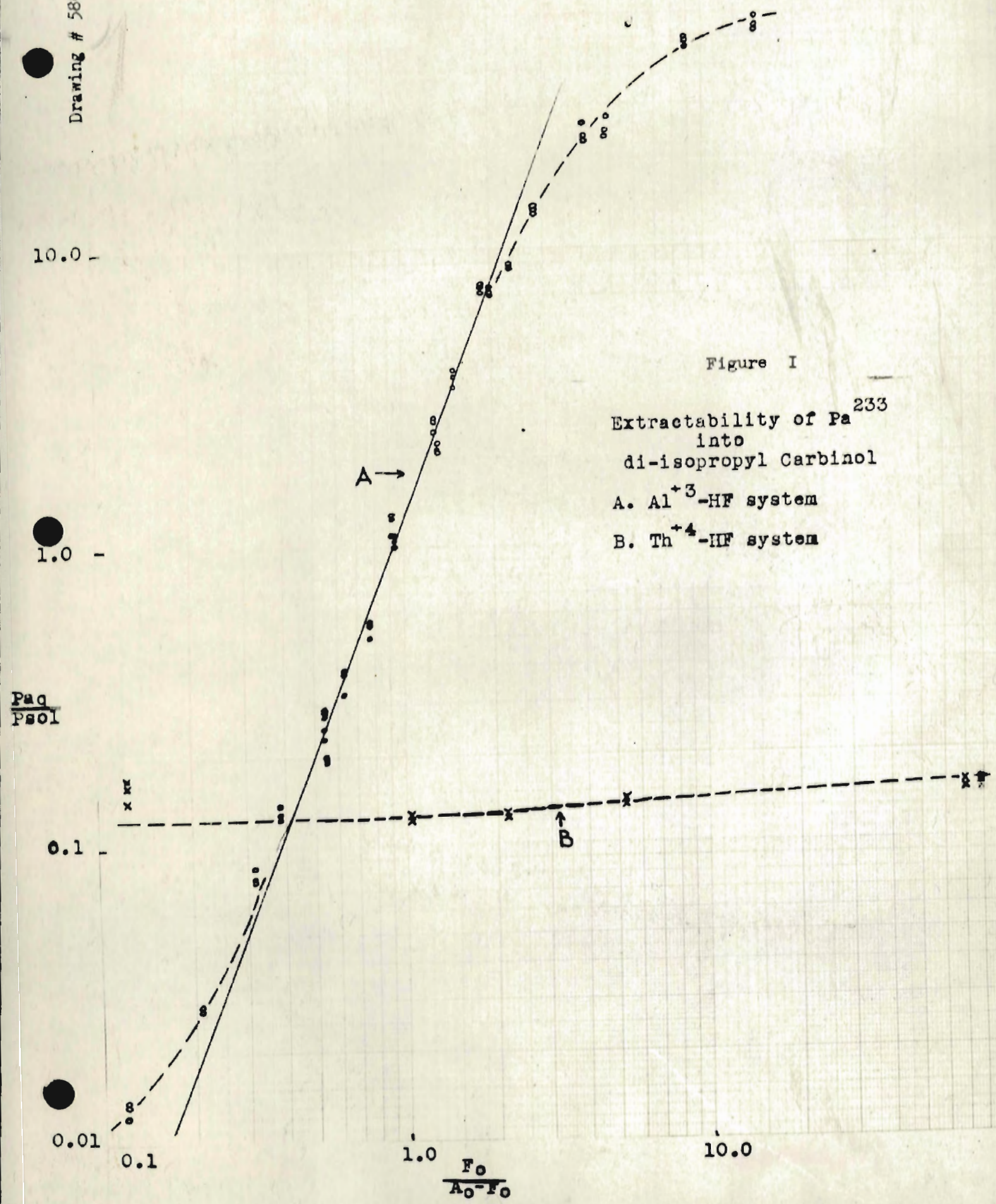

Figure I

Extractability of Pa^{233} into di-isopropyl Carbinol

A. Al^{+3}-HF system

B. Th^{+4}-HF system

[redacted]

where A_o and F_o are the initial concentrations of the metal ions (Al and Th) and of HF respectively.

For the positive ions selected, the constants for the reaction

$$X^{+n} + HF + H_2O \longrightarrow XF^{+(n-1)} + H_3O^+ \qquad \text{(III)}$$

are large. Let

$$K_{XF} = \frac{h\,X_F}{Xf}$$

where $h = [H_3O^+]$, $f = [HF]$, $X = [X^{+n}]$ and $X_F = [XF^{+n-1}]$ (IV)

and brackets indicate concentration.

Dodgen[3] reported K_{XF} for Th^{+4} to be ca 45000 at ionic strength μ = 0.5. From the data of Brosset and Orring[2] (using as acid constant for HF $K_a = 1.159 \times 10^{-3}$ [4]) K_{XF} for Al^{+++} can be calculated to be ca 1600 at ionic strength ca 0.5. These authors also reported that the constants K_{XF_2} for the reaction

$$XF^{+(n-1)} + HF + H_2O \rightarrow XF_2^{+(n-2)} + H_3O^+ \qquad \text{(V)}$$

for these ions are considerably smaller (K_{XF2} = 650 for Th(IV) and K_{XF2} = 120 for Al(III)). At the higher ionic strengths used here, the constants (equation 4) would be different, but probably still sufficiently high to permit the approximations

$$F_o = [XF^{+}(n-1)] \qquad \text{(VI)}$$

and

$$A_o - F_o = [X^{+n}] \qquad \text{(VII)}$$

for small values of R. At large values of R the approximations would not pertain, since then the higher fluoride complexes of the positive ions (see equation 5) would assume importance.

It can be seen from Figure 1 that addition of small amounts of HF to Pa-Al solutions causes a rapid decrease in the extractability of Pa (D_o increases) while addition of similar amounts of HF to Pa-Th solutions has practically no effect on the extractability of Pa.* This negligible effect

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*This is in agreement with the observations of Overholt and Steahly regarding extractability of Pa from HNO_3 - HF-Th solutions.[5]

---

of HF in Th solutions even pertains for R = 70, the largest value of R used.

[redacted]

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The difference between the two types of solutions is qualitatively as expected, since the stronger complexing agent (Th), also more strongly inhibits fluoride interference in the extraction. The conditions of the experiments however, are sufficiently different (e.g., the D_o values, i.e., the distribution coefficients in the absence of HF for the Al and Th systems differ very considerably) to make quantitative comparison not possible. The data intrinsically, however, should permit some conclusions regarding fluoride complexing of Pa, especially for the Al system. The discussion which follows was included to illustrate - in a simplified manner - the relationships involved.

Even in the absence of fluoride ions the aqueous layer of the Pa solution contains probably several species. Let us assume that one of these is extractable. Let P_N be the concentration of all non-extractable species and P_{Cl} the concentration of the extractable one, i.e.,

$$P_{aq} = P_N + P_{Cl} \qquad \text{(VIII)}$$

The distribution coefficient for the extractable species P_{Cl}

$$D^* = \frac{P_s}{P_{Cl}} \qquad \text{(IX)}$$

will remain constant under any set of conditions, although the concentration of P_{Cl} could vary (e.g., with acidity (h) and chloride concentration (b)). For constant h and b the ratio

$$\frac{P_{Cl}}{P_N} = K_{Cl} \qquad \text{(X)}$$

would remain constant.

Addition of fluoride ions produces one (or more) non-extractable species according to a reaction of the type

$$PaO_xCl_m + nHF + nH_2O \longrightarrow PaO_xCl_{m-r}F_n^{+r-n} + rCl^- + nH_3O^+ \qquad \text{(XI)}$$

with equilibrium constants of the type

$$K_{ClF} = \frac{P_F\, b^r\, h^n}{P_{Cl}\, f^n} \qquad \text{(XII)}$$

where P_F is the concentration of the fluoride complex,

$$f = \left[HF\right],\ b = \left[Cl^-\right] \text{ and } h = \left[H_3O^+\right]$$

[redacted]

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For constant b and h equation 12 simplifies to

$$K^*_{ClF} = K_{ClF} \frac{1}{b^r h^n} = \frac{P_F}{P_{Cl} f^n} \qquad \text{(XIII)}$$

Setting

$$P_{aq} = P_N + P_{Cl} + P_F$$

(where for convenience it is assumed that only one non-extractable fluoride complex if formed).
and using equations 10 and 13 one obtains

$$P_{aq} = \frac{P_{Cl}}{K_{Cl}} + P_{Cl} + P_{Cl} K^*_{ClF} f^n \qquad \text{(XIV-a)}$$

Hence, using equation 9 one obtains

$$P_{aq} = \frac{Ps}{D^*} \left[\frac{1}{K_{Cl}} + 1 \right] + \frac{Ps}{D^*} K^*_{ClF} f^n \qquad \text{(XV)}$$

Or

$$\frac{P_{aq}}{Ps} = D_o = \frac{1}{D^*} \left[\frac{1}{K_{Cl}} + 1 \right] + \frac{K^*_{ClF}}{D^*} f^n \qquad \text{(XV-a)}$$

It can readily be shown, using equations 8, 9, and 10 that the first term in equation 15-a

$$\frac{1}{D^*} \left[\frac{1}{K_{Cl}} + 1 \right] = D^o_o \qquad \text{(XVI)}$$

where D^o_o is the observed distribution coefficient at f = o.
Thus

$$D_o = D^o_o + \frac{K^*_{ClF}}{D^*} f^n \qquad \text{(XVII)}$$

Using also equation 4 and setting

$$\frac{K^*_{ClF}}{D^*} \left(\frac{h}{K_{XF}} \right)^n = C \qquad \text{(XVIII)}$$

[redacted]

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we finally obtain the equation

$$D_o = D_o^o + C\left(\frac{X_F}{X}\right)^n \qquad \text{(XIX)}$$

Thus from the slope of a plot of log $(D_o - D_o^o)$ vs. log $\frac{X_F}{X}$ "n", the number of fluoride ions attached to the Pa, could be deduced.

In Figure 1 log D_o was plotted instead of log $(D_o - D_o^o)$. However, for the Al-system the slope of the line in Figure 1 should still yield an approximate value of "n" since log Do-log $(D_o - D_o^o)$ is negligible except for very small values of Do. Up to R = 2 "n" for the Al-system appears to be between 2 and 3. The data at present are not sufficiently precise and the H_3O^+ concentration not kept sufficiently constant to permit a more precise statement. The decrease in slope above R = ca 2 is probably due to the fact equation 4 alone does not yield the HF concentration sufficiently accurately, the higher Al-fluoride complexes also becoming of importance.

For the Th-system, the change in Do was too small to permit evaluation of "n". Thus all that can be said at the present time is that thorium (under the conditions used) removes the interference of HF on the extractability of Pa considerably more strongly than does Al.

Bibliography

(1) A. Garen, K. A. Kraus, reported in CNL-37.
(2) C. Brosset and J. Orring, Svensk Kem. Tid. 55.101.1943.
(3) W. H. Dodgen, MDDC-343.
(4) C. Brosset and B. Gustaver, Svensk Kem. Tid. 54.185.1942.
(5) D. C. Overholt, F. L. Steahly, reported in Mon N-125 and Mon T-253.

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Process Chemistry

Chemical, Physical and Nuclear Properties of Heavy Isotopes
A J. Fry and R. W. Stoughton

A completion report on problem assignment CX10-22 (Complexes of Th(IV) and IO_3^-) is now being written and will be issued shortly.

Process for Recovery of U^{233} from Thorium
E. G. Bohlmann

A summary report on the work done on problem assignment CX9-1 (Recovery of U^{233} from Thorium) is being prepared and will be issued shortly.

The "26" sample has been decontaminated and concentrated. The ignited sample measures eight mr per hour at one inch and is ready for transfer to Y-12 on receipt of further instructions.

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[redacted]

The Recovery of Uranium from Enriched Piles

(H. R. Baxman, G. R. B. Elliott, Jr., J. P. McBride, F. T. Miles, J. M. Ruth)
- P.A. CX5-9

Introduction and Summary:

The process for the decontamination and recovery of uranium from the high flux pile has shown consistently satisfactory results in both semi-works and pilot plant tests. In the latter, the yields have been uniformly high ($>$ 99.9%) and the decontamination factors for the first cycle have been $> 10^4$ for β and $> 3 \times 10^3$ for γ . The second cycle product activity is indistinguishable from the uranium activity showing a decontamination of at least 10^5. The use of diphenylthiourea (DPT) for increasing ruthenium decontamination was tested with satisfactory results in five runs in the semi-works columns. With DPT, the strip column gave ruthenium decontamination factors of 20 to 80. The only pilot plant run with DPT, however, was a failure since precipitation of UO_2SO_4 in the mixing chamber caused mechanical difficulties and the decontamination was not improved as much as had been anticipated.

With the adequacy of the process apparently assured the work in the chemistry division is practically finished and is limited to investigation of possible process improvements and attempts to explain some of the observed effects. The use of organic amines to complex uranium and neptunium has been studied. In this connection the distribution ratios of the complexing agents (2-hexyl pyridine and tri-n-butyl amine) have been measured. It was necessary to develop analytical methods for these amines and their nitrates.

Some additional work has been done on the extraction behavior of ruthenium tracer in order to establish more exactly the equilibria between the different forms and the rates of conversion.

There has been some formation of solids in the process. These solids were examined, and stability tests were made to find conditions which caused the precipitation. This work is reported in CL-GRBE-47.

Complexing of Uranium in Hexone

The distribution ratio of uranium between 1M aluminum nitrate and hexone in the presence of complexing agents and 0.05 M ferrous ammonium sulfate has been studied as a function of the pH of the aqueous phase and the concentration of the complexing agent.

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Pre-equilibration of phases before the addition of tracer, temperature control (25.0 ± 0.2°C.), pH measurement, and titration of acid in the hexone phase were carried out as described in CNL-37. Uranium 233 tracer was used. All counting samples were prepared on platinum plates and flamed to remove the complexing agent, in order to prevent self-absorption in the sample. Careful flaming with a microburner was found to give satisfactory results. Both phases were analysed; the aqueous phase being saturated with aluminum nitrate and repeatedly extracted with hexone which was evaporated and counted.

Hydrazine, 2-hexylpyridine, and tri-n-butylamine were used as complexing agents. Plots of the data are given in Figures 1, 2, and 3. For hydrazine the calculated curves are plotted; for the others, the curves are drawn through the experimental points. Quantitative explanations of the effects of the latter two will be left until their distributions have been studied more completely.

The distribution of hydrazine as a function of pH has been measured and can be expressed using three equilibrium constants (CNL-37). With these constants it is possible to calculate the concentrations of various components of the system at any pH. These are plotted in Figure 4, where the concentration of hydrazine in the aqueous phase plus the concentration in the hexone phase is always 0.47. Small changes of the hydrazine distribution with concentration were neglected in fitting the curve for 0.047 M hydrazine. It is noted that the calculated values of NO_3^- in the hexone disagree with titration values in the high pH range. In fitting the equation to the data, however, the calculated values have been used. Nitric acid in the hexone phase in the absence of hydrazine was obtained from the graph in MonN-432, which was extended to a lower pH range.

With no complexing agent present, the following reactions are assumed:

(1) $$UO_{2aq.}^{++} + 2NO_{3aq}^- + 3H_2O \longleftrightarrow UO_2(NO_3)_2 \cdot 3H_2O_{hex.}$$

$$k_1 = \frac{[UO_2(NO_3)_2 \cdot 3H_2O]_{hex}}{[UO_2^{++}]_{aq.}\,[NO_3^-]^2_{aq}}$$

(2) $$UO_2(NO_3)_2 \cdot 3H_2O_{hex} + NO_{3hex}^- \longleftrightarrow UO_2(NO_3)_3^- \cdot XH_2O_{hex} + (3-X)H_2O$$

$$k_2 = \frac{[UO_2(NO_3)_3 \cdot XH_2O^-]_{hex}}{[UO_2(NO_3)_2 \cdot 3H_2O]_{hex}\,[NO_3^-]_{hex.}}$$

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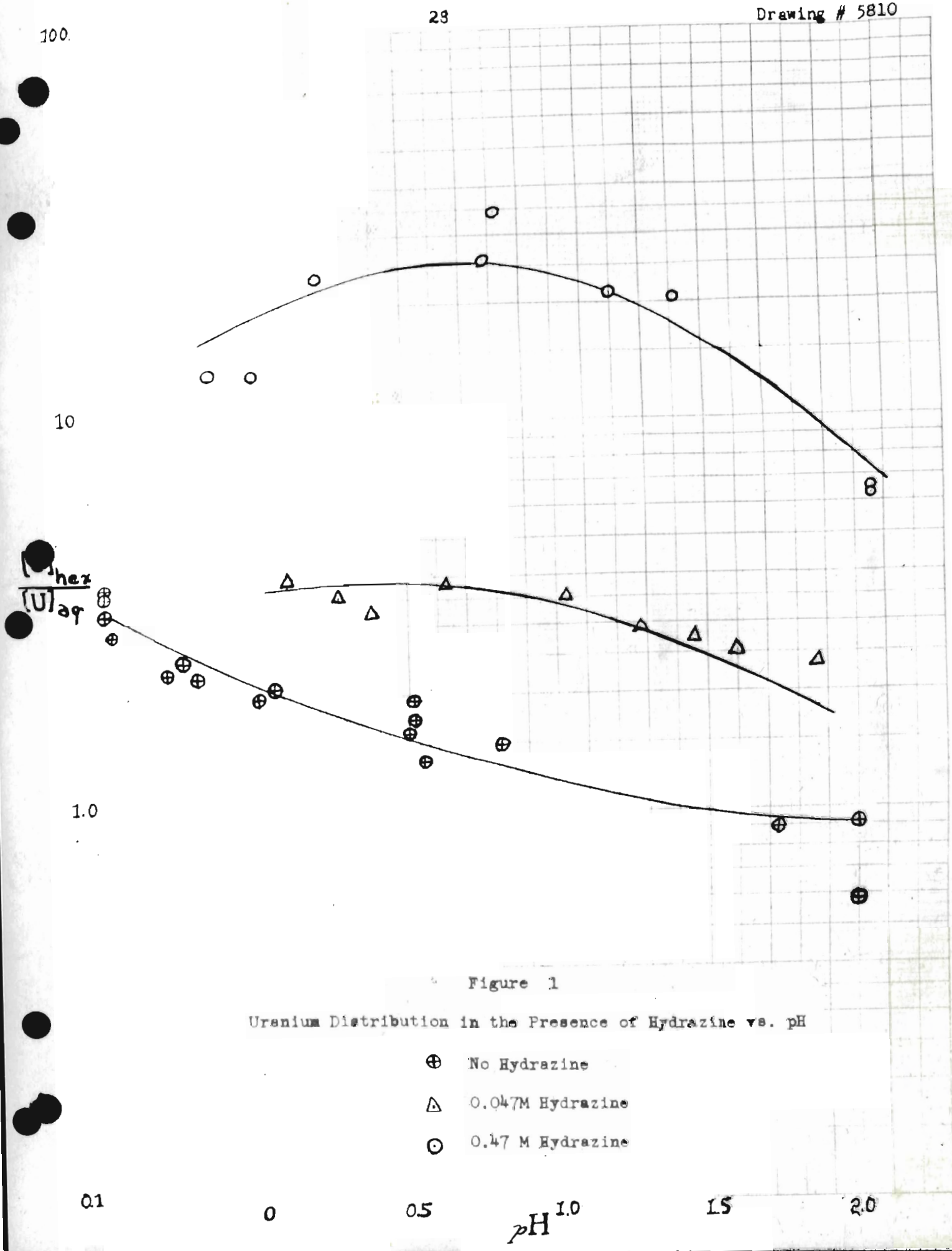

Figure 1

Uranium Distribution in the Presence of Hydrazine vs. pH

⊕ No Hydrazine

△ 0.047M Hydrazine

⊙ 0.47 M Hydrazine

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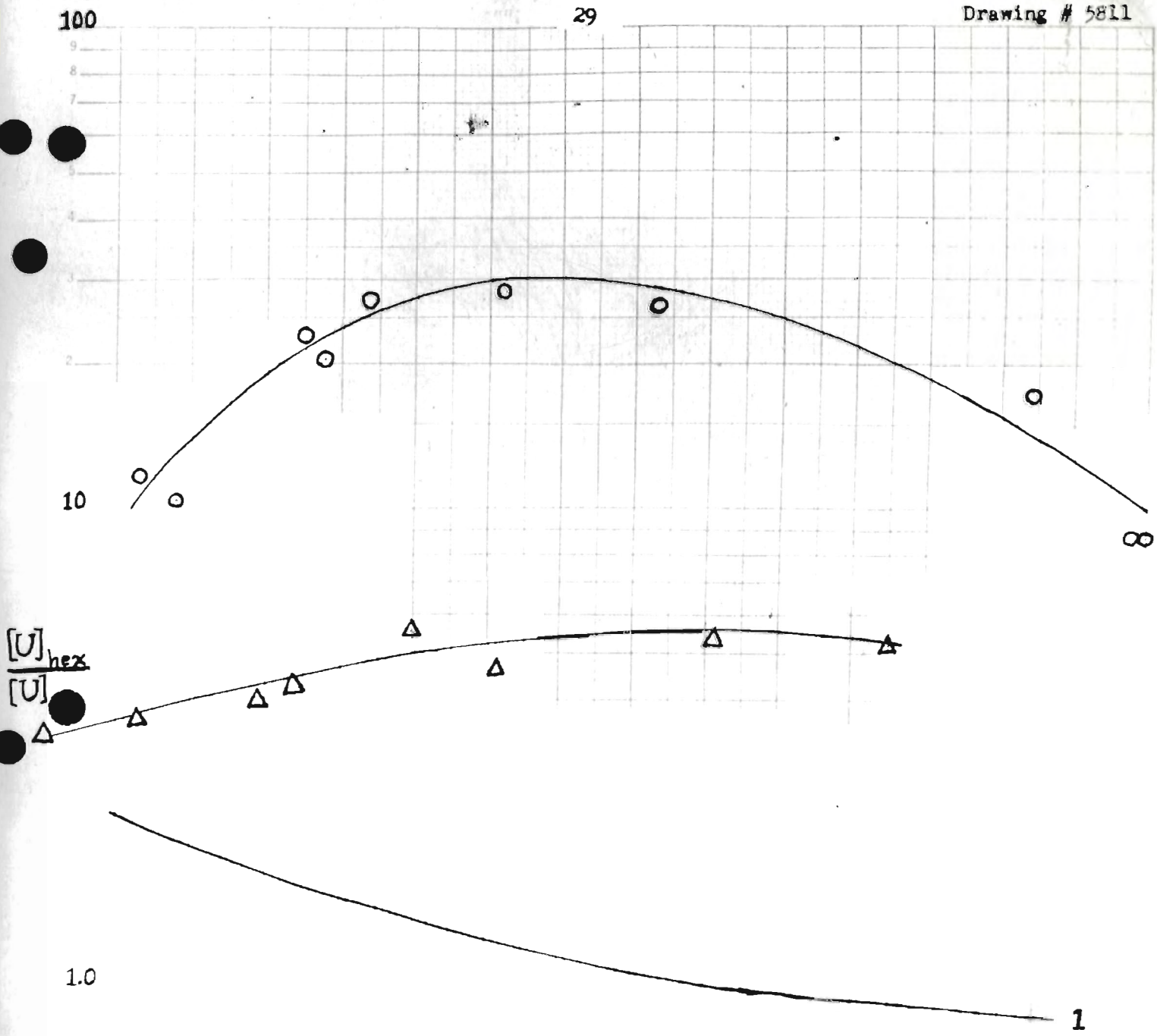

Figure 2

Uranium Distribution in the Presence of 2-hexylpyridine vs. pH

1 No 2-hexylpyridine

△ 0.047M 2-hexylpyridine

○ 0.47 M 2-hexylpyridine

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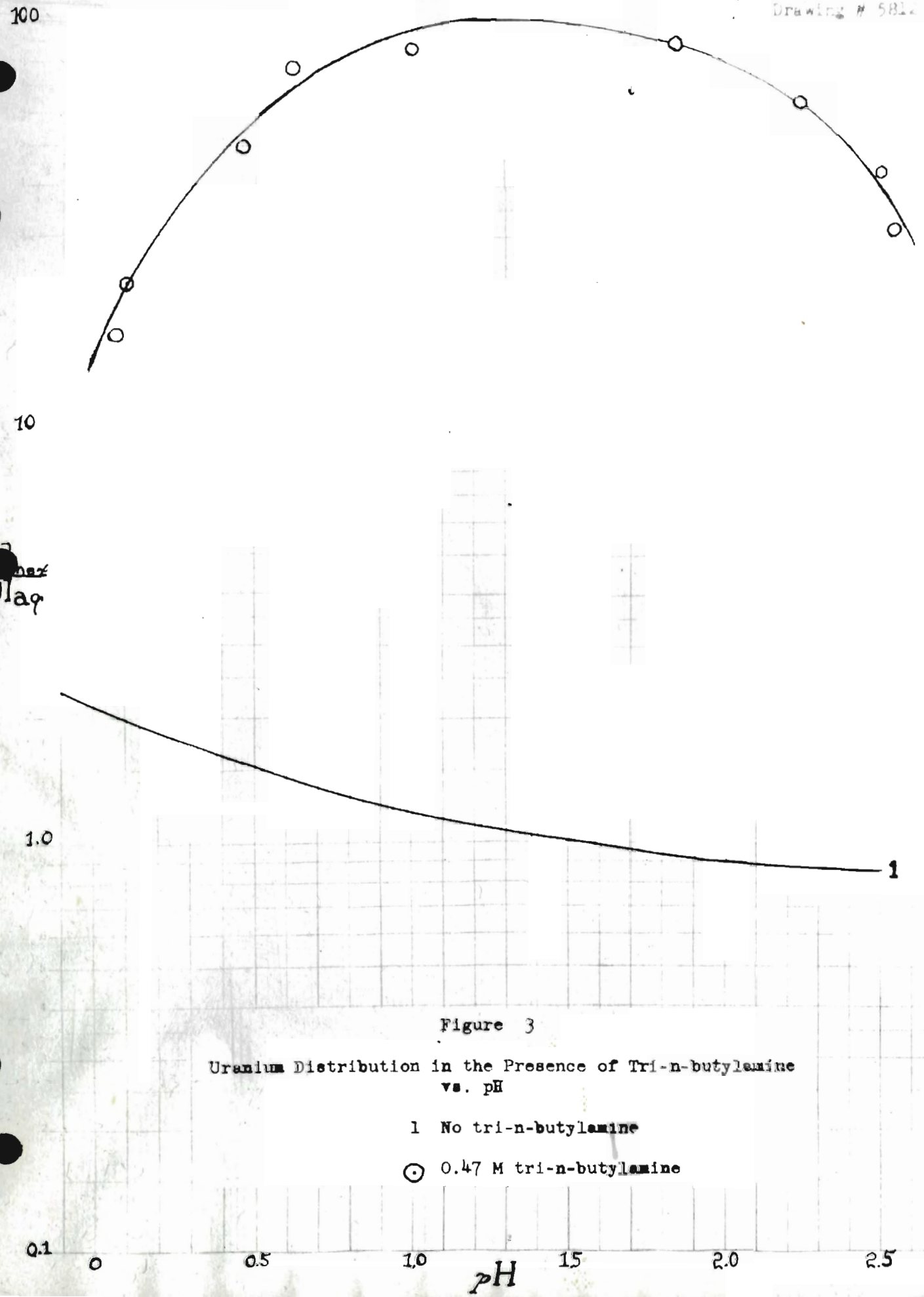


Figure 3

Uranium Distribution in the Presence of Tri-n-butylamine vs. pH

1 No tri-n-butylamine

⊙ 0.47 M tri-n-butylamine

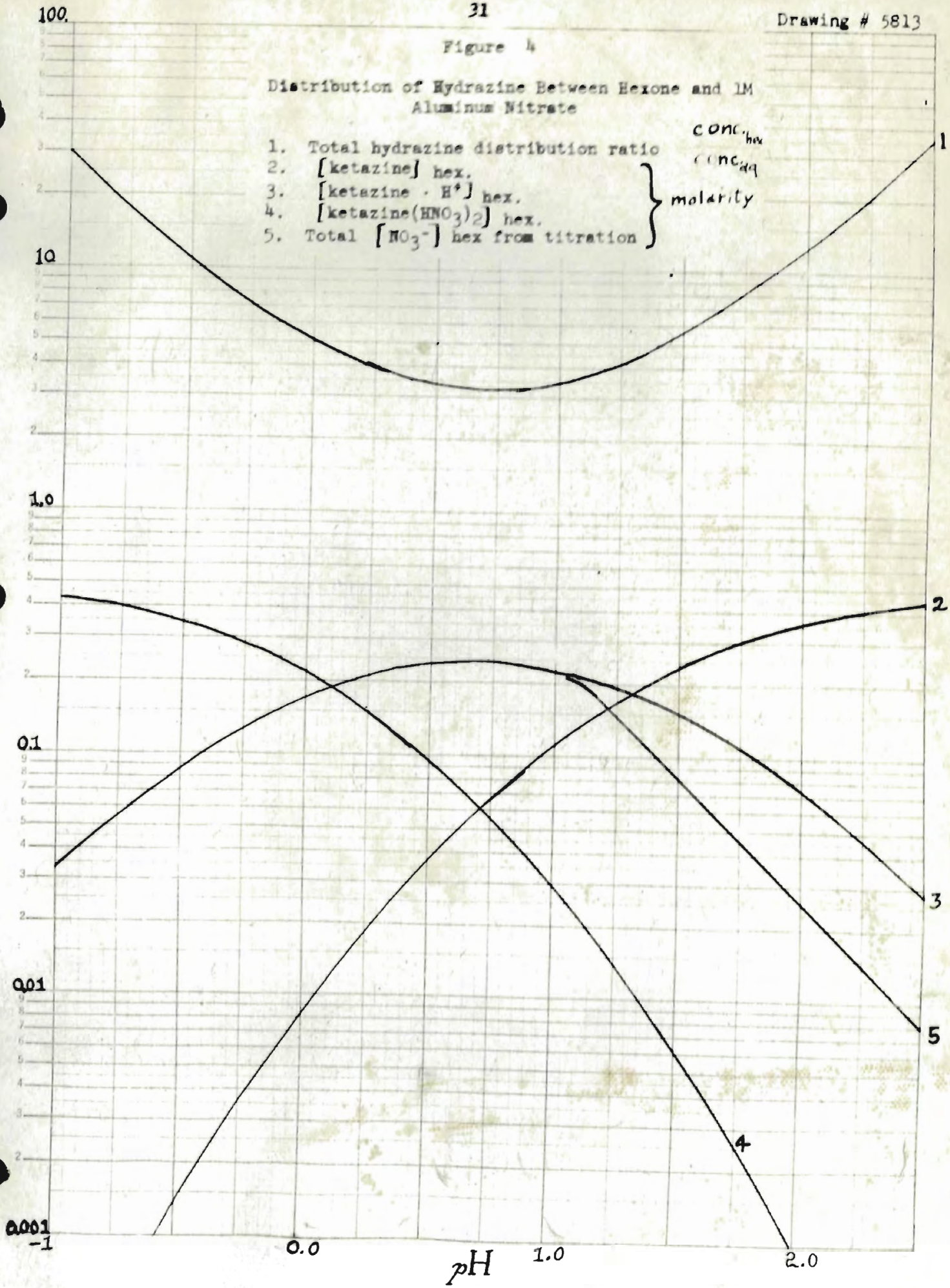
Drawing # 5813

Figure 4

Distribution of Hydrazine Between Hexone and 1M Aluminum Nitrate

1. Total hydrazine distribution ratio $\frac{conc._{hex}}{conc._{aq}}$
2. [ketazine] hex.
3. [ketazine · H^+] hex.
4. [ketazine$(HNO_3)_2$] hex.
5. Total [NO_3^-] hex from titration

} molarity



[redacted]

(3) $H^+_{aq} + NO^-_{3aq} \longleftrightarrow H^+_{hex} + NO^-_{3hex} \xleftrightarrow{k_3} HNO_3\ hex$

$$k_3 = \frac{[HNO_3]_{hex}}{[H^+]_{hex}[NO_3^-]_{hex}} = \frac{[HNO_3]_{hex}}{[NO_3^-]^2_{hex}}$$

$$[NO_3^-]_{hex} = \left(\frac{[HNO_3]_{hex}}{k_3}\right)^{\frac{1}{2}} = \frac{[HNO_3]^{\frac{1}{2}}_{hex}}{k^{\frac{1}{2}}_3}$$

$$D.R. = \frac{[U]_{hex}}{[U]_{aq}} = \frac{[UO_2(NO_3)_2 \cdot 3H_2O]_{hex} + [UO_2(NO_3)_3 \cdot XH_2\bar{O}]_{hex}}{[UO_2^{++}]_{aq}}$$

$$= k_1[NO_3^-]^2_{aq} + k_1k_2[NO_3^-]^2_{aq}[NO_3^-]_{hex}$$

$$= k_1[NO_3^-]^2_{aq} + \frac{k_1k_2}{k_3}[NO_3^-]^2_{aq}[HNO_3]^{\frac{1}{2}}_{hex}$$

The data for the distribution ratio of uranium in the absence of hydrazine reported last quarter can be fitted by an equation of this type; for 1 M $Al(NO_3)_3$ in the aqueous phase:

$$D.R. = \frac{[U]_{hex}}{[U]_{aq}} = 0.8 + 3.7[HNO_3]^{0.6}_{hex}$$

With hydrazine present, using the calculated concentrations of ketazine · 2 HNO_3 in the hexone phase, it seems necessary to assume that only the ketazine mononitrate takes part in the complexing action. This might be explained if the dinitrate were only slightly ionized, while the mononitrate is largely ionized.

The additional nitrate from this source is then equal to [ketazine · H^+]hex.

$$[NO_3^-]_{hex} = \frac{[\text{free } HNO_3]^{0.6}_{hex}}{k^{\frac{1}{2}}_3} + [\text{ketazine} \cdot H^+]_{hex}.$$

$$D.R. = k_1[NO_3^-]^2_{aq} + k_1k_2[NO_3^-]^2_{aq}\left(\frac{[\text{free } HNO_3]^{0.6}_{hex}}{k^{\frac{1}{2}}_3} + [\text{ket. } H^+]_{hex}\right)$$

[redacted]

[redacted]

It was found that the data for total hydrazine concentrations (molarity in the hexone phase plus molarity in the aqueous phase) of 0, 0.047, and 0.47, with 1M $Al(NO_3)_3$ in the aqueous could all be fitted by an equation of this form as follows:

$$D.\ R. = 0.8 + 3.7 \left[HNO_3 \right]_{hex}^{0.6} + 100 \left[\text{ketazine} \cdot H^+ \right]_{hex}$$

Lines calculated from this equation for the three concentrations of hydrazine are plotted in Figure 1 and compared with observed data. These results are in general agreement with the complexing theory first proposed by Chicago (ANL-WMM-193; ANL-WMM-180).

Complexing of Reduced Neptunium in Hexone

The distribution of N^{IV} between hexone and 1.00 M $Al(NO_3)_3$ has been investigated using hydrazine, 2-hexylpyridine and tri-n-butylamine as complexing agents with varying pH.

Two concentrations of N_2H_4 were used, 0.47M and 0.047M where the molarities are equal to the molarity in the organic phase plus the molarity in the aqueous phase. Figure 5 shows a plot of Np distribution ratio versus pH and shows that the distribution has approximately a third power dependence on $\left[H^+ \right]$ aq. Figure 6 gives the plot of the log of the Np distribution against the log of the nitrate ion concentration in the organic phase. This nitrate ion concentration is not the actual titrated value but is the titration minus the calculated ketazine $\cdot$ H_2^{++} concentration at that pH as shown in Figure 4.

Figure 6 shows that the Np distribution has approximately a cube power dependence on the NO_3^- calculated in the manner given above. It also shows that it is apparently independent of the concentration of N_2H_4 except as this determines the nitrate concentration in the hexone phase.

In both of these figures it can be easily observed that fractionation is taking place and that equilibrium in the system has not been reached during the time of equilibration - 2 minutes.

Figure 7 gives a plot of Np distribution versus pH where 2-hexylpyridine was used as the complexing agent. Two cases are shown: one where urea was present as a holding reductant, and one where there was no urea added. One point is also shown where a four hour equilibration time was used. All other points are for two minute equilibrations. It is apparent that equilibrium is not reached in two minutes and possibly not in four hours and also that the distribution ratios obtained with two minute equilibrations are much too low to be of practical value. It will be noticed that higher distributions are obtained for corresponding pH's when no urea is present that when urea is added. This is probably due to the oxidation of the Np by nitric acid to the more extractable +6 state.

[redacted]

Drawing # 5814

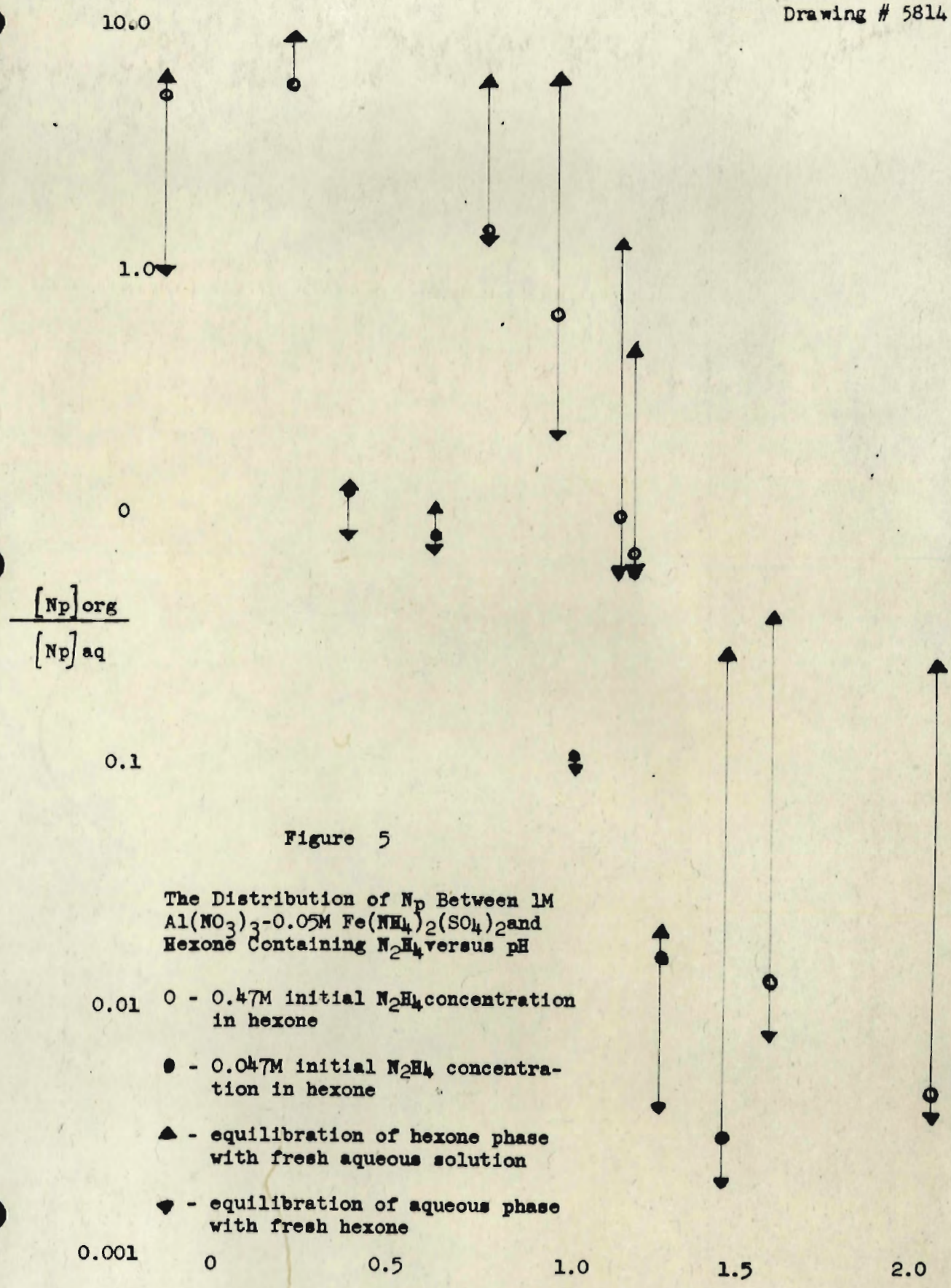


Figure 5

The Distribution of N_p Between 1M $Al(NO_3)_3$-0.05M $Fe(NH_4)_2(SO_4)_2$ and Hexone Containing N_2H_4 versus pH

O - 0.47M initial N_2H_4 concentration in hexone

● - 0.047M initial N_2H_4 concentration in hexone

▲ - equilibration of hexone phase with fresh aqueous solution

▼ - equilibration of aqueous phase with fresh hexone

Figure 6

The Distribution of N_p between 1M $Al(NO_3)_3$ - 0.05M $Fe(NH_4)_2(SO_4)_2$ and Hexone containing N_2H_4 versus Effective Organic Nitrate Concentration ($[NO_3^-]^*_{org}$).

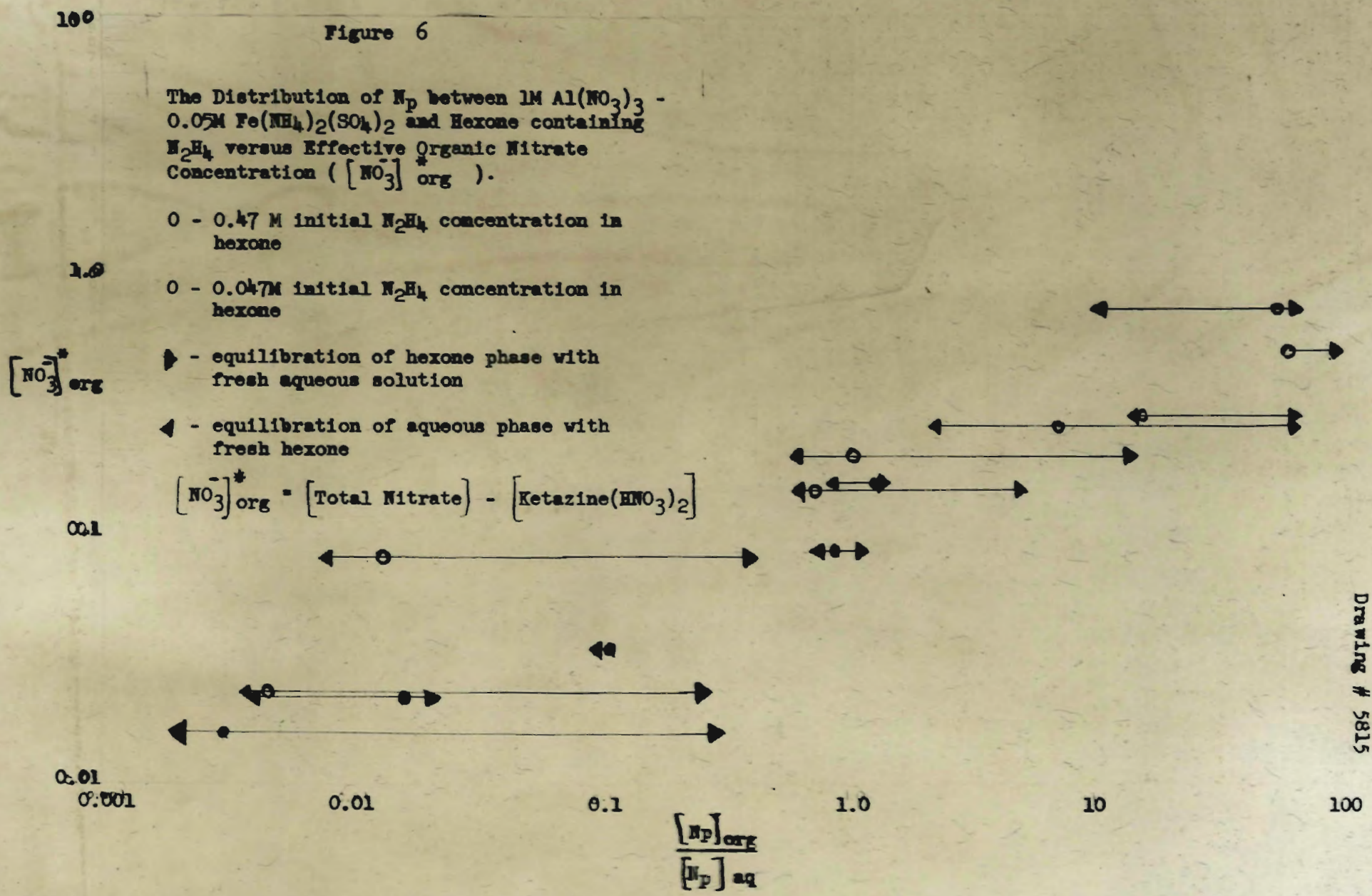
O - 0.47 M initial N_2H_4 concentration in hexone

O - 0.047M initial N_2H_4 concentration in hexone

▶ - equilibration of hexone phase with fresh aqueous solution

◀ - equilibration of aqueous phase with fresh hexone

$$[NO_3^-]^*_{org} = [\text{Total Nitrate}] - [\text{Ketazine}(HNO_3)_2]$$



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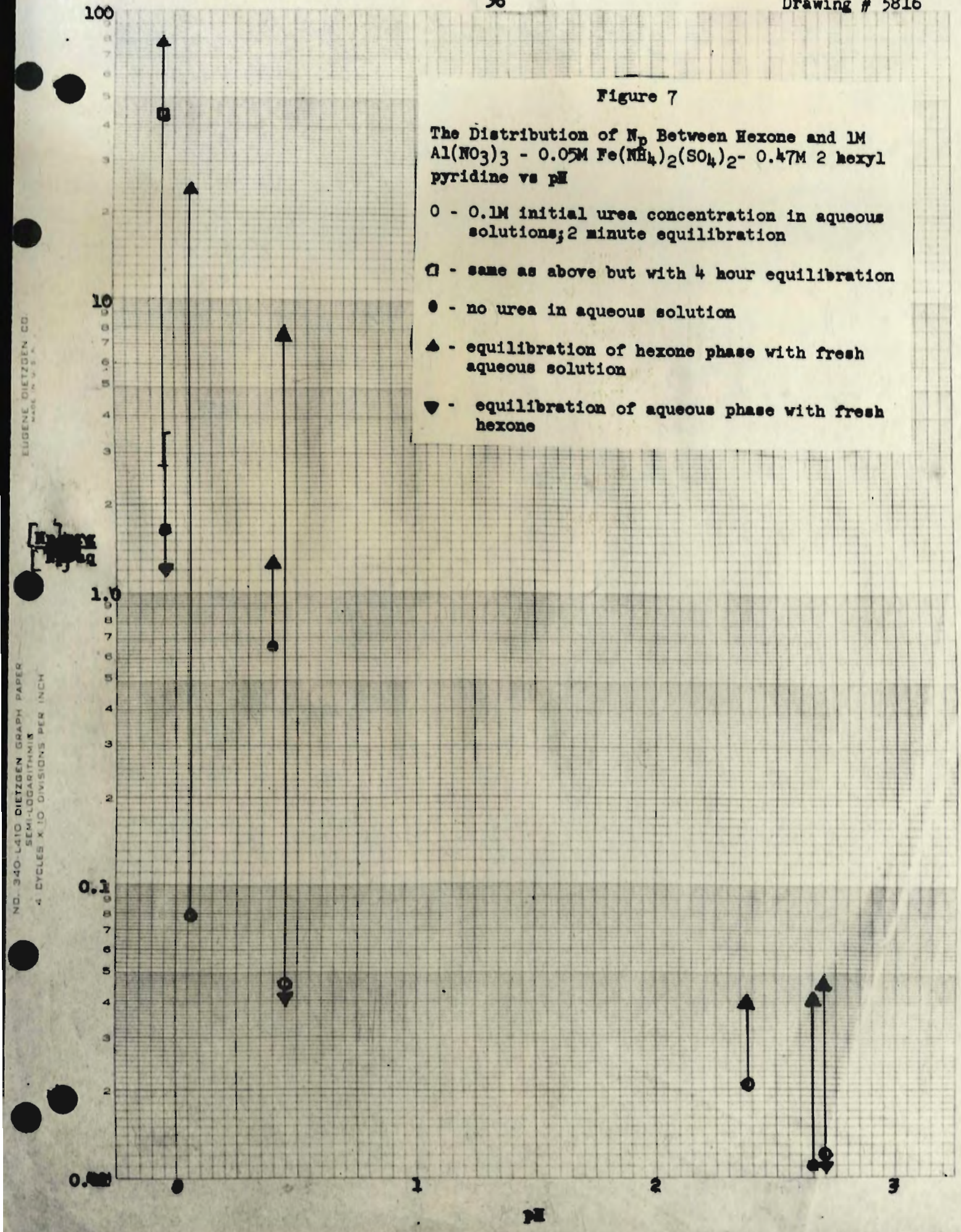

Figure 7

The Distribution of N_p Between Hexone and 1M $Al(NO_3)_3$ - 0.05M $Fe(NH_4)_2(SO_4)_2$- 0.47M 2 hexyl pyridine vs pH

O - 0.1M initial urea concentration in aqueous solutions; 2 minute equilibration

□ - same as above but with 4 hour equilibration

● - no urea in aqueous solution

▲ - equilibration of hexone phase with fresh aqueous solution

▼ - equilibration of aqueous phase with fresh hexone

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In Figure 8 is plotted the Np distribution as a function of pH using tri-n-butylamine as the complexing agent. The graph shows the distribution obtained from the original extraction and also an approach to equilibrium conditions following a four-hour equilibration.

Diagrams of the extractions at the four pH's are shown in Figures 9-12. All lines running from left to right are aqueous phases, those running from right to left are hexone phases. The number directly under the intersections are the observed distribution ratios, those to the right of the intersections are the time of equilibration.

Figures 10, 12 at pH = 1.58 and -0.02 show definite evidence of fractionations. Figure 11 is not self-consistent and no explanation for it can be offered at this time. Figure 9 indicates either that it attained equilibrium in 2 minutes of less or that it is in a metastable state and equilibrium was not approached after 4 hours. At pH - 0.02 (Figure 12) the system appears to be approaching equilibrium with a time greater than four hours. At pH 1.58 (Figure 10) equilibrium is apparently reached between two minutes and four hours. This system can be explained assuming two forms of Np as follows:

$$\begin{array}{ccc} N_{pIaq} & \xleftrightarrow{D_I = 11.} & N_{pIorg} \\ \uparrow \; \downarrow \; \cong .10_5 & & \updownarrow \; k_{org} = \dfrac{[N_{pI}]}{[N_{pII}]} = 23 \\ N_{pIIaq} & \xleftrightarrow{D_{II} = 0.05} & N_{pIIorg} \end{array}$$

$$k_{aq} = \frac{[N_{pI}]}{[N_{pII}]} = \frac{k_{org} \cdot D_{II}}{D_I}$$

Distribution ratios calculated on these assumptions are shown in parentheses on Figure 10 and are in agreement with the observed values.

The Determination of Nitric Acid In Hexone in the Presence of Organic Complexing Agents

Nitric acid may be determind by direct titration in 50% methanol solution containing a small amount of hexone and in the presence of either 2 hexylpyridine, tri-n-butyl amine mono-nitrate, or tetra-n-butyl ammonium nitrate. The potentiometric break using a calomel-glass cell is sharp with all three but is shorter with the 2 hexylpyridine (90 mv) which shifts the end point to the basic side or an apparent pH of about 8.7. The apparent pH is calculated from the millivolt reading assuming that the same pH-EMF relationship holds for 50% methanol solution as for aqueous solutions. The midpoints of the breaks in the presence of the amine and the quaternary ammonium salt occur at apparent pH's of 5.5 and 6.5, respectively. It is to be noted that at the equivalence point, the 2-hexylpyridine is

[redacted]

Drawing # 5817

Figure 8

The Distribution of Np between Hexone and 1M $Al(NO_3)_3$- 0.05M $Fe(NH_4)_2(SO_4)_2$- 0.47 M$(n\text{-}C_4H_9)_3N$ vs pH

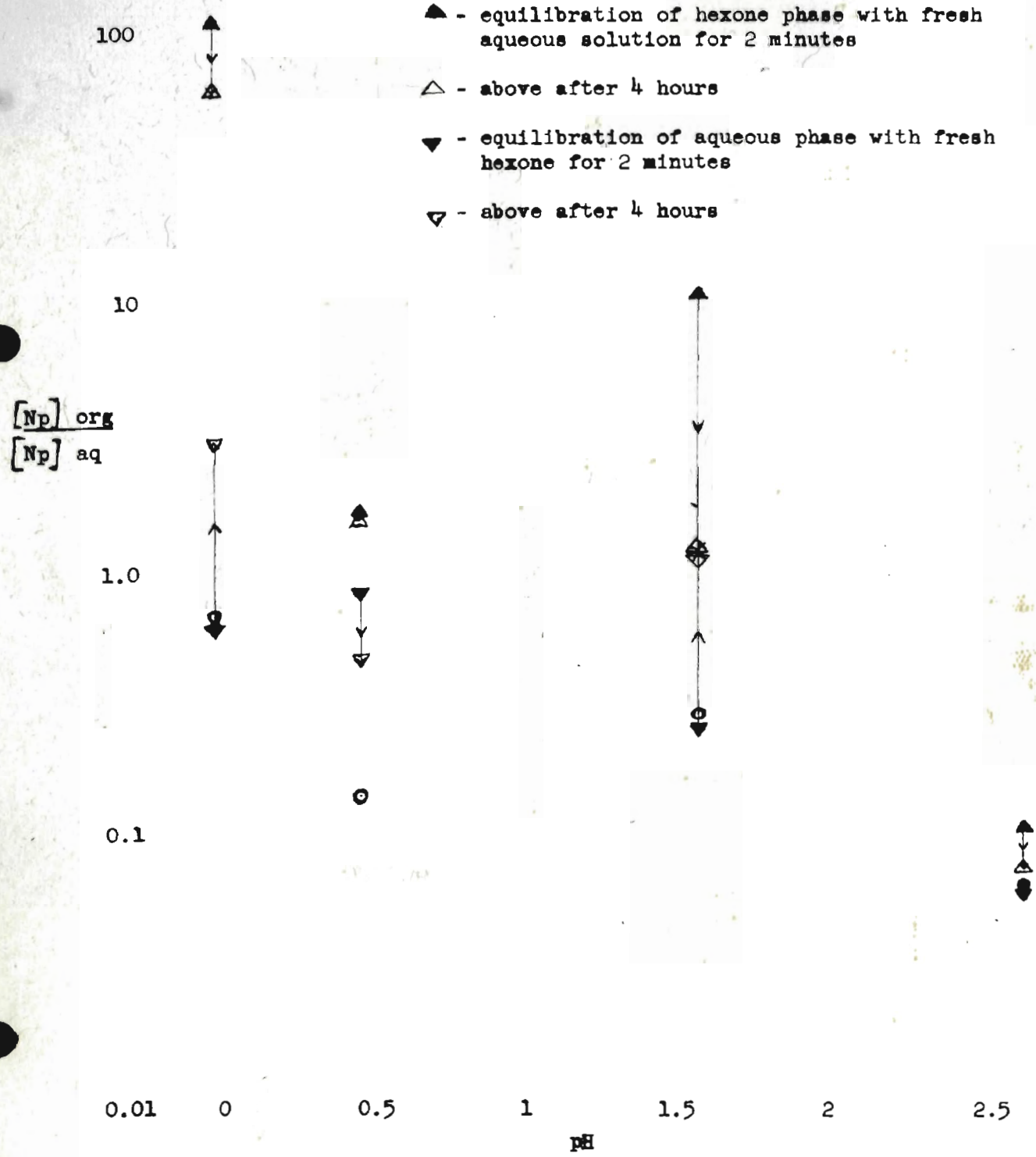
O - 0.1M initial urea concentration in aqueous solution

▲ - equilibration of hexone phase with fresh aqueous solution for 2 minutes

△ - above after 4 hours

▼ - equilibration of aqueous phase with fresh hexone for 2 minutes

▽ - above after 4 hours



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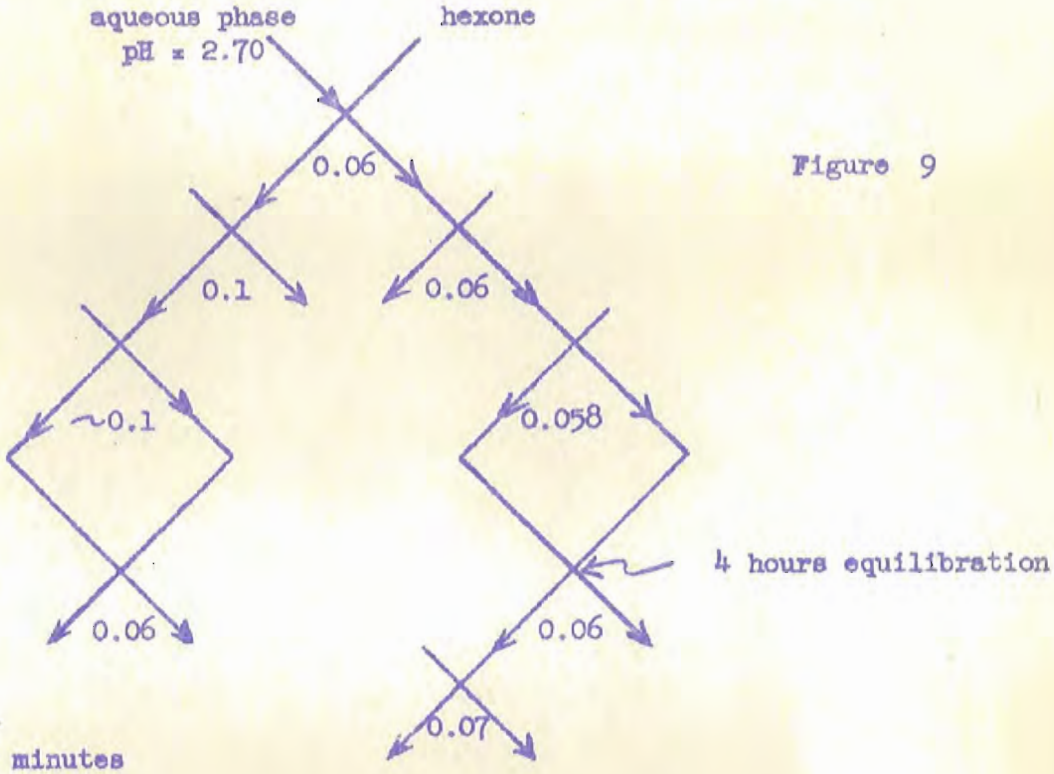

Figure 9

Equilibrations for 2 minutes except as specified.

Arrows follow course of Neptunium

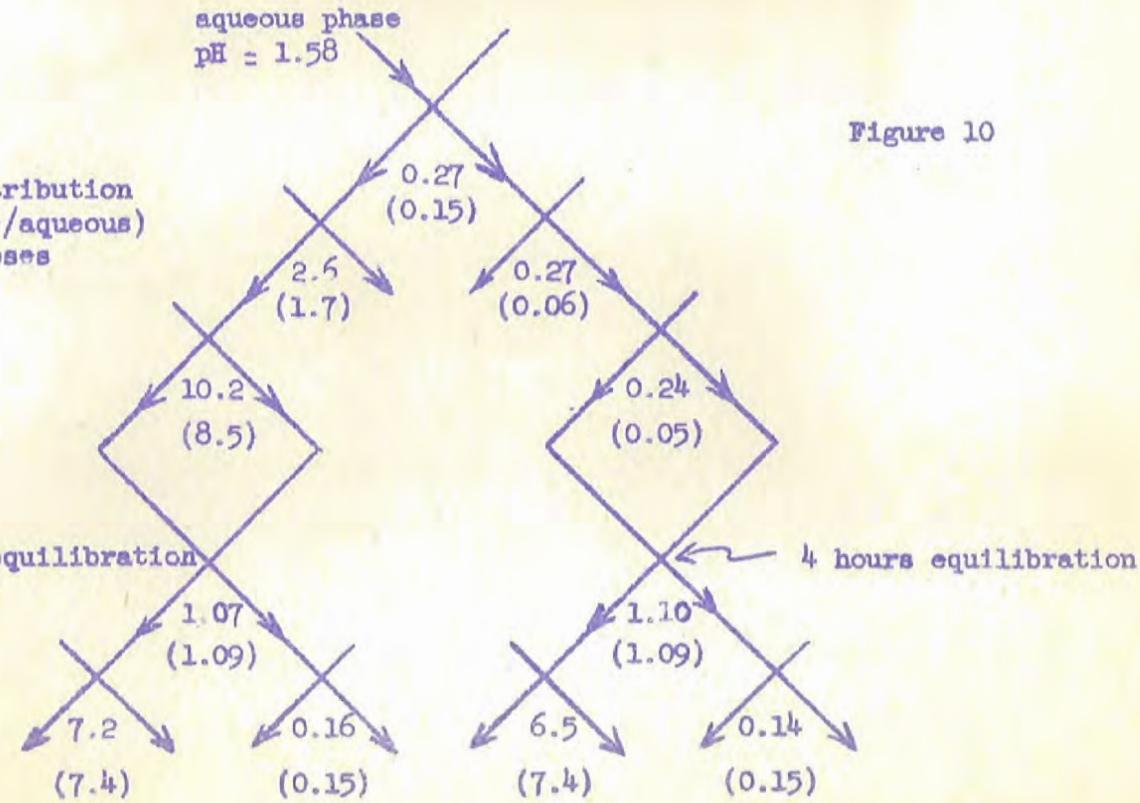

Figure 10

Calculated distribution ratios (organic/aqueous) are in parentheses

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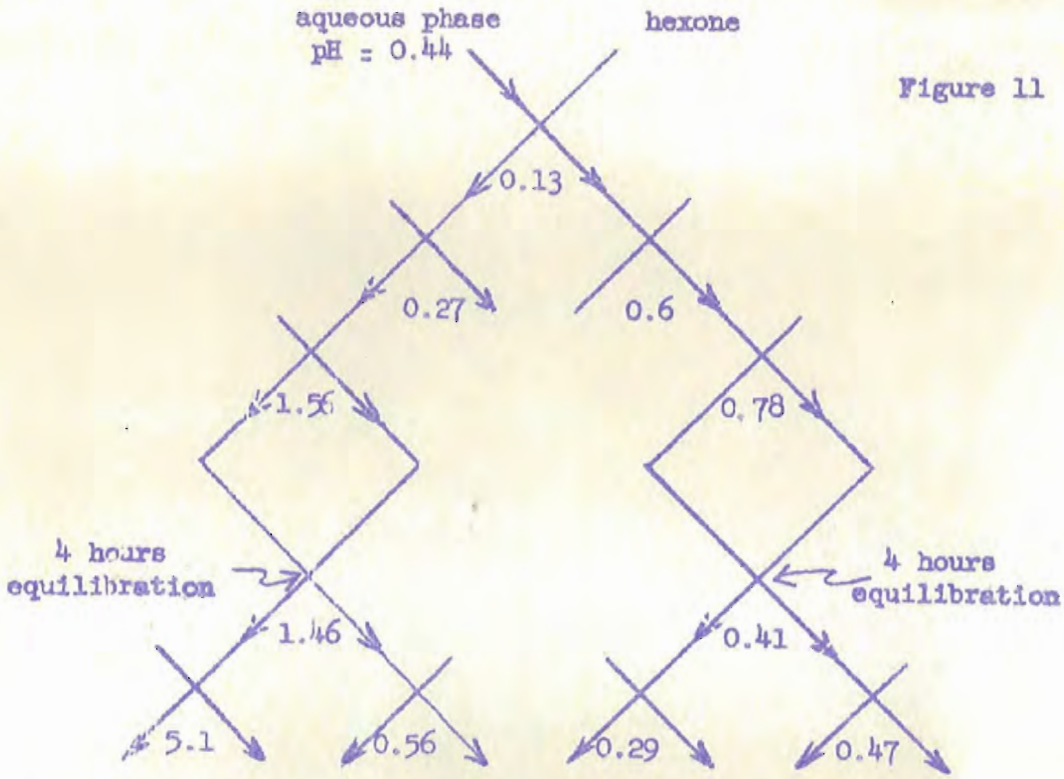

Figure 11

Two minute equilibration except as specified.
Arrows follow course of Neptunium.

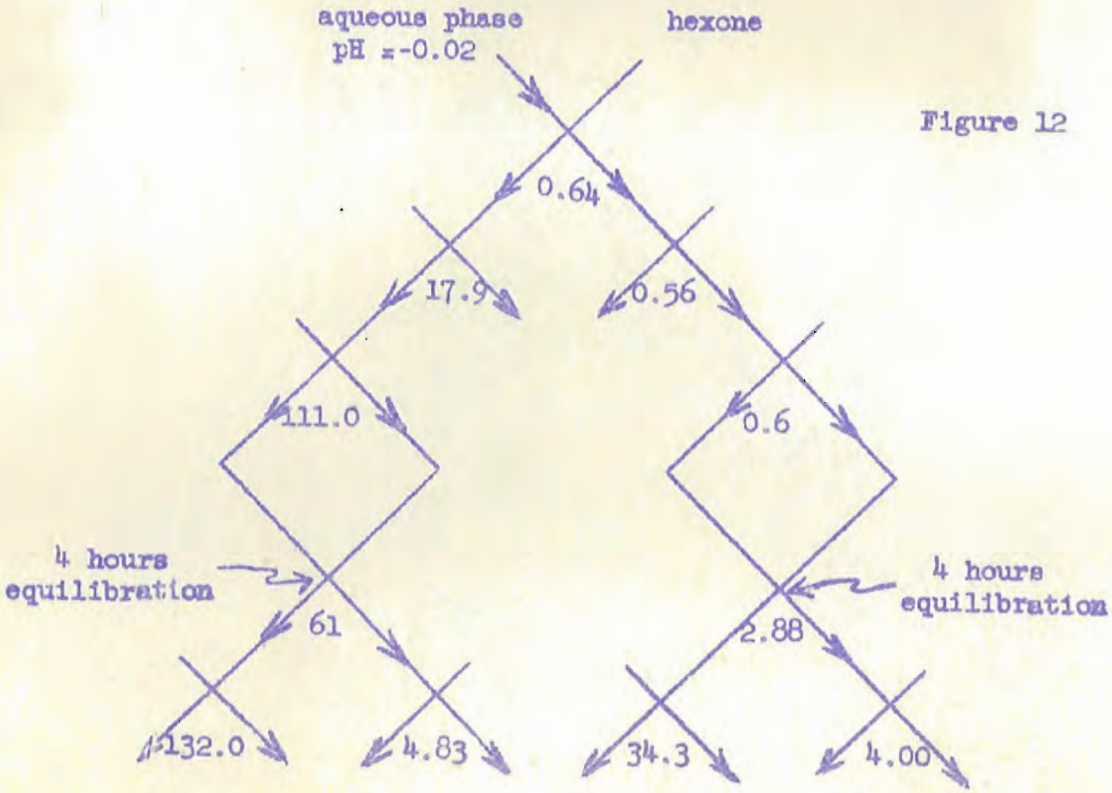

Figure 12

[redacted]

present as the base itself but that the other compounds are present as the mono-nitrates. As one would expect from the above result tri-n-butyl amine itself may be titrated directly with nitric acid to the mono-nitrate. Figure 13 illustrates some typical potentiometric curves for the above titrations.

The Determination of Tri-n-butyl Amine in Hexone-Nitric Acid Solutions

Two methods of determining tri-n-butyl amine in hexone-nitric acid solution were investigated. The first included a study of the determination of total nitrate in the amine-hexone-nitric acid system by the method of Kolthoff, Sandell, and Moskovitz (J.A.C.S. 55, 1454 (1933)). Given the total nitrate concentration one could obtain the amine concentration by subtracting from the total nitrate the excess nitric acid determined by direct titration with base. The total nitrate method, which consists of the quantitative reduction of NO_3^- by Fe^{+2} in hot concentrated HCl, gave a low value, 90% of theoretical, in the presence of the amine.

The second method considered was the steam distillation of the amine from a dilute base solution and the subsequent determination of the amine in the distillate by an acid-base titration. Excellent results were obtained by the procedure developed below.

In the initial experiments 2 ml aliquots of either hexone or methyl alcohol ca 0.5 M in amine were added to 25 ml 0.04 N.NaOH containing 1 meq $NaNO_3$. The mixture was vigorously steam distilled into a 50% methanol solution containing a known excess of nitric acid and was subsequently titrated with standard base. The organic phase came over quickly during distillation and distillation was continued ca 10 mins. Initial results were low (but gave check results for duplicate distillations) when compared with the volume of base required for the methanol-nitric acid solution to which a 2 ml aliquot of the stock amine solution had been added. The addition of 5 ml of hexone to the still pot in subsequent experiments, however, resulted in quantitative recovery of the amine. The additional solvent either aids in carrying over the amine or extracts the amine from the still pot mixture and in that way helps the distillation. That the amine itself distills very inefficiently is shown by check results obtained for different distillation times. Table I lists the results of pertinent determinations.

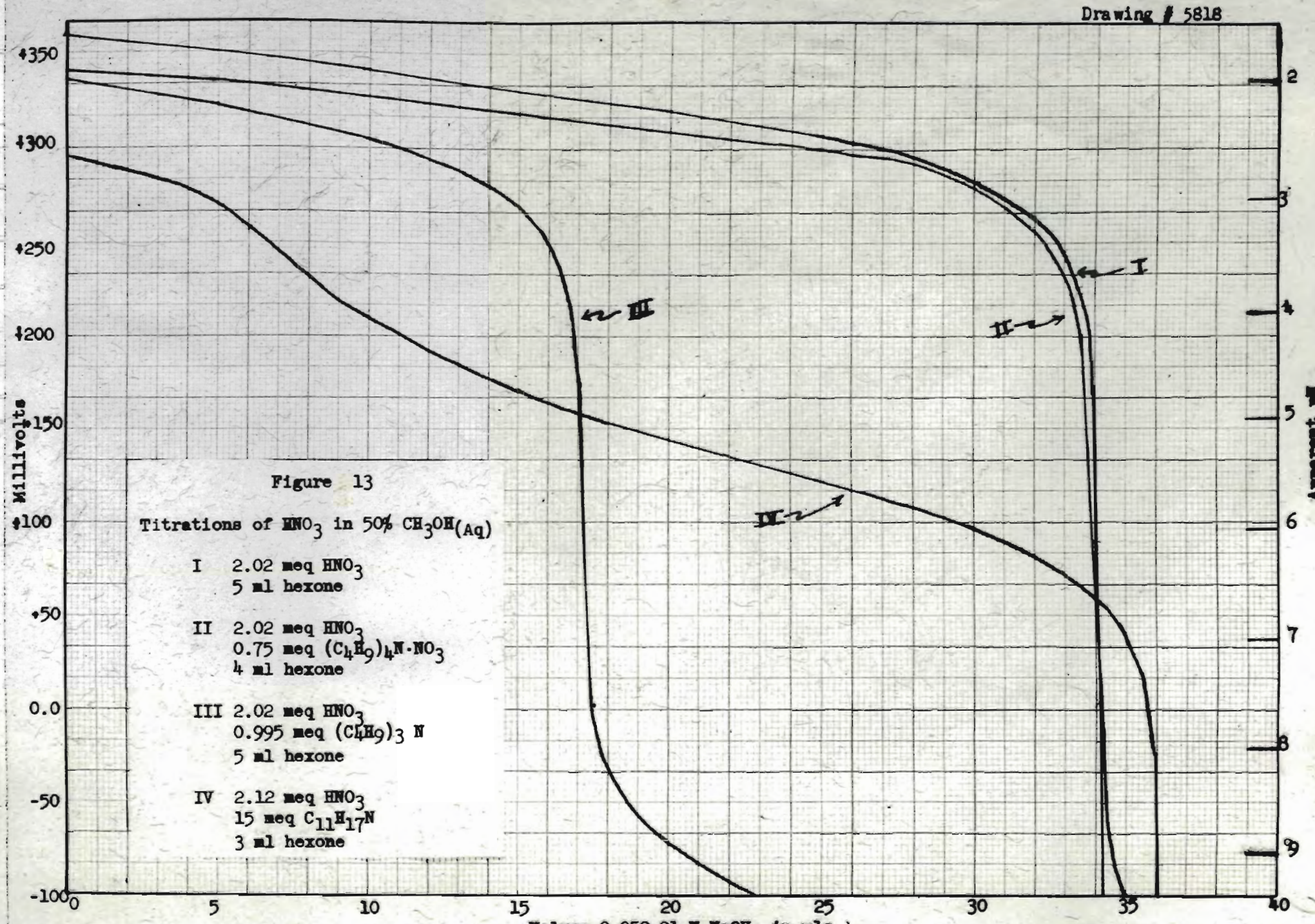

Figure 13

Titrations of HNO_3 in 50% $CH_3OH_{(Aq)}$

I 2.02 meq HNO_3
5 ml hexone

II 2.02 meq HNO_3
0.75 meq $(C_4H_9)_4N \cdot NO_3$
4 ml hexone

III 2.02 meq HNO_3
0.995 meq $(C_4H_9)_3N$
5 ml hexone

IV 2.12 meq HNO_3
15 meq $C_{11}H_{17}N$
3 ml hexone

[redacted]

TABLE I

The Determination of Tri-n-butyl Amine

Procedure: Steam distillation from dilute base into Me OH - HNO_3 and subsequent titration with NaOH

Series	Run	Steam Distillation		Back-titration			
		ml 0.5M stock sol'n	ml hexone added	meq HNO_3 in catch sol'n	meq NaOH for back-titration	meq amine found	% recovery: blank = 100%
Hexone	Blank	2ml	(no steam distillation)	1.958	0.976	0.982	100
	1	2ml	none	1.958	1.076	0.882	90
	2	2ml	none	1.958	1.076	0.882	90
	3	2ml	5ml	1.958	0.977	0.981	100
Methanol	Blank	2ml	(no steam distillation)	1.958	0.978	0.980	100
	1	2ml	none	1.958	1.159	0.799	81
	2	2ml	none	1.958	1.150	0.808	82
	3	2ml	5ml	1.958	0.992	0.966	98

[redacted]

[redacted]

Aging of Tri-n-butylamine - Hexone Solutions

Hexone solutions of tri-n-butylamine become yellow on standing. No effort was made to determine the nature of the aging process but it was noted in the course of the work in the analysis of such solutions that on standing 3 weeks a 0.2 N solution of the amine in hexone became less basic by about 9% and gave evidence of deterioration in that upon addition to excess acid and back-titration with base the potentiometric break was less sharp and required ca 2 ml of 0.06 N solution rather than about 0.5 ml for a 150 mv change.

The Extraction of Tri-n-butyl Amine with Hexone

The organic phases from equal volume equilibrations of a 0.47 M tri-n-butyl amine solution in hexone with 1 M $Al(NO_3)_3$ solutions of various pH's and 0.1 M in urea and 0.05 M in $Fe(NH_4)_2(SO_4)_2$ (cf., Figure 9) were analyzed for HNO_3 and tri-n-butylamine as above. The results are recorded in the following table.

TABLE II

The Extraction of Tri-n-butyl Amine with Hexone

Condition: 1 M $Al(NO_3)_3$, 0.05 M $Fe(NH_6)_2(SO_4)_2$, 0.1 $(NH_2)_2CO$ equilibrated 2 to 4 hours with equal volumes 0.47 M tri-n-butyl amine in hexone.

Solution	Final pH Aqueous phase	Acid Conc. Organic phase	n Butyl Amine Conc. Organic phase	Aqueous phase (0.47-org)	Total NO_3^- Concen. Organic phase; M	D. R. Org/Aqueous
1	2.7	0.002	0.433	0.037	0.435	11.7
2	1.6	0.0292	0.465	0.005	0.494	93.0
3	0.4	0.2692	0.446	0.024	0.715	18.6
4	0	0.9040	0.422	0.048	1.326	8.8

Two significant facts became apparent from the table: (1) The D. R. org/aqueous of the tri-amine reaches a maximum around a pH of 1.6; and (2) the tri-amine is extracted as the mono-nitrate even at a pH as high as 2.7.

The Determination of Tetra-n-butyl Ammonium Nitrate in Hexone

The success encountered in the steam distillation of tri-n-butyl amine as a method of analysis encouraged efforts to analyze for tetra-n-butyl ammonium nitrate by decomposing it to the amine and distilling off the amine.

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A stock solution of tetra-n-butyl ammonium nitrate was prepared from the Eastman Kodak iodide salt by precipitating the iodide in nearly neutral solution by adding $Ag(NO_3)$, determining the exact equivalent point potentiometrically using a Ag electrode vs calomel cell. The break is very sharp - more than 300 mv per drop of 0.07 N $AgNO_3$ solution at the end point. The titration indicated the salt contained 98.6% of the theoretical iodide. 50 ml of a stock solution prepared as above contained 5.538 g of the iodide salt converted to nitrate and was therefore ca 0.3M. 3 ml aliquots of the stock solution were steam distilled from various alkaline solutions with and without an added hexane phase and, also, with and without previous treatment. The distillates were collected in convenient aliquots and added to a known excess of HNO_3 and back-titrated with standard base as in the tri-n-butyl amine determination. Distillation was continued until the amine ceased to come over. The best results obtained indicated only 88% recovery of the theoretical amine and with those conditins as standard, two weighed samples of the iodide salt were analyzed with comparable results. Table III lists the various experiments and their results. Experiments 7, 10,11, and 12 were performed under the conditions used for the determination of the quaternary salt in the extraction experiments described below.

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[redacted]

TABLE III

The Determination of Tetra-n-butyl Ammonium Nitrate

Run	Volume 0.3M salt mls	Stillpot solution	Conditions	Total Volume of Distillate: Aqueous mls	Total Volume of Distillate: Hexone mls	total meq HNO_3 Added to Dis.	total meq of Base Req.	total meq Amine found	% Recovery based on 98.5% purity
1	3	6 N NaOH	Direct Distillation; 5 ml cuts	25	-	4.99	4.91	0.08	9
2	3	6 N NaOH	Steam Distilled; hexone intermittently added to stillpot; 5 cuts	75	25	5.03	5.00	0.03	3
3	3	50g 76% NaOH + 50 ml H_2O	Direct Distillation; 2 10 ml cuts	20	-	1.996	1.379	0.617	69.6
4	3	75g 76% NaOH + 30 ml H_2O	Distilled Directly three 2 ml aliquot collected	6	-	4.02	3.29	0.73	82
5	3	19 N NaOH 5 ml hexone	Distilled Directly; Four 5ml aliquots; one 15 ml aliquot	30	5	4.99	4.29	0.70	79
6	3	50g 76% NaOH 30 ml H_2O	Heated to near boiling, distilled hexone through solution; five 5 ml cuts	9	16	4.99	4.65	0.34	38 +
			(6a) continued steam distillation	50	-	0.998	0.576	0.422	48
							Total		86
7	3	50g 76% NaOH 30ml H_2O	Refluxed 15 minutes at boiling point of solution ca 135°C; flushed column with 10ml hexone	13	9	0.998	0.222	0.772	87.5
8*	3	50g 76% NaOH 30 ml H_2O 10ml Hexone	Refluxed for 15 minutes (135°C) and flushed with ca 12ml hexone steam distilled two aliquots: (a)15ml (b) 20ml	(a) 2	13	0.998	0.890	0.108	(12) +
				(b) 11	9	0.998	0.403	0.595	(67)
							Total		79

* Most of the tri-n-butyl amine comes over with the last portion of hexone and distills but inefficiently initially.

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TABLE III
(Cont.)

Run	Volume 0.3M salt mls	Stillpot solution	Conditions	Total Volume of Distillate: Aqueous mls	Total Volume of Distillate: Hexone mls	total meq HNO_3 Added to Dist.	total meq of Base Req.	total meq Amine found	% Recovery Based on 98.5% purity
9	3	50g 76%NaOH 30 ml H_2O	Refluxed for 15 minutes (135°C); cooled and steam distilled	80	-	3.992	3.339	0.653	74
			(9a) added 10ml hexone; continued distillation	10	10	0.998	0.976	0.022	4 2
							Total		76
10	3	50g 76%NaOH 30 ml H_2O	Refluxed 15 minutes(135°C); flushed column with 10ml hexone; cooled and steam distilled	10	10	1.996	1.213	0.783	88.3
			Iodide Runs						
11	0.495 meq I^-	50g 76%NaOH 30ml H_2O	Refluxed 15 minutes(135°C) flushed column with 10 ml hexone; cooled and steam distilled	11	10	1.996	1.558	0.438	88.5
12	0.502 meq I^-	50g 76%NaOH 30ml H_2O	Refluxed 15 minutes (135°C) flushed column with 10ml hexone; cooled and steam distilled	11	10	1.996	1.582	0.414	82.5

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The Extraction of Tetra-n-butyl Ammonium Nitrate with Hexone

The D. R. organic/aqueous of tetra-n-butyl ammonium nitrate in hexone - $Al(NO_3)_3$ systems has been found to increase inversely with pH. Its solubility has also been found to be sharply pH dependent, at least in 1 M $Al(NO_3)_3$, the solubility in 1M $Al(NO_3)_3$ - 5M HNO_3 being less than 0.004M and in 1M $Al(NO_3)_3$ - 0.8M HNO_3 less than 0.1M.

Four 10 ml solutions were prepared each 0.089 in tetra-n-butyl ammonium nitrate and 1M in $Al(NO_3)_3$ and containing various amounts of HNO_3 and $NaNO_3$. The low pH solutions, 5 and 0.8 M in HNO_3, separated into two phases. In the former case, it was possible to separate the lighter phase which was 0.1 to 0.2 ml in volume. Analysis showed this phase, which was water soluble, to contain 96.5% of the total tetra-n-butyl ammonium nitrate. The other three solutions were equilibrated 2½ hours at 25°C with equal volumes (10 mls) of pre-treated hexone. The phases were separated an analyzed for acid and the tetra salt by the methods developed above. Results of the analyses appear in Table IV. The material balances are based on 87.9% yield for the decomposition of the salt to the trisamine. No significant volume changes occurred during equilibration.

TABLE IV

The Extraction of Tetra-n-butyl Ammonium Nitrate with Hexone

Conditions: 1M $Al(NO_3)_3$, -0.089 M $(C_4H_9)_4$ N.NO equilibrated 2½ hours with an equal volume of pre-treated hexone.

Run	Final pH Aqueous phase	Acid Conc. Organic phase	meq $(C_4H_9)_4$ N.NO_3 Aqueous	Organic	D. R. Organic Aqueous	Material Balance based on 87.9% yield
1	-0.14	0.406	0.037	0.48	13	67%
2	1.69	0.021	0.21	0.55	2.6	97%
3	2.36	0.006	0.21	0.43	2.0	82%

Ruthenium Distribution

Further studies were made on ruthenium distribution ratios, and equilibrium and rate constants which were discussed in Mon N-432, pp.23-28, Figures 14 and 15, show the new data obtained while Figure 16 shows the proposed explanation with the revised constants.

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Four constants relating Ru_A and Ru_B are known experimentally. The probable values of these constants are listed with extra figures for consistency in cross calculations. The values of the constants are dependent at least upon temperature, pH, salting strength, and reagent purity. This dependence helps to account for ranges of values noted.

D_B = distribution ratio of Ru_B (org/aq) = 0.05 ± 20% (from repeated rapid extractions of an organic scrub).

$D_{2\mathcal{D}_\infty}$ = distribution ratio of Ru_A + Ru_B after twelve hour two phase equilibration = 1.15 ± 40%.

D_{org_∞} = distribution ratio of Ru_A + Ru_B where organic phase Ru_A and Ru_B in equilibrium are contacted for a short time with inactive aqueous phase = 5.68 ± 30%.

D_{aq_∞} = distribution ratio of Ru_A and Ru_B where aqueous phase Ru_A and Ru_B in equilibrium are contacted for a short time with inactive organic phase = 0.207 ± 50%.

The three remaining constants were calculated to give the best fit with the above values:

D_A = distribution ratio of Ru_A = 7.43 ± 30%.

Ko = equilibrium constant for $Ru_A \longleftrightarrow Ru_B$ in organic phase = 26.0 ± 50%.

$Ka \equiv \frac{D_B \; Ko}{D_A}$ = equilibrium constant for $Ru_A \longleftrightarrow Ru_B$ in aqueous phase = 0.175 ± 50%.

The rapid extractions of a scrub lead to a distribution ratio of .05 to .06. This distribution ratio should represent the distribution ratio of Ru_B since the Ru_A will have fractionated out and Ru_A is being formed from Ru_B at the rate of only about 1 % (or less) per minute. (The half reaction time of $Ru_B \longrightarrow Ru_A$ in two phases is in the order of an hour as seen in Figure 15.)

Figure 14 is a distribution diagram for initially oxidized ruthenium tracer and is very similar to the diagram on page 24 of the earlier report. Because of the fact that the scrubs of the organic phase were carried out rather rapidly (2½ hours to point where distribution ratio of 15.2 was observed) it is probably that the oxidized ruthenium (Ru_D) did not have time to react to $Ru_A \longleftrightarrow Ru_B$ (See Figure 16). Apparently then, the distribution ratio of 15 represents a combination of Ru_A and Ru_D, almost all the Ru_B having been fractionated out by the rapid scrubs.

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Figure 15 shows the rates of approach to two phase equilibrium. These data might appear to be approaching a two phase equilibrium distribution ratio ($D_{2\phi\infty}$) of about 1.5 but this value of 1.5 does not agree with previous values of $D_{2\phi\infty}$ (.09 to 1.3) nor the relationship of $D_{org\,\infty}$, $D_{aq\,\infty}$, and D_B. For this reason the value of $D_{2\phi\infty}$ was set at 1.15, the point at which the lower curve alone appears to be leveling off. The deviation of the upper curve from the theoretical might then be explained by the presence of Ru_D with a high distribution ratio which is only slowly reacting to Ru_A and Ru_B.

The rates of approach to two phase equilibrium may be expected to be equal since the reaction of $Ru_A \longrightarrow Ru_B$ or the $Ru_B \longrightarrow Ru_A$ should take place mostly in the phase where the rate is faster and independently of the phase in which the form was present initially.

It must be emphasized that all these statements are merely proposed explanations which fit the data reasonably well. The system is at least as complicated and is probably more complex than the diagram.

Formation of Solids

Examination of solid matter formed in the presence of DPT under various conditions has indicated that several types may be formed:

1) In the pilot plant run with DPT an appreciable amount of $UO_2SO_4 \cdot 3H_2O$ was precipitated in the mixing and heating chamber. The formation of sulfate from DPT and nitric acid in hexone has been found to be accelerated by higher temperature, higher acidity, and the presence of stainless steel. This precipitate will redissolve in water.

2) Smaller amounts of a blue insoluble precipitate have been formed on long standing of Hexone - DPT - HNO_3.

3) The black solid formed when DPT was added to hexone from the "23" column appears to be associated with the presence of mercury and/or manganese.

Precipitation of aluminum and iron can be brought about by heating the system $Al(NO_3)_3$ - HNO_3 - hexone - traces of Fe^{+++}.

The memo C1-GREE-47, file 48-5-14, gives a complete report of these studies.

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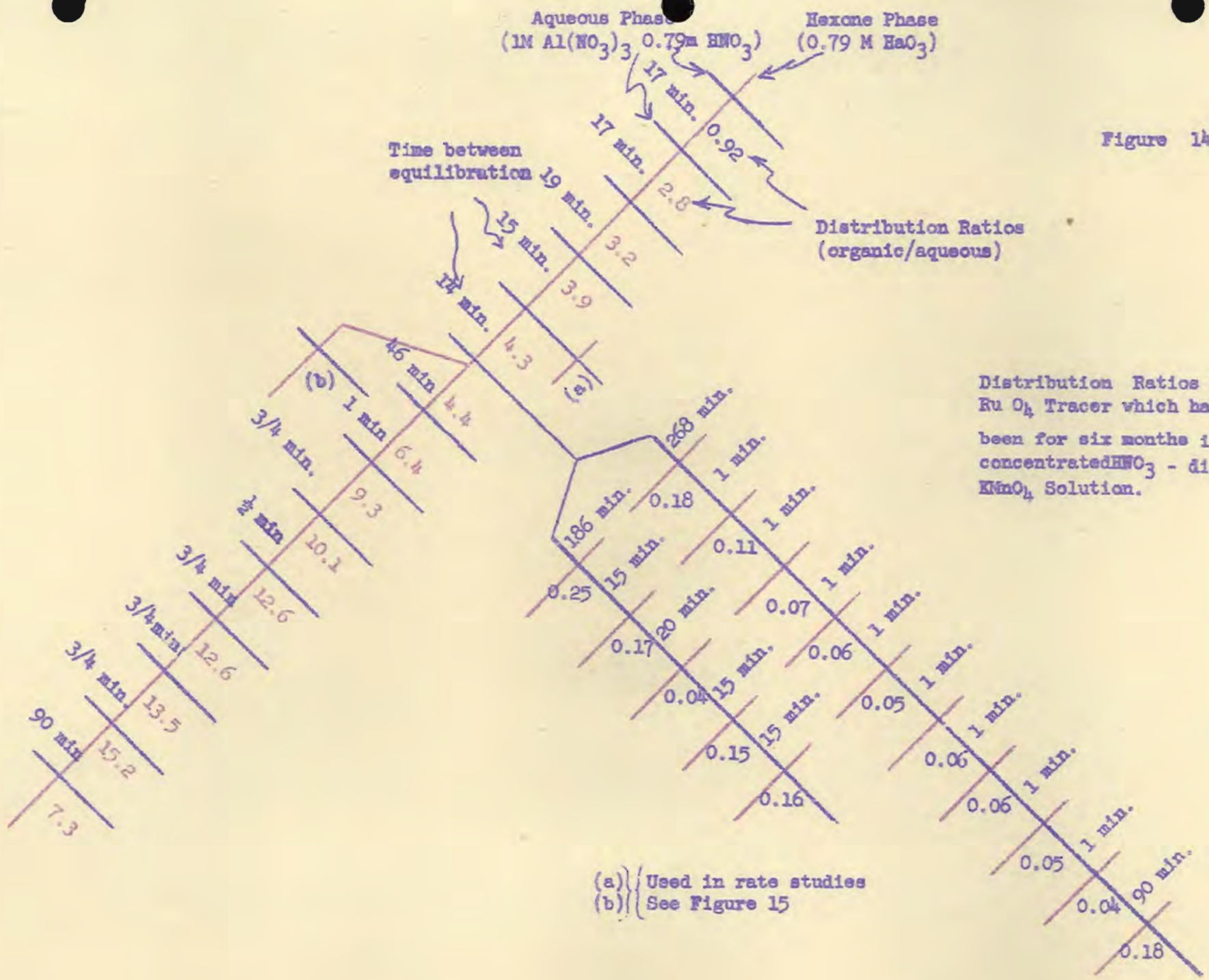

Figure 14

Distribution Ratios for Ru O_4 Tracer which has been for six months in concentrated HNO_3 - dilute $KMnO_4$ Solution.

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Figure 15

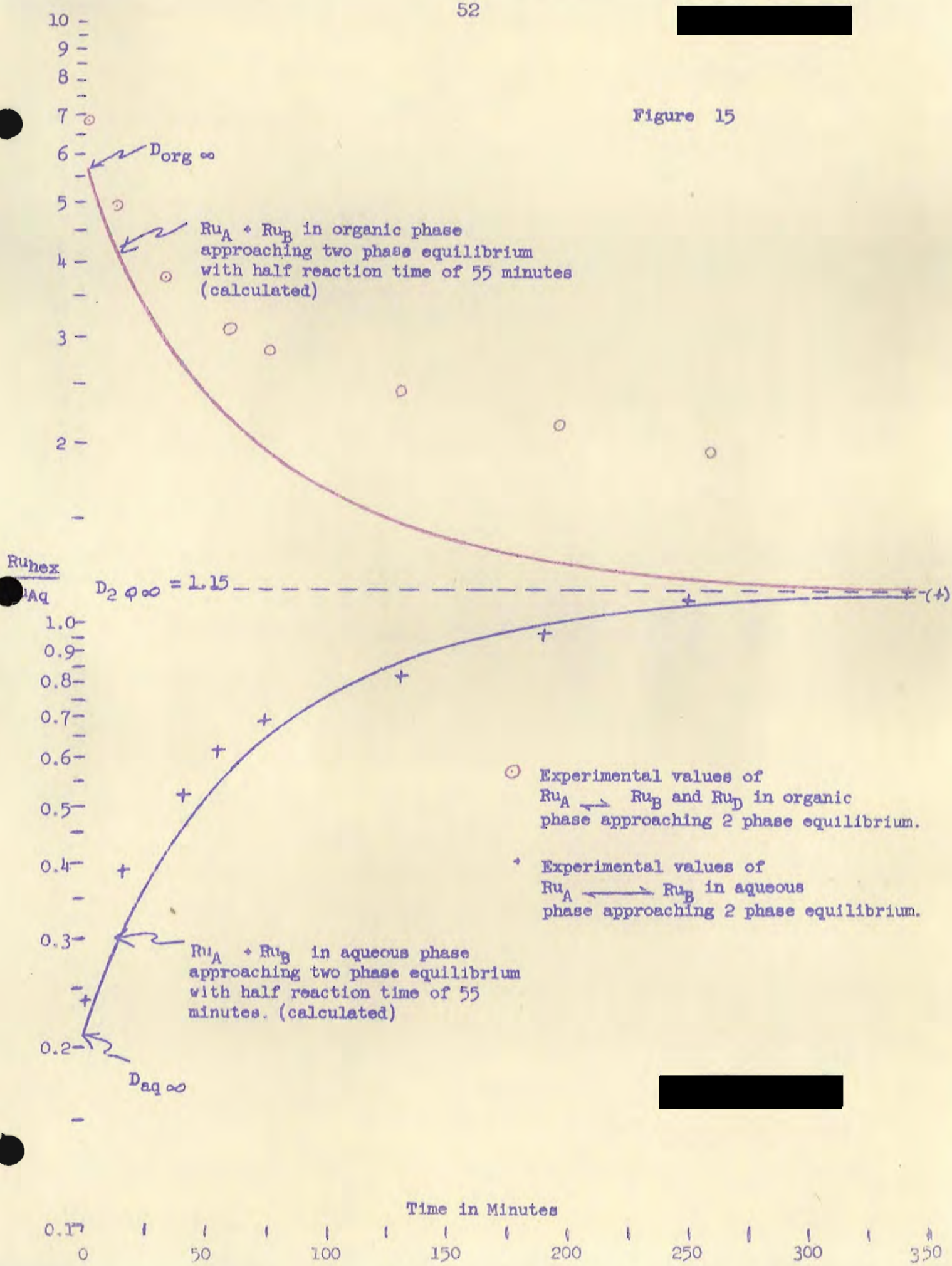

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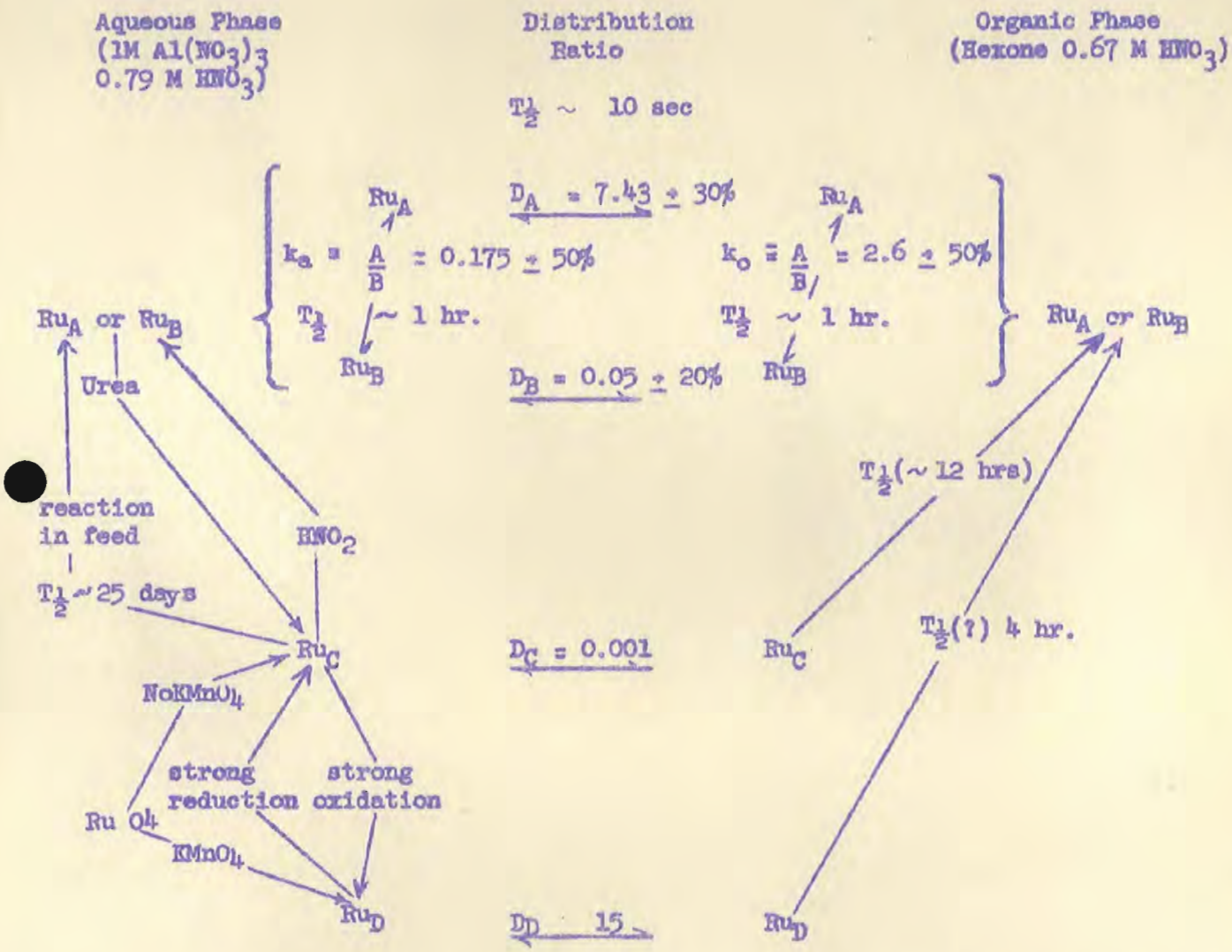
Figure 16

Proposed Explanation for Behavior of Ruthenium



D_A, D_B, D_C, D_D are distribution ratios (organic/aqueous) of Ru_A, Ru_B, Ru_C, Ru_D.

$T_{\frac{1}{2}}$ indicates half reaction time. Parentheses indicate a rough guess chosen to fit fragmentary evidence available.

k_o and k_a are equilibrium constants for reversible reactions in the organic and aqueous phases.

Limits of accuracy are discussed in text. Best values to fit all the data are listed on the diagram and extra figures are carried so that cross calculations will be consistent.

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2. RADIOISOTOPES

A Method of Analyzing Radioactive Decay Curves - (H. Zeldes)

A paper will be released shortly describing a method of computing the A_i and λ_i parameters from radioactive decay curves, where the total activity $A(t) = \sum A_i e^{-\lambda_i t}$ is known as a function of time. The method is to represent $\ln A(t)$ as a polynomial $f(t)$ and then to represent $e^{f(t)}$ by $\sum A_i e^{-\lambda_i t}$ using the least squares criterion to adjust the values of the parameters. This method is simpler (though less objective) than least squaring the original data to $\sum A_i e^{-\lambda_i t}$ to obtain the A_i parameters where the λ_i parameters are known. In addition, it yields the λ_i parameters. The error in the computed values of A_i is discussed and graphically illustrated for the two component case.

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Xenon Cross Sections as a Function of Energy

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

Xe Retention Experiments

During the last quarter, work was directed primarily toward determining the extent to which Xe is released from PdI_2 precipitates and the loss of Xe during the somewhat lengthy precipitation procedure, i.e., toward determining an effective zero time for growth in terms of the precipitation. In order to accomplish this it was necessary to find a system for reference wherein all of the Xe was known to be released. This led to a number of experiments on hydrated NaI for which previous information had indicated complete release of Xe as it formed. Interpretation of these data was hindered by uncertainties in the radiochemical constants of the short-lived Xe^{135} isomer and its relation to the 9.2 hr. Xe^{135} ground state. Consequently, a number of measurements were made, designed to either confirm or revise existing information on the radiochemistry of Xe^{135}.

The basic experimental technique consisted in milking an iodide sample (containing I^{135}) of its Xe^{135} daughter and counting the gas sample thus obtained. The apparatus was comprised of a vacuum system, a source of carrier Xe and one of water vapor, and a large bulb constructed and operated like a McLeod gauge. The gas sample was expanded into this bulb and then compressed with Hg up into a small counting bulb which replaced the closed end capillary of the usual McLeod gauge. This bulb was blown from 2 mm capillary, had a volume of about 0.3 cc, and was estimated to have a wall thickness of several mils and about 20 mg/cm^2. The iodide sample was placed in a small bulb and appropriate connections and stopcocks provided to permit necessary evacuation, dosing with water and Xe, and expansion into the compression bulb. Capillary tubing leading to the small counting bulb passed through a hole in the bottom of a standard lead pig and the bulb itself, inside the pig, was placed with a little better than second shelf geometry relative to a standard G-M tube. The gas sample was compressed into this bulb with Hg which could be reproducibly brought just to the point at which the bulb joined the capillary, thus giving an essentially spherical source. A number of early measurements were vitiated by failure to appreciate the difficulty of completely removing Xe activity from the counting and compression bulb after a count. Evacuation with a mercury diffusion pump, even for considerable periods, proved insufficient to remove all the activity which then was added to the next sample to give inordinately high results. If the counting system was well flushed with air four or five times following a count, this difficulty was avoided and hence such flushing was adopted as standard practice.

Most of the work has been done with NaI as the source of Xe. The preparation and assay of the I^{135} tracer is described in section II below. Several trials were made of the extraction of Xe from a water solution of iodide, but the results seemed to indicate that removal was not complete. Most of the work was done by evaporating a solution of sodium iodide to dryness and then admitting water vapor and carrier Xe to the sample vessel. The water vapor was introduced to insure that the NaI was in the form of the hydrate which previous work had indicated lost all its Xe readily. The procedure generally followed consisted in alternately evacuating and dosing (with water vapor and Xe) the sample for about three cycles comprising a 5-10 second evacuation and about a minute's growth. At the end of the final evacuation, the sample was shut off, given a final dosage of water and Xe and allowed to grow for the desired period of time which ranged from two minutes to twelve hours.

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[redacted]

Whether or not complete release of Xe is accomplished by this procedure is still undetermined. Several pieces of evidence, however, combine to suggest that it is. Reproducibility is excellent, indicating that at least a constant fraction if not all the Xe is removed in each milking. Furthermore, a preliminary result, discussed later in this report, on absolute counting of the 9.2 hour Xe^{135} by coincidence methods gave a result appreciably higher than that calculated from the iodine assay. It is suspected that the high result arises from the presence of conversion electrons which were not eliminated in the counting and that re-investigation will give a good check between the iodine assay and the absolute counting of the Xe^{135}. It thus seems probable that the Xe^{135} is completely released by the hydrated sodium iodide. Certainly the fact that several one minute flushings with water and Xe are sufficient to prevent any appreciable accumulation of Xe in successive growth periods argues for fairly complete Xe elimination. This point requires additional work before an unequivocal answer can be given.

The decay curves of the gas samples were analyzed by several different methods into the two components of 9.2 hour and 15.3 minute half-lives. The most satisfactory method, and the one most used in later runs, was to use the integrated counts over a 20-30 minute period at the beginning of the counting and another integrated count over the same time interval at the end of the counting period. This procedure results in two constants which, in the case of two independent decays, are direct measures of the counting rates of the two activities at zero time. In the case of the Xe decay, where the ground state arises partly from decay of the parent iodine and partly from the decay of the isomer, these two constants are related to the counting efficiencies and the fraction of the decay following the isomer route. By working with different growth periods, it is possible in principle to obtain a value for the fraction of the decay going by the isomer route. In practice, however, it was found that the counting data, thus analyzed, was far too insensitive to variations in the fraction to permit such a determination.

The half-life of the Xe^{135} isomer is variously reported to be between 10 and 15.6 minutes with 13 minutes listed as the preferred value. Since analysis of the decay data from various growth periods required a rather good value for this half-life, a re-determination was made.

Sufficient activity was prepared to permit counting of the gas samples at adequate rates through 6.7 grams of Pb. Under these conditions less than two percent of the original counting rate was due to the 9.2 hr. Xe. Over about ten half-lives the data lead to a value of 15.3 minutes for the half-life of the Xe^{135} isomer. This figure should be good to about 2%. Decay curves were also run with 437 mg of Al, and with 87.6 mg of Al as absorber. There was no evidence for activity other than those of 15.3 minute and 9.2 hour half-lives.

Purity of the 9.2 hour Xe was investigated by determining the half-life and the absorption curve. Both checked published data satisfactorily, and there was no evidence for unexpected activities. About 0.6% of the original counts were due to the 5.4 day Xe^{133} which means that the I^{135} tracer probably contained less than 2% I^{133} as impurity.

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A number of extractions of Xe were made after 15 minute growth periods. These extractions extended over a twenty-three hour period. The zero time counts for both the 15.3 minute and 9.2 hour Xe activities decreased with about a 6.7 hour half-life, thus confirming the fact that both Xe activities are daughters of 6.7 hour iodine.

Since attempts to determine the fraction of the Xe decaying via the isomer route were not successful by counting gas from varying times of growth, the problem was attacked by coincidence methods. Coincidence counting also permits an absolute count of Xe removed from the NaI and hence provides a check on the iodine assay and also on the completeness of removal of Xe from the iodide sample. The electronic equipment for this work was set up by Borkowski and Dandl, of the instrument research group. Proportional counters were used for the β and γ-counting tubes and a coincidence circuit with a resolution time of about 1/2 a microsecond. The β counting tube was filled at atmospheric pressure with CH_4 and the γ tube with an Argon-CO_2 mixture. The γ tube was gold plated and had a 50 mg/cm^2 Au foil over the inside of the window. The estimated γ-counting efficiency for this tube was about 2% at 100% geometry. With an ordinary G.M. tube the counting efficiency for this 0.25 Mev γ-ray is about 0.25%. With this equipment counting was done at rates of 500,000 β counts/min., 10,000 γ counts/min. and 600-800 coincidence counts/min. Unfortunately the random coincidence correction amounted to about 30-40% of the coincidence counts. In spite of this, some useful preliminary data were obtained. Coincidence counts were taken as a function of time for the gas from a six-minute and an eight-minute growth. The coincidence count shows only the 9.2 hour Xe since it is the only one having β-γ coincidences. These curves were analyzed analytically into two components - the growth of 9.2 hr. Xe with a 15.3 minute half-life and the decay of 9.2 hour Xe. In terms of the two constants (k_1 and k_2) it can be shown that the fraction going by the isomer route is

$$F = \frac{1}{\frac{\lambda_2}{\lambda_3 - \lambda_2} \frac{Q_2}{Q_3} \left(\frac{k_1 + k_2}{k_1}\right) - \frac{R_3}{Q_3} + 1}$$

where λ_2 and λ_3 are the half-lives of the 15.3 minute and the 9.2 hour respectively and R_3 is the calculated amount of 9.2 hour activity if all of it was formed through the isomer; Q_3 is that if all the 9.2 hour were formed directly, and Q_2 is the calculated amount of 15.3 minute activity if all the decay were through the isomer route. The six minute and eight minute growth periods yielded values for the percent going by the isomer route of 18% and 20.8% respectively. There is every reason to believe that these values are at least approximately correct. These figures are to be compared with the value of 10% reported in the literature. Re-determination of the fraction by this method is planned in the future under improved experimental conditions.

A preliminary attempt was made to determine the absolute disintegration rate of 9.2 hour Xe by coincidence counting and compare the result with the iodine assay previously developed. A twelve hour growth period for the Xe was used. The results turned out to be too high by as much as thirty percent. There was some evidence that conversion electrons from the 9.2 hour activity had not been experimentally eliminated - a condition that would be expected to lead to high results. This work will be repeated and the interference due to conversion electrons eliminated.

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The loss of Xe during the precipitation of PdI_2 was investigated. The standard procedure for precipitation, reported in the last quarterly report, was followed. Two precipitations were made. The sample of PdI_2, after precipitation and centrifugation, was placed in the apparatus and heated to decomposition. The Xe thus released was counted and the calculated time of growth required to give the amount of Xe found compared with the actual elapsed time from the start of precipitation to the release of Xe. This total elapsed time in one case was an hour and thirty-three minutes and in the other an hour and thirty-five minutes. The actual growth times, computed from the amount of Xe obtained, were 45 minutes and 60 minutes respectively. In the first case this corresponds to 3 minutes after the completion of the half-hour cooling period and in the second case to ten minutes before the end of this period. For the precipitation procedure used, this fixes an effective zero time close to the end of the cooling period. Calculation based on a zero time four minutes before the end of the cooling period should be quite adequate for the purpose in hand. An alternate approach to this is that the experimentally determined amount of Xe is rather close to that calculated on the assumption that 50% of the Xe is lost during the first hour after the start of precipitation. In view of the limited amount of data available at this time, any significant variation in the time schedule of the precipitation would require further investigation.

A precipitate of PdI_2 was left in the apparatus overnight, and the Xe escaping was collected and counted. The amount of Xe collected represented 13% of that expected for such a growth, thus demonstrating an appreciable loss of Xe from dry PdI_2 precipitates at room temperature. Several short collection times were also run at both room temperature and at the temperature of boiling water. These data were sufficiently crude to permit little more in the way of conclusions than that Xe is released from PdI_2 at room temperature and at a somewhat increased rate at 100° C. The increased rate at 100° C over that at room temperature corresponds roughly to an energy of activation of 5000 calories - a not unreasonable figure. An extraction of Xe was also made at the temperature of dry ice. The amount of Xe obtained was 3.76% of that expected if all the iodine had released Xe. The area of this PdI_2 sample was estimated to be 840 Cm^2. If it is assumed that all the I atoms contributing to the released Xe were on the surface of the PdI_2, one obtains a value of 12Å^2 per iodine ion or 3.5Å for the effective diameter of an I ion in the surface. The structure of PdI_2 is not known so this figure cannot be compared to a known value. It does seem somewhat too small, however, as one might expect something in the neighborhood of 5Å for the diameter of the iodide ion. The result, however, does lead one to conclude that at this temperature certainly most of the Xe escaping comes from the surface iodide ions. It suggests a method of measuring surface areas that may have some utility.

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Calibration of Assay Equipment

Introduction

In measuring the Xe^{135} cross section with the crystal spectrometer, it is desirable to know the number of Xe^{135} atoms present in the sample at any given time in order that the cross section can be calculated on an absolute basis. It is expected that of the order of 20 curies of Xe^{135} activity may be used in some of the experiments. The Xe will be formed from the I^{135} parent which will be precipitated as PdI_2. The other fission product I and Xe activities will also be present. None of these activities has been reported to have gamma radiation harder than 0.55 Mev except for I^{135} which has been reported to have a 1.6 Mev gamma ray. It should, therefore, be possible to absorb the soft gamma radiation in a heavy lead shield and measure only the I^{135} gamma radiation. With the instrument calibrated in terms of the number of I^{135} atoms, the number of daughter Xe^{135} atoms at any time after growth has started can be calculated.

Since this method of assay is based on the absence of hard gamma emitters among the longer-lived I and Xe fission products, a check of the published gamma energies (based on Pb absorption data) was made by Peacock with the beta ray spectrometer. His values for the γ ray energies agreed with the published values within 10% in all cases except I^{135}. He found 1.27 and 1.8 Mev γ rays instead of 1.6 Mev as reported before. By measuring the photoneutron yield in Be with Bernstein's apparatus, we were able to show that the 1.8 Mev γ ray occurred in about 4% of the disintegrations. With the confirmation of the presence of hard γ radiation in I^{135} and absence of it in the other longer-lived I and Xe fission products, it was concluded that the proposed method of assay was feasible.

Before an assay instrument could be calibrated in terms of 135 atoms, it was necessary to know the disintegration schemes of I^{135} and Xe^{135}. With the cooperation of Peacock, spectrometer measurements of both of these activities were made. As reported in Mon-432, p. 58, three beta groups were found in I^{135} but these could not be fitted with the γ energies into a definite decay scheme. Xe^{135} was found to have a simple decay scheme with a 0.93 Mev beta followed by a 0.25 Mev gamma ray. The gamma ray was found to be partially internally converted. In spite of the above complications, it was found that the beta counting rate of an I^{135} sample followed the calculated curve within a few per cent (assuming one I^{135} beta per Xe^{135} beta) during the growth and decay of the Xe^{135} daughter. Hence, it was decided to assume that the I^{135} beta counting rate at a known geometry would give the I^{135} disintegration rate. The assay equipment has been calibrated on the basis of this assumption. At the same time work has continued to learn whether the assumption is correct. If it is found to be in error, the calibration can be corrected by the proper factor.

In addition to errors in the absolute counting of I^{135} activity, other sources of error are uncertainties in the decay constants of I^{135} and Xe^{135}. An uncertainty in the assumed precipitation time could also lead to an appreciable error. These errors have been plotted as a function of Xe^{135} growth time in Figure 1. The largest error results from an uncertainty in the I^{135} decay constant because the calculations are based on the plan to measure the I^{135} activity after the neutron spectrometer measurements. This

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was assumed to be 40 hours after precipitation of PdI_2. It appears desirable to assay at the later time because the hard gamma radiation associated with 54 min. $I^{(134)}$ will have decayed. It will also then be possible to follow the decay of the sample and in case foreign activities are present, the decay curve can be analyzed for a 6.7 hr. I^{135} component.

A further possible source of error is the deviation from linearity in the response of the detecting equipment. This could be a serious source of error if the instrument were calibrated at one level of activity and measurements were made at quite a different level. In addition to describing the calibration methods, work which has been done to reduce the two most serious sources of error is described below, i.e. measurements of the half life of I^{135} and determination of the deviation from linearity of response of the instrument.

Equipment

The equipment used for measurement of I^{135} activity in the Xe^{135} assay consists of a conventional high pressure gamma ionization chamber filled with argon and equipped with a vibrating reed electrometer and a Brown recorder. The top and sides of the chamber are shielded from stray radiations with 4 inches of lead. The sample to be measured is placed inside a shield with 4 inches of lead between the sample and the ionization chamber. This sample holder is mounted beneath the chamber and a "portable " shield with 5 inch lead walls rolls into a position from which the sample may be transferred without exposure of personnel.

Calibration

Since the ionization chamber was calibrated with respect to I^{135} beta activity counted at a known geometry, it was necessary to use I^{135} activity of the highest purity. Figure II is a calculated curve showing the per cent contamination in I^{135} beta activity prepared by a two minute bombardment of UNH and separation of the fission product iodine within two minutes after removal from the pile. Immediately after separation, the chief contaminant is 54 min. I and after 8 hours, it is 22 hour I. These two I activities have Te parents with half lives of about an hour whereas the Te parent of I^{135} either has a very short half life or is non existent. The purity of actual preparations of I^{135} activity has been checked by following decay curves both in the presence and absence of Xe daughters. The decay curve of separated Xe activities has also been measured. In all three cases, the amount of impurity was in good agreement with the computed values.

Although the purity of I^{135} activity made by short bombardments and rapid separation was satisfactory, the maximum amount that could be made safely without elaborate equipment was of the order of 30 microcuries at the time of highest purity. This was not enough for precision measurements through 4 inches of lead. By bombarding for 1 hr. and allowing a cooling period of 10 minutes before separation of iodine activity from a uranium salt, it was possible to safely prepare of the order of 2 millicuries of I^{135} activity. At the time of maximum purity about 16% of the beta activity in these samples was from 22 hour I^{133}. A calculated curve showing the change in purity with time after iodine separation is given in Figure III.

Since the amount of contaminating beta activity in the I^{135} samples from 1 hour uranium bombardments was considered to be too high for precision work, the following procedure was adopted. I^{135} activity of the purity shown in Figure II was prepared by a short bombardment of UNH and rapid separation of iodine. The tracer solution contained a small amount of sulfite to prevent loss of I^{135} as iodine and Na_2CO_3 to prevent loss as HI. The solution contained 10 to 15 micrograms of solids per milliliter. It was found that the evaporated tracer solution could be heated or evacuated without loss of I^{135} activity. It was also found that the Xe daughters were not retained in samples kept under ordinary atmospheric conditions. At a time 8 to 10 hours after separation, absorption curves of several aliquots were taken using a mica end window counter. At the same time the decay of a larger aliquot in a reproducible position was followed with an ionization chamber with 1 inch of lead between the sample and the chamber. Just after the I^{135} absorption curves were taken, the absorption curve of an RaE standard sample of known disintegration rate prepared by L. Zumwalt was taken in the same position. The geometry of this position was calculated from the RaE data by the method given by Zumwalt in Mon C-397. Both the RaE and the I^{135} samples were mounted on 0.6 mil polystyrene film and placed in the center of the second shelf using an aluminum mountingcard and spacer. The counting rates were corrected for counting losses, background and gamma ray counts. The mass per cm^2 of the air and mica window between the sample and sensitive volume of the G.M. tube was added to that of the aluminum absorbers and the curves were extrapolated to zero absorber thickness. The extrapolated I^{135} counting rates were corrected for decay to a common time and averaged. This average counting rate was divided by the geometry to give the disintegration rate. The ion chamber measurements expressed as millivolts potential drop across a 10^{11} ohm resistor were corrected to the same time and same aliquot size. The corrected ion chamber measurement divided by the disintegration rate gives the required calibration. Just after each ion chamber measurement, a standard sample was measured in order that corrections could be made for any change in the response of the instrument. The calibration data obtained with five different I^{135} preparations are given in Table I.

Table I

Calibration of Ion Chamber in Terms of I^{135} Disintegration Rate With One Inch of Lead Between Source and Chamber

I^{135} Preparation	β d/min/λ	Volume Measured With Ion Chamber (λ)	Mv With 10^{11} Ohm Resistor	Mv/Millicurie
I-31	19,210	1000	340.2	39,900
I-32	49,740	650	566.0	38,900
I-33	29,380	600	316.7	39,890
I-34	16,710	1000	311.0	41,310
I-35	27,540	1000	500.0	40,320
			Average	40,060
			Standard Deviation	1.96%

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With an ion chamber calibrated for measuring I^{135} activity through 1 inch of lead, it is possible to work with samples containing an appreciable amount of 22 hour I^{133}. When iodine is separated within 15 minutes after a 1 hour bombardment of uranium the error caused by the presence of I^{133} is less than 1%. When measured through 4 inches of lead, the error should be negligible.

In calibrating the chamber for the Xe^{135} assay in the cross section experiments, iodine from a 1 hour UO_2SO_4 bombardment was precipitated with 10 mgs. of carrier iodine as PdI_2. The PdI_2 precipitation was made as described in CNL-37 and centrifuged onto a Selas filter in a 1.5 mm. capillary as planned in the cross section experiments. The capillary tube was placed in a holder of the same design to be used for positioning the PdI_2 in the neutron beam. This holder was placed in a reproducible position with 4 inches of lead between it and the high pressure ionization chamber. The ion current in the chamber was measured for 15 to 20 minutes during the period of highest purity.

In order to assay the PdI_2 for I^{135}, the precipitate was dissolved in 2 M NaCN and the solution was diluted to 25 ml in a volumetric flask. A 100 λ aliquot of this solution was then measured in a standard manner through the 1 inch lead shield. The two ion chamber measurements were corrected for decay to a common time and the potential drop across a 10^{11}ohm resistor per millicurie of activity computed. The results obtained in calibrations with four different I^{135} preparations are given in Table II.

Table II

Calibration of Ion Chamber in Terms of I^{135} Disintegration Rate With Four Inches of Lead Between Source and Chamber

I^{135} Preparation	Mv with 1" Pb 10^{11}Ohm Resistor	Millicuries of I^{135} in PdI_2	Mv with 4" Pb 10^{11}Ohm Resistor	Mv/Millicurie
I-36	249.6	1.56	180.3	115.6
I-38	302.0	1.89	221.0	117.1
I-39	193.0	1.21	144.6	118.5
I-40	270.4	1.69	197.6	116.9

Average 117.3
Standard Deviation 1.2%

Linearity of Response of Ionization Chamber

In calibrating the ionization chamber sources of the order of 1.5 millicuries of I^{135} were used. The samples to be assayed in the cross section experiments are expected to have in the region of a curie of I^{135}. In order for the calibration to be useful, it is necessary either to establish that the ionization current is proportional to the activity or to determine the deviation from linearity over the range in which the instrument is to be used.

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In preliminary experiments, it was found that with ionization current in the range expected (10^{-9} to 10^{-8} amperes) the current was not proportional to the activity of the source. It was also found that the deviation from linearity was a function of source position and probably also of the energy of the radiation. In the determination of the deviation from linearity, it was assumed that the relation between activity and ionization current could be represented by a power series

$$A = k_1 I + k_2 I^2 + k_3 I^3$$

and that an increment in activity ΔA would produce an increment in ion current ΔI. Then

$$A + \Delta A = k_1(I + \Delta I) + k_2[I^2 + 2I\Delta I + (\Delta I)^2] + k_3[I^3 + 3I^2\Delta I + 3I(\Delta I)^2 + (\Delta I)^3]$$

and

$$\frac{\Delta A}{\Delta I} = k_1 + k_2(2I + \Delta I) + k_3[3I^2 + 3I\Delta I + (\Delta I)^2]$$

By measuring the ionization current at various levels before and after adding an increment of activity, it is possible to solve for the constants in the above equations. The deviation from linearity

$$A - k_1 I = k_2 I^2 + k_3 I^3$$

and the per cent deviation from linearity is:

$$\left(\frac{A - k_1 I}{k_1 I}\right) 100 = \left(\frac{k_2}{k_1} I + \frac{k_3}{k_1} I^2\right) 100$$

The corrected ion current I_c which is proportional to the activity of the sample measured will be equal to the observed ion current I plus the correction for deviation from linearity or

$$I_c = I + \frac{k_2}{k_1} I + \frac{k_3}{k} I^2$$

It can be seen that the values of the constants k_1, k_2 and k_3 will be proportional to the strength of the incremental source ΔA. However, the ratios $\frac{k_2}{k_1}$ and $\frac{k_3}{k_1}$ are independent of source strength. Hence, it is not necessary to use sources of known strength in the determination of the correction factors.

In the experimental work a series of radium sources was used as follows The ion current was measured before and after the addition of an incremental source with a nominal strength of 1.88 millicuries. The incremental source was always placed in the standard sample position. Another source was added in a position as close as possible to the standard sample position and the ion current was again measured before and after the addition of the incremental source. This was repeated until the full range of the instrument had been covered.

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The experimental data are plotted in Figure IV as $\frac{\Delta A}{\Delta I}$ versus $2I + \Delta I$. It can be seen that a straight line adequately fits the data and therefore the deviation from linearity is proportional to I^2. Hence, higher terms in the power series can be neglected. The best least squares values for the constants k_1 and k_2 are 2.484×10^9 and 1.142×10^{17} respectively. The corrected ion current is then

$$I_c = I + 4.60 \times 10^7 I^2$$

The standard deviation of the $\frac{\Delta A}{\Delta I}$ values using the above constants was 3.7×10^7. This will lead to a standard deviation of $\left(\frac{3.7 \times 10^7}{k_1}\right)100$ or 1.5 per cent over the range of the instrument.

Since the calibration with a 4 inch lead shield gave 117.3 millivolts per millicurie with a 9.1×10^{10} ohm resistor the I^{135} activity in curies can be expressed as a function of observed ion current as

$$A = 7.75 \times 10^8 I + 3.57 \times 10^{15} I^2$$

It is believed that the chief uncertainty in the correction term arises from the use of Ra activity rather than I^{135} activity in evaluating the constants. Before using this equation in an actual assay, it is planned to follow the decay of a hot I^{135} source. Since the log of the corrected ion current should be proportional to the time this will serve to check the correction term or allow a re-evaluation of it.

Half Life of I^{135}

Because errors of the order of 8% in the Xe^{135} assay are introduced by an error of 2% in the I^{135} decay constant, a careful re-determination of this constant has been made. I^{135} was prepared by a 1 hour bombardment of UO_2SO_4 and extraction of fission iodine within 15 minutes. The iodine was purified by oxidation and extraction into CCl_4 and reduction and extraction into water. This was repeated until the activity in the aqueous phase after extraction of iodine and the activity in the CCl_4 after extraction of iodide was entirely negligible.

The purified source was placed in the 4 inch lead shield and the change in ionization current followed continuously until it reached background. The decay data were fitted to the equation:

$$\text{Log}_{10} A = \text{Log}_{10} A_0 - \frac{0.301\ t}{T_{\frac{1}{2}}}$$

by the method of least squares. Only that portion of the decay curve between the time when 54 min. activity amounted to 0.1% and when the uncertainty in background introduced a 0.2% error was used. The deviation from linearity at the highest ion current was of the order of 0.01% and hence no correction was made. The results obtained in experiments with four different iodine preparations are given in Table III.

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Table III

Half Life of Iodine^{135}

Iodine Preparation	Half Life (min)
I-25	398.4
I-26	400.5
I-27	401.1
I-29	402.1
Average	400.5
Standard Deviation	0.34%

It is doubtful whether the mean value obtained for the half life is as reliable as is indicated by the standard deviation. This is because constant errors such as unsuspected impurity are a common source of error in half life measurements.

The fact that the mean value is within 0.4% of the value given by Glendenin and Metcalf (CC-2219) and by Katcoff, Dilland, Finston, Finkle, Seiler and Sugarman (CN-2379) gives confidence that the error in the Xe^{135} assay from this source would not be greater than 2%.

Recovery of Cs^{135}

It is estimated that sufficient quantities of Cs^{135} (about 3×10^{16} atoms) will accumulate from the Xe project to detect a half life of 2.10^9 y. and also to obtain a good cross section measurement if the Cs is isolated without carrier.

Work is in progress on a process for removing the high level iodine and xenon activities and for isolating the Cs without carrier.

It is doubtful that any radiations from Cs^{135} have been detected. W. E. Grummitt and G. Wilkinson (Nature, August 1946, p. 163) report a 0.8 Mev β with a 100 y. half life for Cs^{135}. However, several project investigators working with Cs from the 135 chain have reported lower limits for the half life greatly exceeding 100 y. if the β energy is moderately great. These include L. E. Glendenin and R. P. Metcalf (PPR Vol. 9B, 7.32.2 (1946)) who report $t_{\frac{1}{2}} > 2 \times 10^3$ y., B. Finkle and N. Sugarman (PPR Vol. 9B, 7.40.1 (1946)) who report $t_{\frac{1}{2}} > 1.2 \times 10^3$ y. and D. W. Engelkemeir (PPR Vol. 9B, 7.40.2 (1946)) who reports $t_{\frac{1}{2}} > 3.5 \times 10^6$ y. In addition, Engelkemeir reports $t_{\frac{1}{2}} > 2.5 \times 10^4$ y. if the β energy exceeds 30 Kev.

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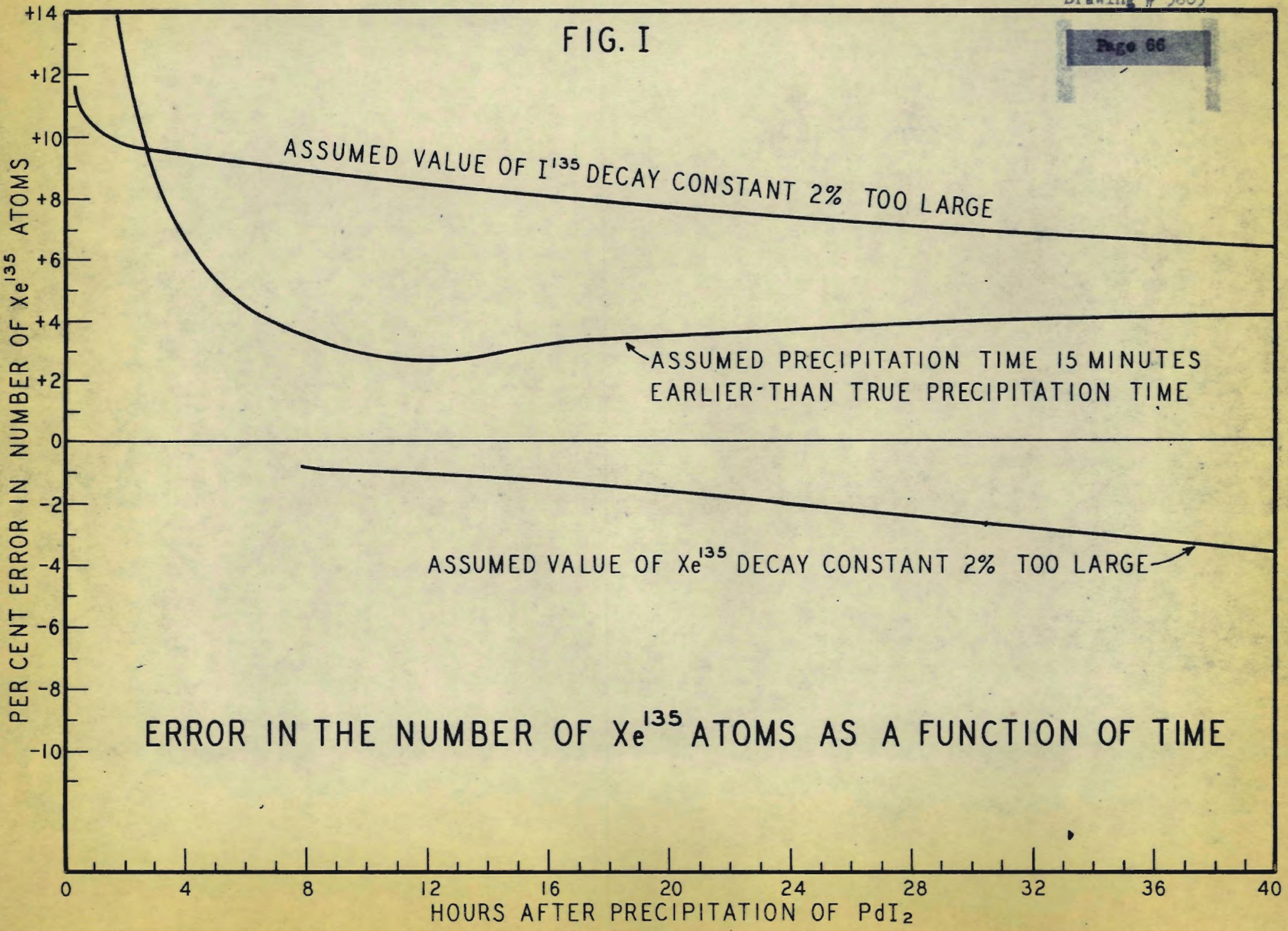
Drawing # 5805

Page 66

FIG. I



Drawing # 5804

FIG. II

PURITY OF I^{135} SEPARATED WITHIN 2 MINUTES AFTER A 2 MINUTE PILE BOMBARDMENT OF UNH

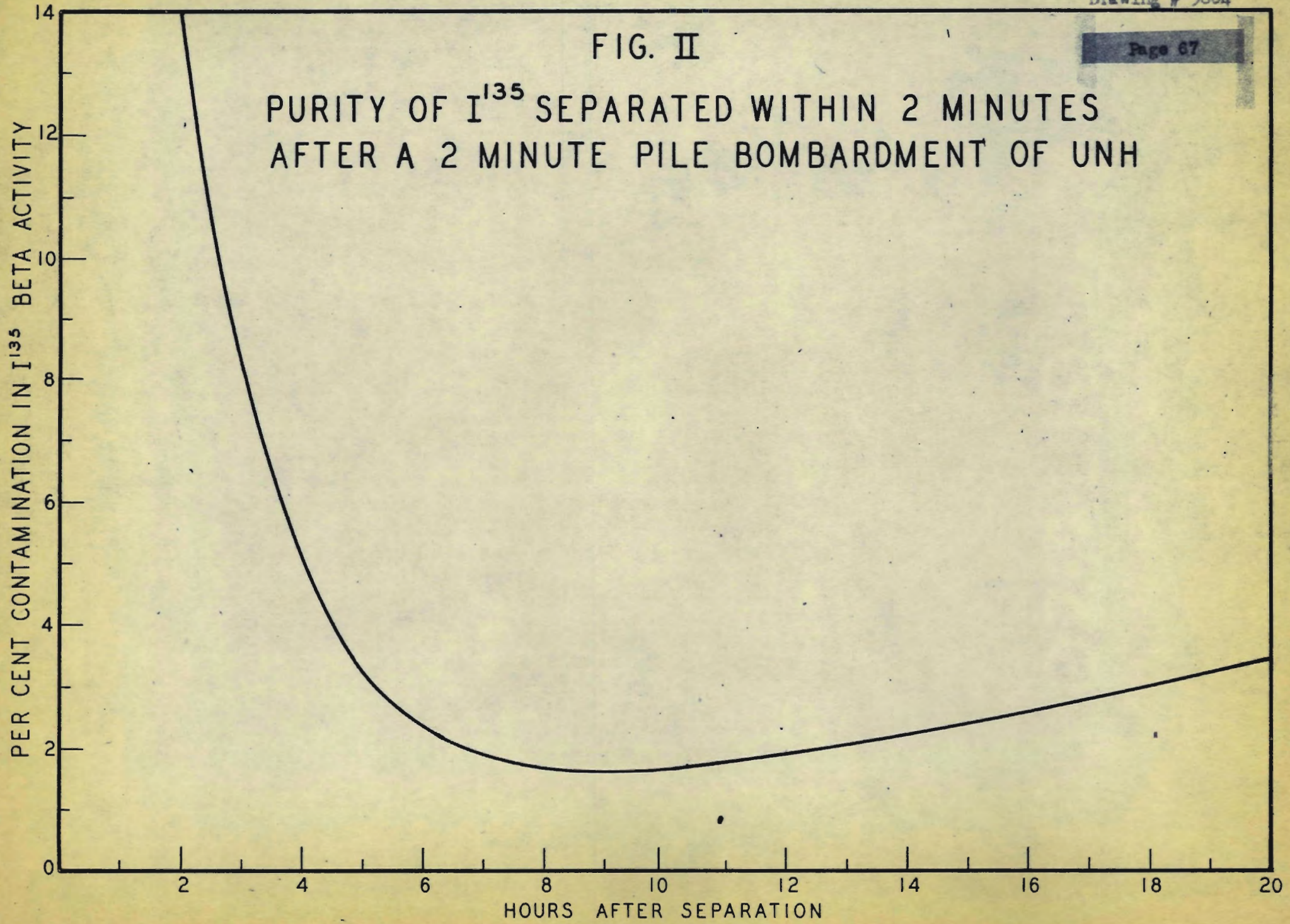
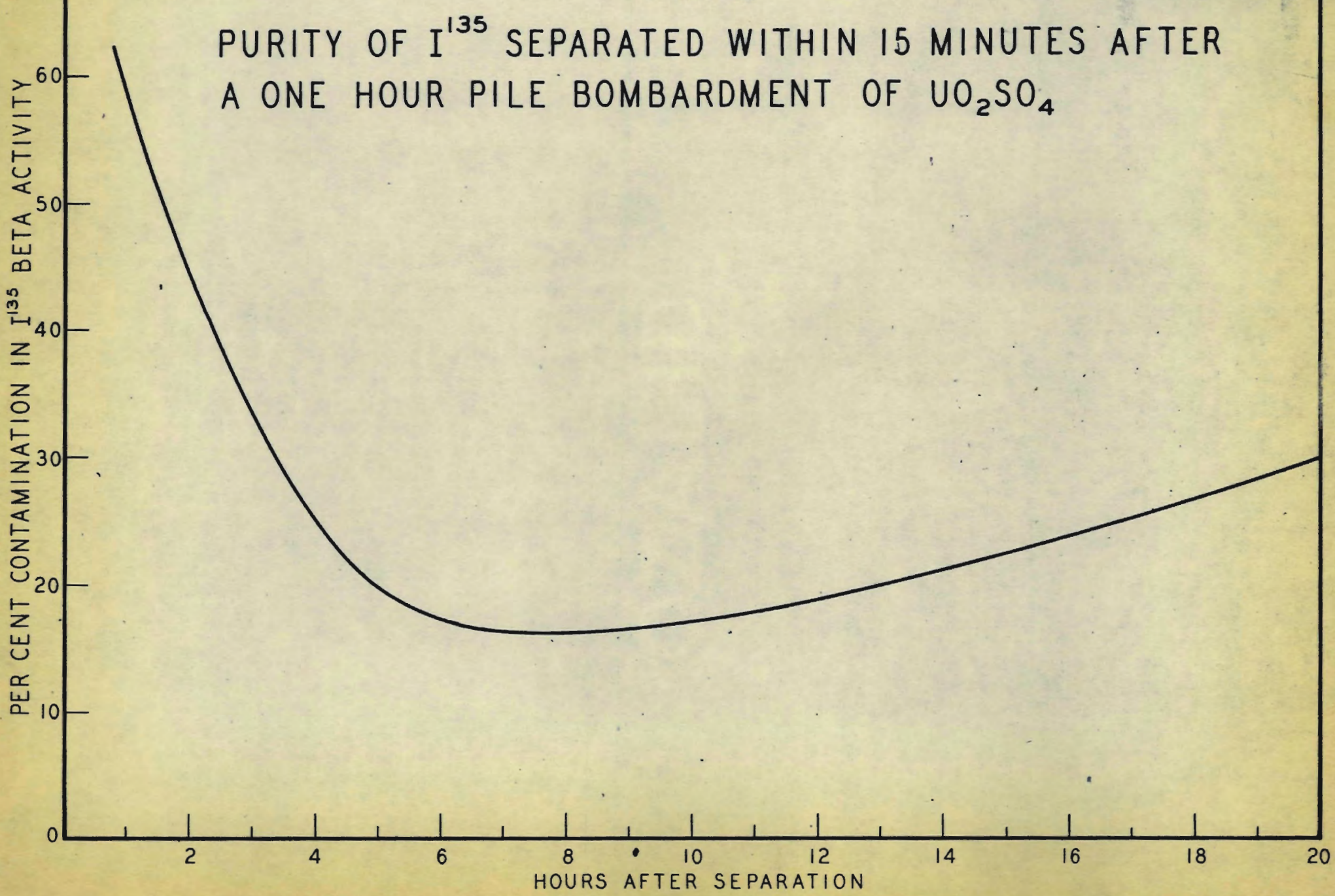


FIG. III

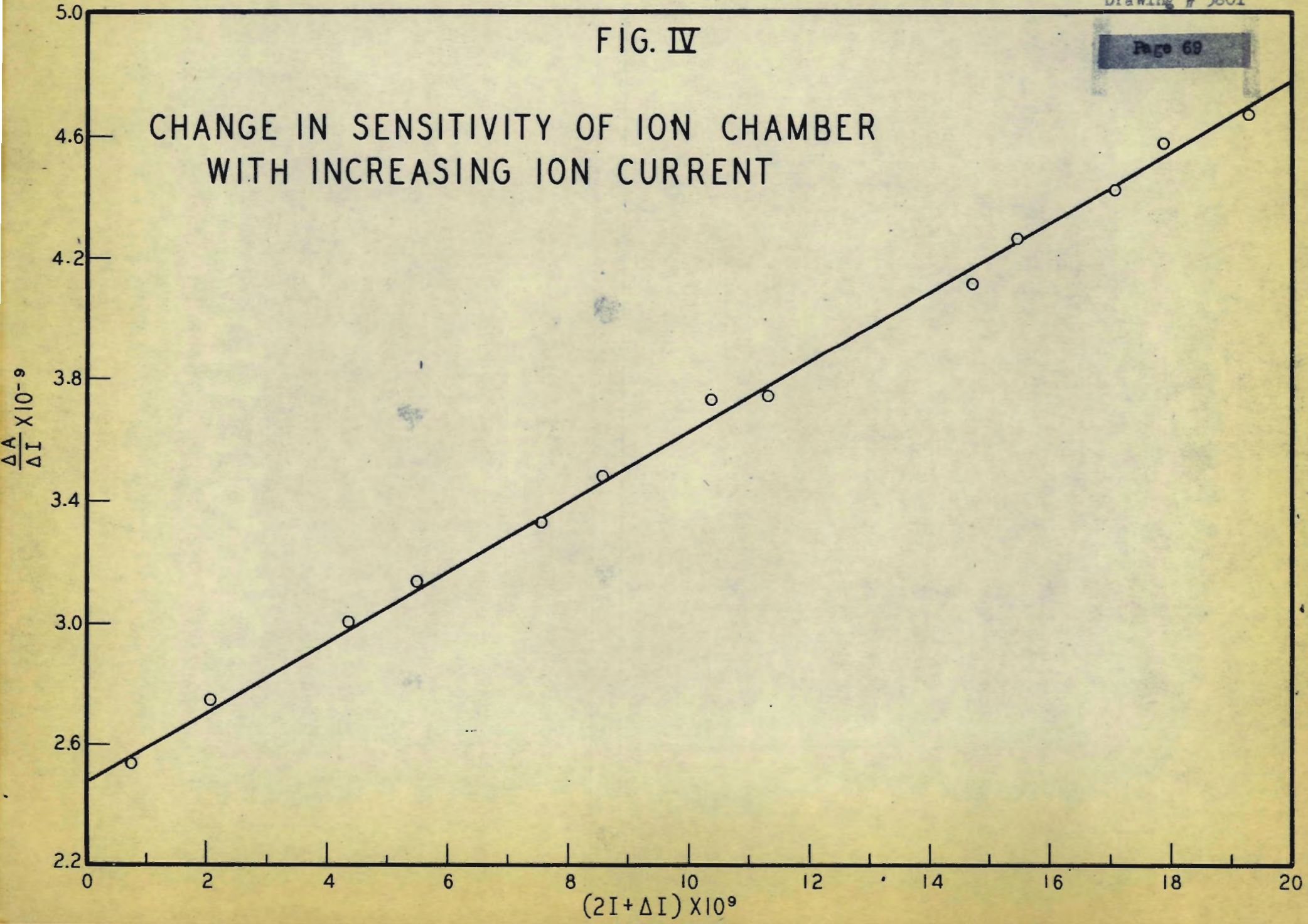
PURITY OF I^{135} SEPARATED WITHIN 15 MINUTES AFTER A ONE HOUR PILE BOMBARDMENT OF UO_2SO_4



Drawing # 5801

FIG. IV

CHANGE IN SENSITIVITY OF ION CHAMBER WITH INCREASING ION CURRENT



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Research Relating to Radioisotope Production

The Removal of Alpha Emitters from Fission Products: (H.W. Kohn, J.A. Swartout)

The cation-exchange procedure which was described in the last quarterly report, CNL-37, for the preparation of radiochemically pure yttrium has been adopted by the Operations Department.

A more extensive separation of rare earth fission activities and alpha emitters, Pu, Y, Eu, 61, Am, Nd, Pr and Ce, has been effected. These were adsorbed from a 5% citric acid solution with pH adjusted to 1.0 on an 86 cm x 4 mm (diam.) column of the 80-150 mesh fraction of a recently obtained, experimental batch of more completely sulfonated Dowex-50. The adsorbed ions were eluted with 5% citric acid, pH adjusted to 3.0, at a flow rate of 0.3 $ml/cm^2/min$. All of the beta and gamma emitting fission elements were recovered essentially free from alpha activity with the exception of 61, which was contaminated with Am. Likewise, all except Eu and Y were recovered at least 99% free from each other. Equilibrium constants, K_d, determined[1] for this newer type of resin from the elution data are given in Table I. The identity of the radioisotope constituting each elution peak was established not only by location of the peaks but also by decay and/or absorption measurements.

A plot of the integrals of the elution curves on "arithmetical probability" paper gave essentially straight line plots and enabled us to easily determine volumes of eluant needed for any percent recovery (See Fig. I). Calculations of the rate of movement, $\frac{\Delta D(cm)}{\Delta C(col.\ volumes)}$, of any activity band and the amount of eluant used in eluting each band showed that at any point, D, on the column the widths, W, of the various activity bands are essentially equal for those ionic species used here (See Table I). Since the rate of spreading of the band can also be calculated[2], it is possible to design a disjointed column such that once the "chromatograph" is developed, the activities may then be specifically eluted. The use of disjointed columns of this type should be a great time saving device and the separations should still be essentially complete as shown by calculations of distance of the bands from the top of the column (D), width of the band at this point (W_2) and position of the band (E). These positions were determined at C = 13.5, the number of column volumes required to move the yttrium peak to the bottom of the column. Since the band position of the ionic species involved is a function only of the ratio of K_d's, variations of factors difficult to control such as pH of elutriant, temperature effects and mold formation would still leave the activities in the relative positions indicated. This method should supply a rapid means for separating the alpha emitters, Pu and Am, from all the rare earth fission products except 61, which has not yet been fractionated from Am by citrate elution from Dowex 50.

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(1) S.W. Mayer and E.R. Tompkins, J. Am. Chem. Soc. 69, 2866 (1947).

(2) "The Effect of Several Column Variables", E.R. Tompkins, D.H. Harris and J.X. Khym. (To be published). The width of the elution curve is directly proportional to the square root of the length of the column.

[redacted]

[redacted]

Program: Experimental investigation of the effectiveness of the proposed "disjointed column procedure" will be undertaken.

Table I

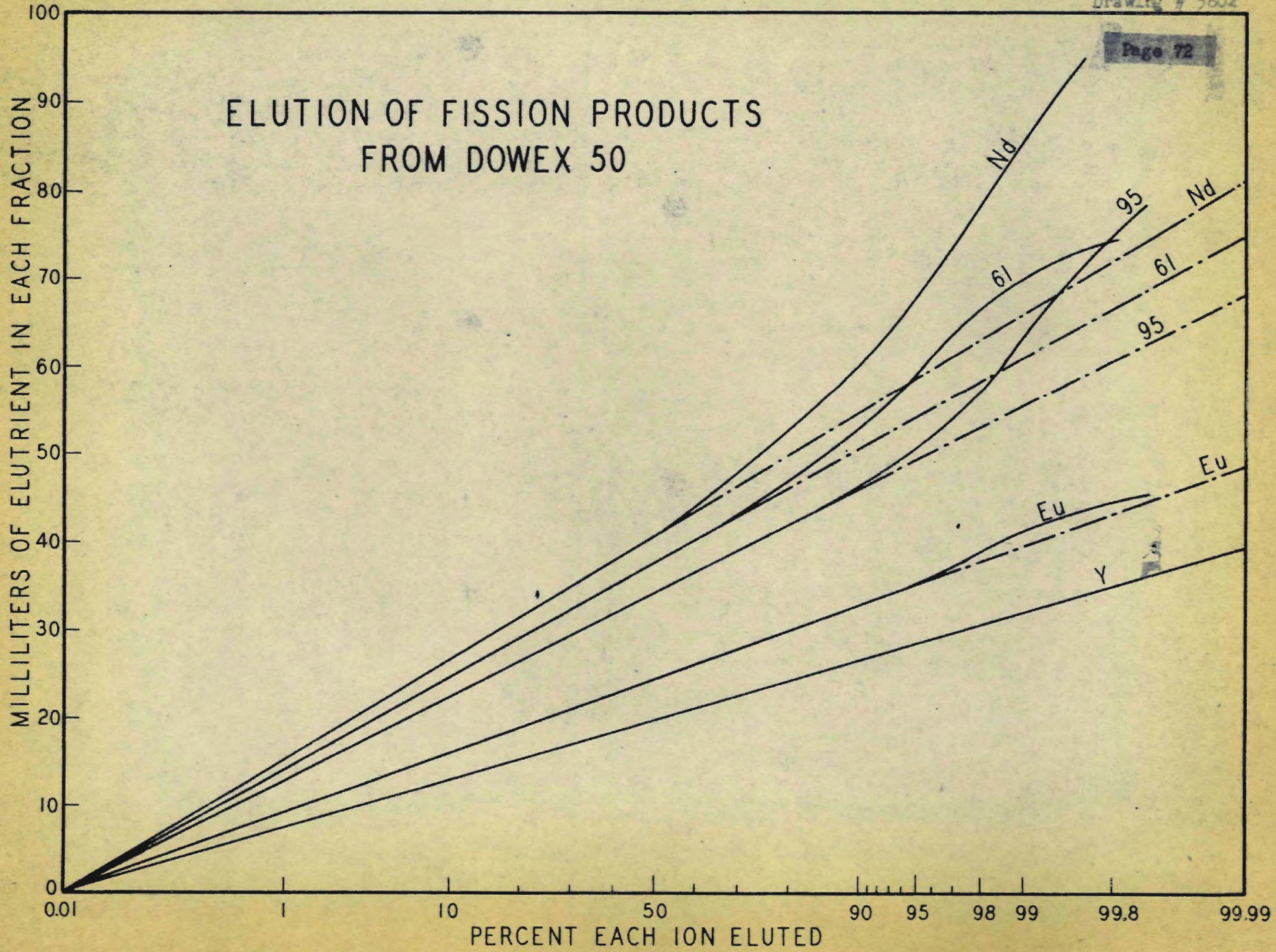
Equilibrium Constants and Calculations on Activity Bands

Element	$\frac{\Delta D}{\Delta C}$ (cm/c)	C at peak (col. vols.)	K_d	W_1 (cm)*	D (cm)**	W_2 (cm)**	Position of Band from top of 86 cm. column E (cm)
Pu	78	1.1	1.87	--	--	--	--
Y	6.36	13.5	23.0	14.8	86	14	79-86
Eu	5.5	15.6	26.5	15.5	73.5	13	67-79.5
61	3.66	23.5	39.9	15.7	57.5	11.5	51.8-62.3
Am	3.46	24.7	42.0	13.7	54.5	11.0	49.0-60.0
Nd	2.58	33.4	56.7	12.2	40.5	9.6	35.7-45.3
Pr	1.53	56.0	95.0	--	24.1	7.4	20.4-27.8
Ce	1.07	80.0	136.0	--	14.5	5.7	11.8-17.4

* Calculated from experimental data. Mean value = 14.3.

** Calculated relative to yttrium peak, C = 13.5.

[redacted]


ELUTION OF FISSION PRODUCTS
FROM DOWEX 50
MILLILITERS OF ELUTRIENT IN EACH FRACTION
PERCENT EACH ION ELUTED
0
10
20
30
40
50
60
70
80
90
100
0.01
1
10
50
90
95
98
99
99.8
99.99
Nd
95
Nd
61
61
95
Eu
Eu
Y

[redacted]

Recovery of Ru^{106} from Metal Wastes: (J.F. Savolainen, H.M. Rice, J.A. Swartout)

A. Electrodeposition

The electrodeposition method described in the previous report (CNL-37) for recovery of Ru^{106} from the ORNL metal waste supernate does not appear to be as effective as precipitation methods which are in operation at the present time and it is doubtful that it could be developed to find application within a reasonable time. In view of this fact, further work on this method has been postponed.

B. Electrolytic Oxidation and Distillation

Anodic oxidation of Ru contained in the acid solution of the ferrous hydroxide carrier used by the Operating Division to concentrate Ru from ORNL metal waste supernates appears promising as an alternate for the $KMnO_4$ oxidation-distillation process. In a preliminary experiment, 54.6% of the Ru was collected in 2 hours and 65.2% in 4 hours.

The Ru containing solution obtained from the Ru recovery process was placed in a half cell containing a Pt anode. The anode half cell was connected to the cathode half cell through a sintered glass disk. The cathode half cell containing a Cu electrode was filled with 2 N H_2SO_4. A potential of 14.4 to 14.6 volts was used giving a current of 1.1 to 1.2 amperes. The current density on the anode was 0.22 to 0.23 amperes/sq. cm.

The solution appears to be completely oxidized at the end of the first thirty minutes of operation. The solutions at this time had a color similar to MnO_4^- probably due to the oxidation of traces of Mn. The oxygen evolved at the anode was conducted through traps containing reducing solutions to absorb the Ru. The temperature increased during electrolysis to about 90° C; no localized boiling was observed. About 3.4% of the total activity diffused to the cathode side of the cell and 0.3% was plated on the cathode.

C. Concentration by Precipitation

Determinations of the carrying of Ru activity by eight metal hydroxide precipitates were made and compared with that of $Fe(OH)_2$. It was assumed that the Cs activity would not be carried by the precipitates. Since 12.7% of the beta activity is Ru in the W-7 tank supernatant and 78.6% is Cs, the effectiveness of Ru carrying was considered to be directly proportional to the percent of total activity removed by the precipitates.

Data are given in Table I for the relative efficiency of the various hydroxides in carrying Ru^{106} from the alkaline waste solution. In all cases the amount of cation added corresponded to 0.01 M in the final volume. Mixtures of cations, each in concentrations of 0.01 M, were also tried. Results for these are given in Section B of Table I.

[redacted]

[redacted]

Table I

Carrying of Ru^{106} from ORNL Metal Waste Supernate by Hydroxides

	Metal Cation	Percent Activity Removed*			
		Exp. 1	Exp. 2	Exp. 3	Exp. 4
A.	Ni^{++}	7.9	10.1		
	Co^{++}	5.9	6.5		
	Cu^{++}	2.6	2.8		
	Cd^{++}	8.3	11.3	8.1	8.6
	Hg^{++}	1.2	1.9		
	Bi^{+++}	4.2	5.2		
	Ce^{+++}	4.8	4.9		
	Ce^{++++}	6.7	9.1		
	Fe^{++}	12.6	12.4	11.2	13.9
B.					
Bi^{+++}	Fe^{++}	13.0	13.5		
Pb^{++}	Fe^{++}	12.6	11.8		
Cd^{++}	Fe^{++}	12.5	15.5		
Zn^{++}	Fe^{++}	12.1	12.4		
Sn^{++}	Fe^{++}	11.9	12.8		
$(VO_2)_2SO_4^{-}$	Fe^{++}	12.1	12.0		
Sn^{++}	Cd^{++}	14.9	16.0		
Sn^{++}	Hg^{++}	3.2			

* Ru^{106} beta activity constitutes 12.7% of total beta.

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From the first portion of Table I it is apparent that "$Fe(OH)_2$" is a more efficient carrier for Ru from this solution than any of the others. With two exceptions, the mixtures of cations gave no greater carrying of Ru than with Fe^{+2} alone. Mixtures of Bi^{+3}- Fe^{+2} and Cd^{+2}-Sn^{+2} gave higher carrying, exceeding the fraction of beta activity contributed by Ru^{106}. Because of this apparent carrying of some Cs and, also, because of the nature of the precipitates, these are considered to be inferior to the ferrous precipitate.

Recovery of Cs^{137} from Metal Wastes: (J.F. Savolainen and J.A. Swartout)

After removal of ruthenium from the metal waste supernates, almost all the remaining detectable activity is due to Cs^{137}. Extraction of the cesium at this point is desirable, not only because a large source is thus available, but also to reduce the level of radioactivity in the solution discarded into the waste disposal system. The large volumes of waste solution involved and the lack of common insoluble cesium salts precludes use of precipitation procedures. Investigation of potentially feasible methods was undertaken, starting with ion-exchange.

Cation-Exchange:

An indication of the effectiveness of cation-exchangers in concentrating and isolating Cs is afforded by two preliminary experiments.

A filtered sample of the supernatant from tank W-7 was passed through a 13.5 cm. Dowex #50 resin column in the Na form. The H form of the resin cannot be used with this solution because of the high concentration of carbonates which would result in the liberation of CO_2. When 3.1 wet resin column volumes of W-7 had passed through the column 50% breakthrough occurred.

After washing the column with H_2O the Na was removed with 4.5 column volumes of 0.2 M HCl. The Cs^{137} was then removed with 6 M HCl in one column volume giving a recovery of 50% of the total Cs^{137} adsorbed.

The solution from the W-7 waste tank was diluted 1 to 10 and passed through a Dowex #50 resin column which had been conditioned to the Na form. The resin column was 54 cm long and contained 14.3 ml. of the wet resin. 32 column volumes of the diluted W-7 solution had passed through the column when the Cs activity level reached 50% of the feed solution. As would be expected, diluting the W-7 solution did not increase the capacity of the resin for the Cs activity when calculated on the basis of the undiluted solution.

While this method can be used to remove the Cs activity from the anions and from a substantial amount of the Na present in the W-7 solution, the low capacity of the resin does not give a substantial volume reduction.

Program: Investigation of various solvent-extraction procedures using complexing agents is in progress.

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

I. Introduction:

Interest in pure fission rare earths, particularly of europium and samarium, has resulted in a study of feasibility of isolating these in relatively large quantities, either by adaptation of existing laboratory procedures or by development of new methods more amenable to remote operation.

II. Ion-Exchange:

Because of mechanical difficulties inherent in operation of ion-exchange columns at, or near, the boiling point of solutions flowing through the bed, direct adaptation of the procedure of Ketelle and Boyd[1] to remote operation does not appear practical. Therefore, in order to select optimum, practical conditions, measurements of the equilibrium constants for the distribution of each rare earth between Dowex 50 and buffered citrate solutions as functions of pH and temperature is necessary. In preliminary experiments, difficulty has been encountered in obtaining reproducible results.

Several rare-earth rich fractions were obtained from the "all-ion-exchange" fission product factory of the Operations Department. An initial attempt to isolate europium and samarium from these using a steam heated column under the conditions of Ketelle and Boyd revealed considerable contamination of each fraction by yttrium. Because of the much greater abundance of yttrium in fission even a slight leakage through the column results in appreciable contamination of Eu and Sm. Therefore, means for thoroughly separating Y prior to the Eu and Sm isolation are under study.

III. Solvent Extraction with TTA for the Preliminary Separation of Y from Eu:

Single stage equilibrium measurements on the distribution of Y and Eu between benzene solution (0.2 M TTA) and aqueous solution (0.1 M Na Cl) indicated a ratio of the distribution coefficients of Y to Eu to be 2.2 at pH 3.7 (Table I). While this will not permit great separation of these two elements with one or two extraction stages, the separation to be expected in any given number of stages can be calculated (ORNL-5).

A compromise between the amount of work required and the degree of fractionation resulting was made for 8 stages counter-currently. The results for pH 3.8 and 3.65 (shown in Table II) reveal neither the expected distribution coefficient (in both cases the observed was higher than the expected) nor the expected separation (D.C. for Eu was practically the same as for Y) was obtained.

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

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No explanation is offered for these discrepancies but greater ranges of distribution may be sought in using citrate buffer in the aqueous solutions.

Table I

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

Benzene 0.2 M TTA
Aqueous 0.1 M NaCl

pH	Observed Y	D. C. Eu	Ratio D. C. Y/Eu
3	0.042	0.019	2.2
3.7	3.12	1.38	2.26
5	468	132	3.55

Table II

Distribution of Y and Eu in 8 Stage Counter Current Extraction

Benzene 0.2 M TTA
Aqueous 0.1 M NaCl
20 ml. each phase in each tube

Tube Number	Fraction in tubes at pH 3.8		Fraction in tubes at pH 3.65	
	Y	Eu	Y	Eu
0	0.500	0.432	0.375	0.325
1	0.394 (A)	0.447 (B)	0.450 (C)	0.430 (D)
2	0.104	0.120	0.155	0.197
3			0.024	0.048

Observed distribution coefficient Benzene/Aqueous

A. 10

B. 11

C. 4.3

D. 3.7

[redacted]

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

I. Introduction

Since the previous work[1,2] has shown the H_2SO_4 - CrO_3 process[2] to give quantitative or nearly quantitative recovery of C^{14} from irradiated Be_3N_2 and to be suitable from a chemical standpoint, the scaling up of this process was continued.

Experiments on unirradiated Be_3N_2 were made to test the larger scale apparatus and to determine:

1. The amount of inactive carbon introduced by the sweep gas and the reagents.
2. The amount of inactive carbon contained in the unirradiated Be_3N_2.

II. Testing of Larger Scale Apparatus (20-25 gms Be_3N_2)

A. Blank Runs - Carbon in Reagents and Sweep Gas:

A new apparatus having a 1 liter pot and a capacity of from 20-25 g. of Be_3N_2 (H_2SO_4 - CrO_3 process) was designed, built and leak tested.

Tests of the sweep gas and the reagents gave the results shown in Table I.

The reagents used were made as follows:

H_2O	Freshly boiled distilled H_2O cooled in a loosely stoppered bottle.
18 N H_2SO_4	1 part of 36 N H_2SO_4 diluted with 1 part of distilled water, boiled and cooled in a loosely stoppered bottle.
Saturated CrO_3	1 g. of CrO_3 dissolved in 1 ml of freshly boiled distilled water.

The sweep air was passed through a Drierite-Ascarite column, through a CuO tube at 800° C and then through another Drierite-Ascarite column.

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(1) Weinberger, A.J., and Swartout, J.A., "C^{14} from Beryllium Nitride", MonN-370, MonN-432, CNL-37.

(2) Fries, B.A., "The Recovery of C^{14} from Irradiated Beryllium Nitride", BC-43, March 7, 1947.

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Table I

Inactive Carbon in Sweep Gas and Reagents

1. Flow rate of sweep gas was approximately 20 cc. per min.
2. The apparatus was swept for 3 hours to clear it of untreated air.

Procedure	Sweep Time	Mg. $BaCO_3$ Recovered
Add 250 ml. freshly boiled distilled water.		
Add 450 ml. of 18 N H_2SO_4.		
Boil the solution and sweep with air.	34 hrs.	0.7
Add 8 ml. saturated CrO_3 solution.		
Boil the solution and sweep with air.	21 hrs.	4.1
Boil the solution and sweep with air.	20 hrs.	0.2

From Table I it appears that very little carbon was introduced by the H_2O, the H_2SO_4 and the sweep gas. It is unlikely that the carbon which appeared when the CrO_3 solution was added was all introduced in the CrO_3 solution itself. It is more likely that traces of organic material already present in the pot were oxidized when the CrO_3 was added. This point will be settled later by adding two portions of CrO_3 solution.

B. Blank Runs - Carbon in Unirradiated Be_3N_2:

Two runs were made using 25 g. portions of unirradiated Be_3N_2, Clinton prepared, heat decanned and crushed to a powder in a jaw crusher. The powder contained some Al not removed in the decanning operation. This material was supplied by S. F. Beall of the Technical Division.

1. First Experiment: 25 g. of Be_3N_2 was slurried into the pot with 250 ml. of water. The pot was boiled and swept (20 cc. per min.) with air for 2 hours to clear the system. Some gas was evolved from the slurry during this operation. The CO_2 was not trapped.

450 ml. of 18 N H_2SO_4 was added to the pot in 5 ml. portions. Pressure regulation was very difficult and at one time some gas was allowed to escape to relieve the large positive pressure which developed in the pot. The released gas smelled of NH_3 and somewhat like acetylene. The boiling pot was aerated for 6 hours. The CO_2 was collected but was left in the $Ba(OH)_2$ trap.

8 ml. of saturated CrO_3 solution was then added uneventfully and the boiling solution was swept for 20 hours.

This run produced 533.7 mg. of $BaCO_3$ corresponding to 0.13% carbon in the nitride. This figure is low because of the gas lost.

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During the run, 1 to 2 ml. of a condensate, probably H_2O, appeared after the CuO tube.

At the end of the run, the solution was clear except for a slight residue. When the pot cooled, a voluminous precipitate appeared.

2. Second Experiment: A bubbler containing 10 ml. of 18 N H_2SO_4 and a few drops of saturated CrO_3 solution was placed in the line after the CuO tube before Run 2 was started, since it was possible that the condensate might hold some CO_2.

Since so much gas was evolved from the boiling water slurry and during the first stages of the acid addition, it was suspected that the nitride might contain some ammonium or beryllium carbonate or both. Therefore, 25 g. of the dry nitride was placed in the pot which was then heated and evacuated for several hours. The hot dry pot was then swept overnight with CO_2 free air. No CO_2 was collected.

250 ml. of H_2O containing 5 ml. of 18 N H_2SO_4 was then added to the cooled pot. The slurry was swept for 3 hours. Only a small amount of $BaCO_3$ appeared in the $Ba(OH)_2$ trap. The pot was then boiled and swept for 7 hours after which no more $BaCO_3$ appeared to be forming in the trap. During this operation the H_2SO_4 - CrO_3 bubbler solution turned green indicating that reducing constituents were passing through the CuO tube. An additional 1 or 2 ml. of H_2SO_4 was added and the pot was swept for another hour. No more $BaCO_3$ appeared to be forming in the trap.

This treatment produced a total of 56.9 mg. of $BaCO_3$. The trap was refilled and the pot was again started boiling. Only a small amount of $BaCO_3$ appeared in the trap after several hours of aeration.

Thus it may be that some carbonates, not removed by the heating, evacuation and sweeping of the hot dry nitride, are present. However, the fact that the treatment should remove the carbonates and the fact that the H_2SO_4 - CrO_3-bubbler solution turned green indicate that some other effect caused the production of the carbon containing gas. It is reported in the literature that hot water decomposes Be_3N_2. Thus it may be that due to fines present in the nitride powder, the initial attack by hot water is appreciable and that the rate of attack drops off sharply when these fines have been decomposed.

A run with irradiated Be_3N_2 should settle this question since the $BaCO_3$ produced should contain little or no C^{14} if the effect is due to carbonates.

To the boiling water slurry, 245 ml. of 18 N H_2SO_4 was added slowly in 5 ml. portions. During the dissolving, the sweep air was deoxidized by hot Cu. The rate of sweeping was reduced to a minimum before addition of each 5 ml. portion and was kept at a minimum until the reaction subsided. Satisfactory pressure regulation could be maintained but required careful manipulation. The total aeration time for the dissolving step was 24 hours. This step produced 231.3 mg. of $BaCO_3$.

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An additional 200 ml. of 18 N H_2SO_4 was added fairly rapidly to the boiling pot. Then 8 ml. of saturated CrO_3 solution was added. The boiling pot was swept with air for approximately 20 hours. This oxidation step produced 339.1 mg. of $BaCO_3$.

The total amount of $BaCO_3$ obtained from the run was 627.3 mg. This corresponds to 0.15% carbon in the Be_3N_2.

The pot was again boiled and swept with air for 5 hours. A plug-up occurred and the apparatus was shut down. The 5 hours of aeration produced only 0.1 mg. of $BaCO_3$, indicating that the run was complete and that the apparatus had developed no leaks.

There was only a slight residue not in solution at the end of the run. When the pot cooled, however, a voluminous precipitate appeared.

A solution back up during the final shut down made the removal of the CuO tube necessary. An examination of the CuO showed that the wire particles for an inch or two on the inlet side were smaller than the others and were sintered together. While this was not the cause of the plug-up, it is undesirable and shows that since the tube was held at 800° C, the flow rate of combustible gas per square cm. of CuO was too high. A proper admixture of O_2 would probably solve the difficulty but since this is undesirable because of the danger of a hydrogen explosion during the dissolving step, the only solutions are to decrease the dissolving rate or to increase the size of the CuO tube.

The solution in the H_2SO_4 - CrO_3 bubbler was found to be strongly acid after the run. A few added drops of CrO_3 solution were not decolorized even when additional concentrated H_2SO_4 was added, thus indicating that the reducing constituents which passed through the CuO tube either were limited in quantity, were oxidized by the O_2 in the air used as a sweep gas in the oxidation step or were swept out of the bubbler. Additional CrO_3 solution will be added to the bubbler to determine whether these reducing constituents are limited in quantity.

A spectroscopic examination of the $BaCO_3$ produced in the dissolving and oxidation steps of Run 2 was made by N. Murray. This analysis showed Be, Ag, As, Au, Bi, Cd, Co, Ir, Li, Mn, Mo, Na, Pb, Sn, Ta, Ti, V and Zn to be absent. Only trace amounts of Al, B, Ca, Cr, Cu, Fe, Mg, Ni and Si were found. Sr was present in large amounts. Other elements were not sought.

The apparatus was modified after the plug-up occurred so that the H_2SO_4 - CrO_3 bubbler solution could no longer back up. The reagent addition system was also rebuilt so that varying amounts of CrO_3 solution could be added and so that the H_2SO_4 solution could be added slowly and continuously.

III. Summary.

Tests of the H_2SO_4 - CrO_3 process on a 25 g. Be_3N_2 scale showed

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that the reagents and sweep gas introduce only a negligible quantity of carbon compared with that present in the unirradiated nitride samples which were found to contain as much as 0.1% carbon.

There is some evidence that the Be_3N_2 contains some carbonaceous material rapidly decomposable by boiling, very dilute H_2SO_4 or by boiling water.

Some reducing constituents can pass through the CuO tube.

The H_2SO_4, especially the first 100 ml., must be added very slowly to prevent the rapid reduction and subsequent sintering of the CuO particles and to permit satisfactory pressure regulation within the system.

Spectroscopic examination shows that the $BaCO_3$ produced by this process is quite pure.

After completion of the testing of this larger scale apparatus with irradiated Be_3N_2, a search for and investigation of more suitable target materials will be undertaken.

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

Summary

The reduction of $C^{14}O_2$ to methanol by lithium aluminum hydride has been accomplished on a tracer scale. Ethanol has been prepared by reducing acetoxymagnesium iodide with lithium aluminum hydride. Consistent yields of 65-70% formaldehyde have been obtained by the pyrolysis of methyl triphenyl-methyl ether.

The rearrangement of carbonyl-labelled benzalacetophenone epoxide in alkaline solution has been studied and results have been obtained which eliminate certain possible mechanisms of the reaction.

The Van Slyke method of oxidation of organic compounds has been modified for vacuum-line work. The amount of carbon dioxide from the oxidation is measured manometrically.

One hundred and four millicuries of purified barium carbonate have been prepared by the controlled reprecipitation of stock materials. The specific activity of the first (larger) fraction was increased from .009 to .0106 mc. per mg. The final chemical purity was 98% barium carbonate.

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

Methanol and Ethanol (R. F. Nystrom, W. J. Skraba)

In experiments conducted on a tracer scale, it was found that the specific activity of the methanol was 16% lower than that of the starting material. At first glance, it appeared that a dilution had occurred and a blank run was made on the reagents. The latter showed that methanol was present to the extent of 0.8% and water to the extent of 10%. Work is in progress to explain this large variation in the specific activities.

A scheme previously suggested for the preparation of ethanol from acetoxy magnesium iodide and lithium aluminum hydride has been tested and found to give the desired product. Work is in progress on the preparation of both singly and doubly labelled ethanol by this method.

Experimental

Reduction of CO_2 to Methanol. The apparatus and equations for the preparation of methanol from carbon dioxide and lithium aluminum hydride has been described in the last report. $BaC^{14}O_3$ was calibrated by converting it to carbon dioxide and transferring the latter to an ionization chamber. Nitrogen gas was used as a diluent. The specific activity of the $BaC^{14}O_3$ was found to be 1.15 uc./mmol. Dry carbon dioxide, diluted with helium, generated by adding 30% perchloric acid to 2.016 grams (10.2 millimoles) of $BaCO_3$ (containing 11.7 uc of C^{14}) was passed through a solution of 0.9 gram

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of $LiAlH_4$ in 90 cc. of diethyl carbitol (b.p. 95°C./34mm.). The time required for the addition of the carbon dioxide was 65 minutes. Thirty minutes after the last addition, 60 cc. of n-butyl carbitol (b.p. 126°C./26mm.) was added dropwise. The still-pot temperature was then held at 145°C. for two hours after which the traps containing the distillate were sealed off and attached to the vacuum-line. The methanol was vacuum distilled and collected in a graduated receiver. A yield of 0.42 cc. of methanol was obtained. Two separate fifty milligram samples of $C^{14}H_3OH$ were oxidized to carbon dioxide using the van Slyke method of oxidation of organic compounds. The resulting radioactive carbon dioxide was introduced into an ionization chamber which was then attached to a vibrating-reed electrometer. The specific activity of the $C^{14}H_3OH$ was 0.99 uc./mmol.

An analysis of the lithium aluminum hydride furnished the following results: % purity = 94.5; $\%Cl^-$ = 1.2; and % CH_3OH = 0.8.

Reduction of Acetic Acid to Ethanol. A 200 cc. flask containing a magnetic stirring bar and provided with a dropping funnel and suitably arranged gas inlet and outlet connections was employed. The latter was attached to a trap cooled to -195° and thence to a bubbler flow indicator. In the flask was placed an ethereal solution of methyl magnesium iodide (12 mmol.) and 12 mmol. of acetic acid (b.p. 117°C/740mm.). The ether was removed by heating at 100°C./40mm. for one hour and then the solid residue cooled in a stream of helium. After adding 0.9 gram of $LiAlH_4$ in 100 cc. of diethyl carbitol (b.p. 95°C./34mm.) the mixture was heated at 90°C for two hours with stirring. Then the temperature was allowed to drop to 25°C and 60 cc. of n-butyl carbitol (b.p. 126°C/26mm.) added after which the temperature was held at 150°C. for two hours. The product was collected by vacuum distillation and there was obtained a 73% of ethanol -- micro b.p. 77.5°C; and n_D^{20} 1.3593.

Formaldehyde (A. R. Van Dyken)

It was previously reported(1) that triphenylmethyl carbinol yielded up to 70% formaldehyde on thermal decomposition. Further work has shown that this yield cannot be obtained consistently and results are not predictable. Use of P_2O_5 or Al_2O_3 in the thermal decomposition results in the formation of very little or no formaldehyde at all. Loss of weight of the starting material indicates that dehydration is taking place, but the probable product, triphenylethylene has not yet been recovered in pure form. The erratic behavior of the thermal decomposition of triphenylmethyl carbinol makes its use as a source of radioactive formaldehyde inadvisable.

Norris has reported(2) the formation of CH_2O together with some methanol and carbon monoxide from the thermal decomposition of methyl triphenylmethyl ether. Experiments carried out here in the manner described for triphenylmethyl carbinol have given consistent yields of 65-70% formaldehyde according to the following equation:

$$O_3COCH_3 \longrightarrow O_3CH + CH_2O$$

(1) Report CNL-37, pp. 84-86.
(2) Norris, J. F. and Cresswell, J.A.C.S. 55, 4946-51 (1933)

[redacted]

Aliquots of the aqueous solution of the dissolved volatile products from the pyrolysis were analyzed for formaldehyde as previously described(1) and for total oxidation by cold alkaline potassium permanganate as described by Oesper(3). The oxidation equivalent of the formaldehyde was subtracted from the total oxidation, and the difference was calculated as methanol. The CO was measured by oxidation to CO_2 in a CuO furnace and precipitation as $BaCO_3$ after all other products were absorbed in water and liquid nitrogen cooled traps. Most of the material not found as formaldehyde could be accounted for as CO and CH_3OH, which were formed in approximately equal molar proportions. Al_2O_3 which lowers the temperature of decomposition decreased the yield of formaldehyde.

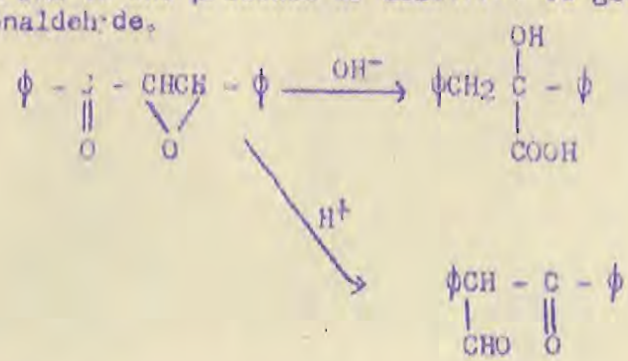
It is reported(4) that 9,10-dihydro,-9,10-dimethoxy,-9,10-diphenyl anthracene yields formaldehyde on thermal decomposition. This compound was prepared and decomposed thermally. Thirty per cent yield of formaldehyde was obtained. Decomposition of the monomethyl ether of 9,10-dihydro,-9,10-dihydroxy,-9,10 diphenyl anthracene rather than the dimethyl ether yielded a negligible amount of formaldehyde.

Methyl tribiphenylmethyl ether was prepared by dissolving triphenyl carbinol in a 50% mixture of methanol and benzene, adding a small amount of conc. HCl and refluxing the solution for two hours. On cooling, the product which crystallized melted 163.5-164°C. and showed no change in melting point after recrystallization from ligroin (b.p. 70-90°C). Thermal decomposition of this material at 400°C in the usual manner yielded 15% CH_2O. Tribiphenylmethane was recovered from the residue.

The Study of Reaction Mechanisms with C^{14}

Rearrangements of Chalcone Epoxide

It has been reported that the epoxide of benzalacetophenone (chalcone) reacts in the presence of alkali(5,6) to give α, β diphenyllactic acid and in the presence of acid(7,8) to give α, β diphenyl, β-keto propionaldehyde.

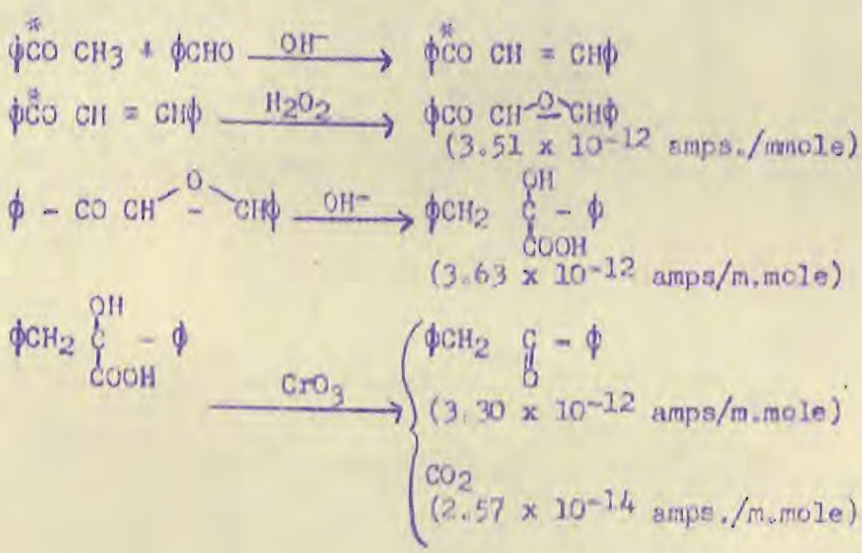


(3) Oesper, Newer Methods of Volumetric Analysis, pp. 55-65 (1938)
(4) Hurd, Pyrolysis, p. 200
(5) Wheeler, et. al., J. Chem. Soc., 1882 (1938)
(6) Robinson and Baker, ibid. 1798, (1932)
(7) Weitz and Schaeffer, Ber. 54, 2344 (1921)
(8) Wislicenus ibid. 308 (229-30) (1899)

[redacted]

The similarity of the basic reaction to the important benzilic acid rearrangement and of the acid reaction to the pinacol rearrangement makes the study of these transformations with the aid of C^{14} of considerable interest.

Considerable progress has been made in the elucidation of the mechanism of the alkaline reaction. Carbonyl-labelled acetophenone was allowed to react in the presence of base with benzaldehyde to give chalcone. This was converted to the epoxide by treatment with alkaline hydrogen peroxide in methanol solution. The epoxide was rearranged in alkaline solution to the acid which was decarboxylated with chromic acid to desoxybenzoin. The carbon dioxide from the decarboxylation was precipitated as $BaCO_3$, dried and weighed. The released CO_2 showed activity only slightly above background. The molar specific activity of the desoxybenzoin was approximately equal to that of the acid, thus demonstrating that the carbon atom of the carboxyl group in the acid is not the one present in the carbonyl group of the chalcone epoxide. This shows that the alkaline rearrangement does not proceed by migration of the phenyl radical attached to the carbonyl group. Below are the reactions which have been carried out and the radioactivity assay, as determined in the vibrating reed electrometer, which have been made. Work on the proper assignment of the position of the C^{14} in the desoxybenzoin is in progress.



Experimental

Carbonyl labelled Chalkone Epoxide. Two hundred forty two milligrams of carbonyl labelled chalkone which had been prepared from carbonyl-labelled acetophenone by the procedure of Kohler and Chadwell[9] were dissolved in 2.80 ml. of absolute methanol. To this solution was added 0.48 ml. of two normal sodium hydroxide. Twenty-four milliliters of approximately 30% hydrogen peroxide were added dropwise and the mixture was stirred until the temperature reached 24°C. After 12 minutes, 0.2 ml. of hydrogen peroxide was added and in five minutes another 0.1 ml of hydrogen peroxide was added

(9) Kohler and Chadwell, Org. Syn. Coll. Vol. I, p. 78

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with stirring. Two ml. of water was then added and the mixture was cooled in the ice box. The crystalline material so obtained was collected on a filter. The yield, when dry, was 163.1 mg. of white chalkone epoxide. The melting point was 81 to 84°C. The crystallization of this material from 2 ml. of ethyl alcohol yielded 117.8 mg. melting 86.5-87.5°C.

α, β Diphenyllactic Acid Fifty milligrams of carbonyl-labelled chalkone epoxide, 0.5 ml. of absolute ethyl alcohol and 0.1 ml. of a solution of 1 g. of sodium hydroxide and 4 ml. water were heated under reflux for 1 hour and 25 minutes. Two ml. of distilled water was then added and the solution was saturated with carbon dioxide by adding a few small pieces of dry ice. The solution was extracted twice with 2 ml. portions of ethyl ether. Two-tenths of a milliliter of 6 HCl were then added and the mixture was extracted with 3 ml. of ether. The ether layer was washed with 1 ml. of water and the water layer was extracted with 3 ml. of ether. The ether layers were combined, washed with water and evaporated to dryness in a tared flask. Crystals so obtained were desiccated over P_2O_5 for 24 hours yielding 51.3 milligrams of α, β diphenyllactic acid. Yield: 95% of theoretical. This material was then dissolved in 3.0 ccs. of benzene. A minute amount of norite was added to this warm solution which was filtered through a talc pad on a centered glass funnel. Flask and funnel were washed with 0.65 ml. of warm benzene and then through the same funnel was poured 5.0 ml. of low boiling petroleum ether. Upon cooling, white crystals of the acid appeared. This material was filtered on a clean tared funnel and desiccated over P_2O_5 for 24 hours. The yield was 39.5 milligrams of material whose melting point was 165 to 166°C. Yield on crystallization was 78%.

Oxidation of α, β, Diphenyllactic Acid to Desoxybenzoin and Carbon Dioxide. A .01777 g. sample of the acid was placed with 5 mg. of dry CrO_3 in the flask of the combustion apparatus. The combustion flask was connected through a condenser and Dry Ice trap to two $Ba(OH)_2$ bubbler tubes. Two milliliters of acetic acid were allowed to flow upon the dry mixture and the flask was warmed slightly until solution of the materials was effected. Nitrogen gas was allowed to bubble through the solution for a period of ½ hour in order to sweep the evolved nitrogen into the $Ba(OH)_2$ solution. At the end of this time, the bubbler tubes were disconnected and the $BaCO_3$ was collected by centrifugation. After being washed, the precipitate was dried over night in the Abderhalden drying pistol. The weight of $BaCO_3$ was .01560 g. This was then decomposed with phosphoric acid and the CO_2 was passed into an ionization chamber for assay. No observable activity. To the residue was added 10 cc. H_2O and 10 cc. ethyl ether. The layers were separated and the aqueous layer was washed 3 times with 2 cc. portions ether. The ether layer was washed once with 4 cc. H_2O and then 4 times with 2 cc. portions saturated sodium bicarbonate solution, followed by two water washings (4 cc. portions). The ether was taken to dryness and desiccated. Yield, 19.0 mgms. crude product, which was dissolved in 0.4 cc. methanol. This solution was filtered. The flask was washed with 0.35 cc. methanol and the washings added through the funnel to the solution. Next, 0.75 g. water was added and the solution was heated until had a turbid solution with no precipitate. Methanol was then added dropwise with agitation until a clear solution resulted. On cooling in ice-box, 7.2 mg. desoxybenzoin-7-C^{14} m.p. 52-53° were obtained. Ionization chamber determination of radioactivity showed an activity of 3.30×10^{-12} amp/mole.

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Development of Analytical Procedures

Oxidation and Assay of Low Molecular Weight Compounds Containing C^{14} e.g. Methanol (H. F. Nystrom, W. J. Skraba)

Methanol-C^{14} has been analyzed by converting it to $C^{14}O_2$ by the van Slyke method of oxidation. Due to the volatility of methanol vacuum-line technique was employed. A known weight of methanol-C^{14} was vacuum distilled into the oxidation chamber, the combustion liquid added, and the resulting $C^{14}O_2$ swept through a trap filled with 30 mesh zinc at -40°C. and collected in three traps cooled by liquid nitrogen. After the $C^{14}O_2$ evolution was complete, the system was evacuated and isolated. The liquid nitrogen baths were removed and the amount of $C^{14}O_2$ measured manometrically. Next the $C^{14}O_2$ was transferred to an ionization chamber which was attached to a vibrating-reed electrometer and the activity of the $C^{14}O_2$ determined.

Purification of $BaC^{14}O_3$ (W. J. Skraba)

The purification of $BaC^{14}O_3$ was undertaken in order to provide the Bureau of Standards with a homogeneous primary standard for the standardization of C^{14} counting methods. Heretofore, stock $BaC^{14}O_3$ has been of questionable chemical purity and consequently of variable specific activity. In our procedure, the specific activity was increased from 2.94% to 3.47% and the final chemical purity was 97-98%. The procedure used in this purification is as follows:

Approximately 100 mcs of $BaC^{-14}O_3$ was purified. Eight batches of $BaC^{14}O_3$ as received from the "C^{14} factory" were tumbled together in a covered glass jar for 24 hrs. and a sample taken for analysis. Results on 11.4 gms. showed 103 mcs C^{-14} with an isotopic ratio of 2.94%.

A water slurry of the $BaC^{14}O_3$ was treated with 70% $HClO_4$ and the evolved $C^{14}O_2$ swept through a hot solution of very dilute $Ba(OH)_2$. The apparatus was arranged so that during the precipitation of $BaC^{14}O_3$, the solution was agitated with a steady stream of CO_2 free air. Excess $C^{14}O_2$ was used in precipitating the $BaC^{14}O_3$ and the unreacted $C^{14}O_2$ was collected in a second precipitation. The above conditions were needed to obtain pure crystals of $BaC^{14}O_3$ that were easily filtered and washed. The precipitate was washed with boiled distilled water until absence of $Ba(OH)_2$ was indicated by pH determination. It was then removed from the precipitator and dried in a desiccator under vacuum over calcium hydride to constant weight.

Eight and six tenths gms. of $BaC^{14}O_3$ (97-98 purity) was obtained from the first precipitation and contained 91.7 mcs. C^{14} with an isotopic ratio of 3.47%. This material will now be used as a primary standard for calibration of various C^{14} counters.

One and two tenths gms. $BaC^{14}O_3$ was obtained from the second precipitation and contained 12.2 mcs. C^{14} with an isotopic ratio of 3.27%. Since conditions of precipitation were not controlled in the second precipitation, the resulting $BaC^{14}O_3$ did not attain the degree of purity of the primary standard.

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3 - SUPPORTING CHEMICAL RESEARCH

Inorganic, Physical and Radiochemistry

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

I. Introduction:

Polarographic studies on the upper valence states of ruthenium have previously been reported. The results which were obtained indicated that the ruthenate-perruthenate potential was probably the only reversible potential amongst the upper valence states. The potential for this couple is to be investigated by setting up the following cell:

$$Hg_{(l)}, HgO_{(s)}, KOH \parallel RuO_4^-, RuO_4^=, Pt$$

If it were possible to obtain one of the other potentials (4-6, 4-7, 7-8) in addition to the 6-7 couple, these values could be combined to give additional thermodynamic data for ruthenium systems in the higher valence states.

II. Review of Thermodynamic Measurements for Analogous Manganese Systems:

Since similar systems and couples had been previously investigated for the upper valence states of manganese, an intensive study of the literature was made on this work.

Sackur and Taegener[1] in 1912 investigated the following reactions:

I $\quad 2\ KMnO_4 + 2\ KOH \longrightarrow 2\ K_2MnO_4 + H_2O + \frac{1}{2}\ O_2$

and II $\quad 3\ K_2MnO_4 + 2\ H_2O \rightleftharpoons 2\ KMnO_4 + 4\ KOH + MnO_2$

These workers had no success in obtaining equilibrium data. This was largely due to the fact that they were unable to determine small amounts of $MnO_4^=$ in the presence of large amounts of MnO_4^-, and vice versa. They therefore resorted to electrochemical methods to attack the problem.

Equation I can be broken down into 2 simpler reactions:

I (a) $\quad 2\ MnO_4^- + 2\ e \rightleftharpoons 2\ MnO_4^=$

I (b) $\quad 2\ OH^- \rightleftharpoons H_2O + \frac{1}{2}\ O_2 + 2\ e$

The potential for the oxygen electrode in 1 MKOH (equation Ib) is known and is 0.41 volts. Therefore it was necessary to obtain the potential for the

couple in equation I (a). The following cell was used to obtain this potential:

$$Pt,\ K_2MnO_4,\ KMnO_4\ (1.5\ MKOH)\ \|\ KOH(0.8M),\ HgO,\ Hg$$

Potentials constant over several hours were obtained; furthermore, they obeyed the Nernst equation: $E = E_0 + \frac{RT}{nF} \ln \frac{MnO_4^-}{MnO_4^=}$

The liquid junction potentials were of the order 2-5 mv. The authors also assumed that the ionic concentrations (activities) of MnO_4^- and $MnO_4^=$ were both proportional to their total concentrations and that both salts were dissociated to the same extent. The range of salt concentrations employed were: K_2MnO_4, 0.015 - 0.054 M; $KMnO_4$, 0.014,-0.15 M; and KOH, 1.5 - 5.8 M. A value of 0.61 volts was obtained for the I (a) couple. When this value was combined with that for the oxygen electrode, (i.e. tantamount to setting up the cell: Pt, $MnO_4^=$, MnO_4^-, KOH(IN), O_2 (1 atm), Pt) an E value of 0.61 - 0.41 = 0.20 volts was obtained. This gave a value of $K = 2.8 \times 10^3$ for reaction I and leads to a value of $K_{Diss.Pressure O_2} = 6 \times 10^{13}$ atmospheres. Therefore, since a pressure of oxygen of 6×10^{13} atmospheres is required to reverse reaction I, the reaction is irreversible.

Similarly equation II can be broken down thus:

II (a) $2\ MnO_4^= \rightleftharpoons 2\ MnO_4^- + 2\ e$ 0.61 volts

II (b) $2\ H_2O + MnO_4^= \longrightarrow MnO_2 + 4\ OH^- - 2\ e$

The potential for II (a) had been obtained above. Therefore it was only necessary to obtain a value for II (b). Considerable difficulty was encountered in getting a reproducible potential and plating the Pt electrode with MnO_2 gave no better results. Somewhat constant potentials were obtained in 4-8 N KOH using a clean Pt foil electrode and pure $MnO_4^=$ solutions. The workers assumed a figure of 40% dissociation in 8 N KOH and 80% dissociation in 0.8 N KOH (for standard electrode). Junction potentials were of the order of several hundredths of a volt. A potential of 0.50 volt was obtained for II (b). It is obvious that since this value is also greater than 0.40 volt (oxygen electrode in IN KOH), it is impossible to oxidize MnO_2 to $MnO_4^=$ by means of oxygen alone. By combining the potentials obtained for II (a) and II (b), an equilibrium constant of $K = 1.4 \times 10^{-4}$ was calculated for Equation II. Furthermore, the values of 0.50 and 0.61 can be combined to give a calculated potential for the MnO_4^-, MnO_2 couple of 0.54 volts.

Ruby[2] in 1921 assayed the work of Sackur and Taegener. His conclusions were that the value for $MnO_4^=$, MnO_4^- couple could be taken as fairly reliable, but that the potential for equation II (b) above was only a rough approximation. He then investigated the equilibrium in equation II, where $K = \frac{(MnO_4^-)^2\ (OH^-)^4}{(MnO_4^=)^3}$. Obviously analyses for the various ions must

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(2) Ruby, J. Am. Chem. Soc., 43, 294 (1921).

be accurate. Ruby analyzed for $MnO_4^{=}$ and MnO_4^{-} in an equilibrium mixture as follows:

(1) Mixture was filtered to remove MnO_2.
(2) A weighed portion was titrated to Mn(II) with standard reducing agent; hence $4x + 5y = A$ (titer), where x is conc. of $MnO_4^{=}$ and y is conc. of MnO_4^{-}.
(3) Another weighed portion was reduced to Mn(II), oxidized with $NaBiO_3$ to MnO_4^{-}, and then titrated with standard reducing agent. This gave total manganese, or $5x + 5y = B$ (titer). The error in (2) was considered to be 0.05% and those in (3) were considered to be 0.5%.
(4) OH^{-} was determined by adding 3% H_2O_2 to precipitate MnO_2, adding excess H_2SO_4, filtering and then titrating with standard base. Corrections were necessary for the acidic material present in the H_2O_2 and the alkali produced by the decomposition of MnO_4^{-} and $MnO_4^{=}$ to give MnO_2. The error in this determination was considered to be 0.5%. However, it is obvious that the errors in (4) are additive and depend on those in (2) and (3).

The concentrations employed by Ruby were: KOH, 0.4 - 0.8 M; K_2MnO_4, 0.003 -0.025 M; and $KMnO_4$, 0.005 - 0.016 M. Equilibrium was attained from both sides of equation II; K obtained from one side varied from 23-90; from the other, K varied from 16-81. Fortuitously, the average of all values in one case was 54.6 and in the other 51.6. Using a value of K = 53, and employing the potential of 0.61 volts obtained by Sackur and Taegener for the manganate-permanganate couple, Ruby calculated the potential for the manganate, manganese dioxide couple to be 0.66 volts, considerably different from the value of 0.50 volts previously obtained electrochemically by the above authors. Ruby also calculated the potential for the permanganate, manganese dioxide couple to be 0.647 volts.

Schlesinger and Siems(3) in 1924 attacked this equilibrium problem with a new and novel approach. Their method depended on these facts: (1) $BaMnO_4$ is very insoluble; (2) the concentration of all components in solution would be so low that 100% ionization could be assumed; and (3) the errors due to the decomposition of MnO_4^{-} or $MnO_4^{=}$ are avoided, because these ions are in equilibrium between solid $BaMnO_4$ and its decomposition in solution is compensated by further reaction of the solid with H_2O. The equilibrium is similar to that written above:

$$3\ BaMnO_4 + 2H_2O \rightleftharpoons Ba(MnO_4)_2 + 2Ba(OH)_2 + MnO_2$$

To determine the concentration of the three species in solution necessary to obtain K, the authors employed these analytical methods: (1) Barium was determined by the sulfate precipitation, and the concentration of $MnO_4^{=}$ was calculated by using the solubility product value of 2.4×10^{-10} obtained in the first part of the paper; (2) permanganate was determined

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

colorimetrically; and (3) OH^- was determined conductimetrically by a method employed previously by Harned, i.e., titration with standard $Ba(OH)_2$ after adding excess H_2SO_4 to the equilibrium mixture.

The first section of the paper was concerned with the solubility product determination of $Ba\ MnO_4$. This was obtained by measuring the equilibrium concentrations in the reaction:

$$BaMnO_4 + K_2CO_3 \rightleftharpoons Ba\ CO_3 + K_2MnO_4$$

Since the solubility product for $Ba\ CO_3$ is known, that for $BaMnO_4$ can be calculated from the equation

$$S.P._{BaMnO_4} = S.P._{BaCO_3} \times \frac{\gamma 1\ (MnO_4^{=})}{\gamma 2\ (CO_3^{=})}$$

assuming that either $\gamma_1 = \gamma_2$ or their ratio was constant during the conditions of the experiment; furthermore, both salts are of the uni-bivalent type and should be dissociated to the same extent. These assumptions were checked by varying the concentration of both salts (up to 0.1M), and using the sodium salts in place of the potassium compounds. A constant value for the solubility product of $BaMnO_4$ was obtained. The largest error in determining the concentration of $MnO_4^{=}$ was involved in the gravimetric determination of Ba as $BaSO_4$. The precipitates of $BaSO_4$ weighed between 1.6 mg-16 mg so that a weighing error of 0.1 mg produced an error of 15-20% in the value of K (equilibrium).

The conductimetric titration employed in (2), (the 2nd part of the paper), was quite tricky and involved the construction of a special titration vessel. However, the authors state that they were able to obtain values accurate to 0.4% on titration of solutions as dilute as 0.00005 N in KOH.

Values of K obtained for the equilibrium varied from 10-25, the average being 16. The ionic concentrations employed by these authors were: KOH, $0.8\text{-}4.1 \times 10^{-3}$M; MnO_4^-, $0.03\text{-}0.87 \times 10^{-3}$M; Ba^{++}, $0.43\text{-}1.1 \times 10^{-3}$M; and $MnO_4^{=}$, $2.2\text{-}5.7 \times 10^{-7}$N.

Andrews and Brown[4] in 1935 investigated the permanganate, manganese dioxide couple. They prepared a manganese dioxide electrode by dipping platinum foil in $Mn(NO_3)_2$ and then heating the foil in HNO_3 and $HClO_4$. This served as the electrode for the permanganate couple in the following cell:

$$Pt,\ MnO_2,\ MnO_4^-, \| KOH,\ HgO,\ Hg$$

These workers obtained potentials reproducible to $\pm$ 0.001 volt. Whether or not the couple is reversible appears questionable, despite the reproducibility of the potentials and their adherence to the Nernst equation. A potential

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(4) Andrews and Brown, J. Am. Chem. Soc. 57, 254 (1935).

of 0.588 volts was obtained for the couple and using Schlesinger's value of K=16 for the equilibrium discussed above, potentials of 0.564 and 0.600 volts were obtained for the manganate-permanganate and manganate-manganese dioxide couples, respectively.

III. Program for Investigation of Ruthenium System:

The manganate-permanganate system has been discussed in so much detail since the analogies to ruthenium are very obvious. The ruthenate-perruthenate couple, since it appears to be reversible from polarographic data, will first be investigated. With this potential available, two lines of attack are open. One is to determine the equilibrium constant for the reaction, $3\ K_2RuO_4 + 2H_2O = 2\ K\ RuO_4 + 4KOH + RuO_2$, if equilibrium exists as in the manganese system. This is open to question, due to the instability of RuO_4^- in solution. The presence of an upper volatile valence state, Ru(VIII) is, no doubt, the primary reason for this instability. Furthermore, the accuracy to which the ionic concentrations of the various constituents can be determined leaves doubt as to the validity of the K which would be obtained. Perruthenate and ruthenate could be determined by a combination of 2 methods: (1) Reduction to Ru(III) in an iodide titration to obtain $3\ x + 4\ y = A$, and (2) total ruthenium by using Ru tracer as a specific activity method. The determination of OH^- remains the major obstacle. A pH meter is probably no more accurate than 0.05 units and obtaining an absolute value of pH to ± 0.02 units in the region pH 10-12 would be quite difficult. The conductimetric titration, although it involves special techniques, would probably give more accurate results. The 2nd line of attack, which is probably easier, is to prepare an electrode with RuO_2 similar to that used by Andrews and Brown. This electrode could then be used to obtain a potential for either the ruthenate, ruthenium dioxide couple, or for the perruthenate, ruthenium dioxide couple. Either one of these potentials, if obtainable, could be then used with the ruthenate-perruthenate potential to obtain considerable thermodynamic information about the upper valence states of ruthenium.

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Ion-Exchange Separations: Rare Earth Purification (D. H. Harris and G. E. Boyd) P.A. CX3-5

The following quantities of spectrographically pure rare earth sesquioxides have been produced during the quarter now elapsed:

Tm_2O_3	0.827 g.
Er_2O_3	6.353
Ho_2O_3	1.276
Dy_2O_3	1.652
Y_2O_3	8.118
Tb_4O_7	0.335
Sm_2O_3	16.279

The above earths were collected in a number of fractions, so that the actual purity of some portions is probably much greater than indicated depending on the position in the elution zone.

It was hoped to have Lu and Yb available at this time, thus completing the yttrium earth group (Lu-Tb plus Y). These will be prepared soon.

The Sm_2O_3 was made by crystallization of the magnesium nitrate double salt. It was carefully checked for Eu; the amount of this element was reported to be not more than 0.1%.

It is of interest to note that the amounts of Tm_2O_3 and Er_2O_3 given were derived from the same amount of source material (viz., Commercial yttrium salts probably from Texas gadolinite). The natural ratio of Tm to Er is thus 1:8.

In all results on 19 column separations have now been obtained. These show many interesting differences from those results found when only milligram quantities were being fractionated.

General Radiochemistry: Heavy Rare Earth Radioisotopes (B. H. Ketelle and G. E. Boyd) P.A. CX4-3

Gadolinium

The separation of the rare earths between holmium and gadolinium was previously reported (B. H. Ketelle and G. E. Boyd, J. Am. Chem. Soc., 69, 2800 (1947)) but some uncertainties existed concerning the assignment of the terbium and gadolinium peak because so little was known concerning the half-lives of the active gadolinium isotopes. In order to clarify this problem several additional column separations of these elements have been made. Slow neutron activated rare earths were used, and, in order to facilitate the identification of yttrium, the 105 day isotope Y^{88} obtained from cyclotron bombarded strontium was used.

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In these separations yttrium was found to fall between holmium and terbium; the dysprosium peak was almost superimposed upon the peak of yttrium but may have lagged slightly behind.

Two separations yielding highly purified gadolinium show the presence of two activities with half-lives of 18 hours and about 240 days. It is possible that the longer lived activity is the same as the activity shown by Ingraham and Hayden (Phys. Rev., 71, 643 (1947)) to belong to Gd^{153}.

Ytterbium:

Bothe (Z. Naturforsch., 1, 173 (1946)) has assigned the 34 day activity of ytterbium to the isotope of mass 169 because the X-rays emitted, following K-capture were those characteristic of thulium. This assignment has been confirmed by the reaction:

$$Tm^{169}(d,2n)Yb^{169}.$$

Ytterbium free thulium fluoride was subjected to a 100 μA hr bombardment in the Berkeley cyclotron and an ytterbium-thulium separation was made on the ion exchange column. Two peaks of activity were desorbed from the column. The first peak was due to activity having a half life of $32\frac{1}{2}$ days. Absorption curves further identified the activity to be identical with the 32 day activity produced by slow neutron bombardment of ytterbium. Activity of the second peak appears to be identical with the 1.0 Mev β 125 day activity of thulium.

Erbium and Thulium

In the last quarterly report (CNL-37, p. 94) probable mass assignments and radiation characteristics were given for the 7.5 hr and 9.4 day erbium activities. Further, it was stated that the 700 day thulium activity was probably the daughter of the 7.5 hr Er^{171}. Further work has been done to confirm these assignments.

A sample of erbium was bombarded in the pile for 138 days to produce the long lived thulium. Following the bombardment the sample was allowed to cool for 35 half lives of the 7.5 hr activity before the thulium erbium separation was made. The decay of the erbium sample was followed in an ionization chamber and the proportional beta counter until it tailed out to a very long lived activity. The latter was present to the extent of only 0.00057 of the 9.4 day erbium activity. If the 9.4 day activity decayed to the 700 day activity, the latter should have about 0.0135. Therefore, it is felt that the long lived activity is either a trace of thulium impurity in the erbium, that it is a third erbium activity, or that it is the long-lived Ho^{163} isotope. Its decay has not been followed sufficiently long to give a value of the half life.

In another experiment the thulium erbium separation was made as rapidly as possible after bombardment and the decay of the erbium fraction was again followed. The results of this experiment cannot be reported until the 9.4 day activity has decayed to a low level relative to any long-lived activity which may be present.

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[redacted]

In conclusion, it is believed that the 9.4 day erbium does not decay to the 700 day thulium. Furthermore, since it was shown that this erbium is a beta emitter, its assignment to mass 169 in agreement with the previous assignment made on the basis of its energy is probably correct.

Thulium activity obtained from the first of the two above mentioned bombardments was sufficient for study on the beta ray spectrometer. It appears to be a pure beta emitter whose maximum energy is 0.100 Mev. The calculated value of ft for this isotope is 1.2×10^6 so the transition is probably first forbidden.

Finally, the β spectrum of a source of Tm^{170}, 125 day half life, was determined on the beta ray spectrometer. Its maximum energy is 0.98 ± 0.01 Mev. With the product ft equal to 6.8×10^8 this appears to be a second forbidden transition.

The Separation of Hafnium and Zirconium by Citrate Precipitation

It was reported in the open literature that a precipitation of zirconium by citric acid would not carry hafnium and that very good separation could be achieved.

In order to test this statement a half a gram of commercial zirconium nitrate was equilibrated with hafnium tracer in hydrofluoric acid. The hydrofluoric acid was then displaced by fuming with perchloric acid and the residue taken up in water. Since a trace of fluoride remained, it was removed by repeated precipitation of the hydroxide and resolution in nitric acid. Finally, the precipitation was made by the addition of a half gram of citric acid monohydrate. Since the precipitation was slow to form, several centrifugations were made and the precipitates were numbered. Finally, the supernatant solution after several weeks standing gave no more precipitate until phosphoric acid was added. The following table gives the reading in mv. on the gamma ionization chamber set on $10^{11}\Omega$ resistance.

Table I

Precipitation of Hf in Zirconium Citrate

Precipitate Number	Mv.	% Hf in Precipitation
1st Citrate	37	32
2nd Citrate	6	5.2
3rd Citrate	3	2.6
4th Citrate	8	7.0
5th Citrate	1	0.9
Phosphate	60	52
Supernate	0	

[redacted]

[redacted]

At best the separation is poor, certainly not the clear cut separation that was reported by the early experimentors. Since the quantities of precipitates formed were not determined, it is not possible to give a separation factor. However, qualitatively it can be said that the amount of hafnium carried was proportional to the precipitate volume.

[redacted]

[redacted]

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

Introduction

During the past quarter work has continued on the extraction of various metals into benzene solutions of TTA (symbol, HT) according to the reaction

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

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

$$K_{Me} = \frac{[MeT_n]_B [H^+]^n_A}{[Me^{+n}]_A [HT]^n_B}$$

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

Yttrium studies

The equilibrium constant for the extraction of yttrium with TTA-benzene was determined using Y^{91} tracer. A series of nine experiments (Table I) in which the extraction ratios (benzene/aqueous) were varied from 5×10^{-4} to 50 by appropriately adjusting TTA and H^+ concentrations gave an average value of

$$K_Y = \frac{[Y]_B [H^+]^3}{[Y]_A [HT]^3} = 1.94 \times 10^{-7}$$

The precision obtained (average deviation = ± 3%) is much higher than is justified by the accuracy of pH measurements. The limit of sensitivity of the pH meter used is no better than 0.02, and this deviation will introduce an error of 15% in the value of K_Y.

TABLE I

No.	Conc. TTA in benzene $(HT)_B$	pH	Distribution Ratio $(Y)_B/(Y)_A$	$K_Y \times 10^7$
1	0.10	3.19	0.107	1.87
2*	0.10	3.84	9.5	1.85
3	0.20	2.86	0.088	2.04
4	0.20	3.20	0.905	2.02
5*	0.20	3.59	12.1	1.84
6	0.50	1.74	0.000516	1.92
7	0.50	2.32	0.0278	1.98
8	0.50	2.86	1.14	1.98
9*	0.50	3.43	57.5	1.95
			K_{ave}	$= 1.94 \pm .06 \times 10^{-7}$

*Equilibrium approached from the benzene phase

(1) CNL-37

[redacted]

Lanthanum Studies

The value quoted in the last quarterly report[1] for the equilibrium constant for the partition of La^{3+} tracer between aqueous solutions and TTA-benzene was found to be in error because of the presence of impurity in the tracer used. A redetermination of K_{La} with use of carefully purified tracer (Table II) gave 7.9×10^{-10} with an average deviation of ± 6%. These data are consistent with the data of Werner and Perlman[2] if their measurements are assumed to have been made at an ionic strength of 0.05 molar. Although the agreement among the various values in Table II is well within the accuracy of the pH determinations, there may be a trend to lower values of K_{La} at higher pH values.

TABLE II

No.	$(HT)_B$	pH	$(La)_B/(La)_A$	$K_{La} \times 10^{10}$
1*	0.20	3.02	0.00105	8.1
2	0.20	3.18	0.0031	7.8
3	0.20	4.07	1.55	8.4
4	0.20	4.09	1.53	7.4
5	0.50	3.01	0.0152	9.2
6*	0.50	3.14	0.0352	8.9
7	0.50	3.33	0.121	8.2
8	0.50	3.42	0.204	7.5
9	0.50	3.54	0.495	7.9
10	0.50	3.57	0.554	7.2
11	0.50	4.01	11.8	7.3
12	0.50	4.06	16.9	7.4

$K_{ave} = 7.9 \pm 0.5 \times 10^{-10}$

*Equilibrium approached from the benzene phase

Zirconium-hafnium separation

An approximate value was obtained (Table III) for the equilibrium constant for the extraction of hafnium tracer from HCl solutions to check on the possible useof a TTA procedure for the separation of zirconium and hafnium. Unfortunately, hafnium extracts at a very slow rate, considerably slower than does even zirconium, and $K_{Hf} \sim 7 \times 10^6$ is not sufficiently different from K_{Zr} ($\sim 2 \times 10^7$)[3] to allow a simple separation. A procedure involving repeated fractionation may, however, be practical. Since hafnium is the less extractable and also the slowest to extract, a better fractionation may be achieved by operating at non-equilibrium conditions. Since there is some chloride complexing in strong HCl solutions, fractionation may also be improved by extracting from non-complexing aqueous phases such as $HClO_4$ solutions.

A further complication was introduced when the extraction was attempted with a Zr + Hf concentration of 10 mg/ml. As soon as a TTA-benzene solution was added to the 1 N HCl containing these macro quantities, a precipitate was formed. The composition of this precipitate has not been determined.

(2) BC-1

(3) Mon-N-311

[redacted]

TABLE III

No.	$(HT)_B$	$(H^+)_A$	$(Hf)_B/(Hf)_A$	K'_{Hf}
1	0.01	1	45	7.1×10^6
2	0.05	1	0.07	7.0×10^6

Dithenoylmethane

Dithenoylmethane has been obtained and will be tested as a complexing agent to supplement TTA. Preliminary indications are that the much lower solubility of DTM (saturated solution $\sim$0.2M) in benzene will limit its applicability.

Reports issued

A compilation of abstracts of project literature on β-diketone extractions has been issued as ORNL-36.

[redacted]

[redacted]

Hard Gamma Rays from Y^{88} - (H. A. Levy, M. H. Feldman)

The apparatus previously described[1] for measuring γ-radiation by counting neutrons from the (γ,n) reaction on deuterium oxide has been used to investigate hard γ-radiation from 105d Y^{88}. This isotope is reported[2] to emit gammas of 0.9, 1.89, and 2.8 Mev, the latter in a fraction 0.01 ± 0.005 of the disintegrations.[3] The 2.8 Mev γ is the only one detectable by (γ,n) on deuterium, and this method offers the possibility of precision considerably greater ($\sim$5%) than that of the previous work.

The Y^{88} was obtained from a Sr target bombarded with deuterons in the 60" Berkeley cyclotron and was separated by a solvent extraction procedure with TTA. The counting rate in the hard γ apparatus was very low, $\sim$100 counts per hour; consequently long counts are necessary. Counts were taken for 10 successive 10-hour periods several times over a 3-month interval. The data were subjected to statistical analysis by usual methods.[4] Some data of questionable value according to Chauvenet's Criterion were discarded as probably arising from defects in the instrument. Periodic measurements of total γ were also made with a high-pressure ionization chamber[5] equipped with a vibrating-reed electrometer.

In Figure 1 are shown the observed measurements as a function of time. The lower curve represents the hard γ measurements, points X being counting rates obtained from the first 10-hour count of each measurement and points O those from the average of 10 such counts. As is to be expected, the former show greater fluctuation. The upper curve represents the total gamma radiation.

Since the slopes of the two curves are not alike, there is doubt as to the origin of the hard γ measured. Further measurements are underway in an effort to clarify the question.

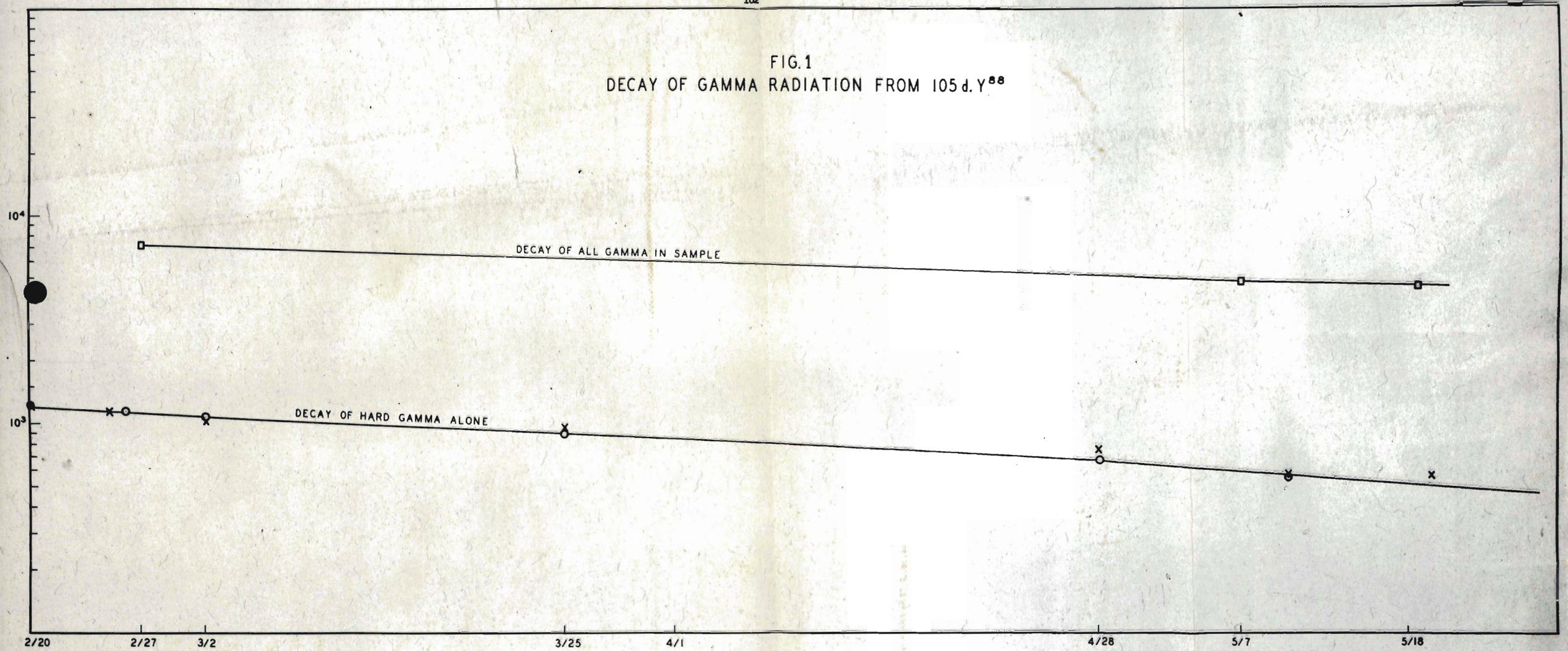
Radiations from Ba^{141} - (H. A. Levy, B. Zemel)

In order to make satisfactory measurements of the energy of 18 m Ba^{141}, it has been found necessary to devise a continuous method of removing the 3.5 hr. La daughter. This has been found possible if the Ba^{141} is counted from solution, and this solution is continuously circulated through a vessel containing suspended $Fe(OH)_3$ at pH 8-9. Equipment for achieving this has been devised and tested. The details, together with results of absorption measurements, will be reported later.

1. Mon-432, p. 100; CNL-37, p. 100
2. Downing, Deutsch and Roberts, Phys. Rev. 60, 470 (1941)
3. Gammertsfelder, Phys. Rev. 66, 288 (1944)
4. A. A. Jarret, Lecture #9 in Radiochemistry, Clinton Laboratory Training Program.
5. Jones, Clark, Zumwalt and Overman, ORNL Report in Preparation.

Drawing # 5827

FIG. 1
DECAY OF GAMMA RADIATION FROM 105 d. Y^{88}



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

In a previous attempt to prepare anhydrous $BaRuO_4$ by heating the monohydrate, it was found that oxygen is evolved and a phase approximating $BaRuO_3$ is formed. X-ray diffraction patterns of this material showed that it was either non-crystalline or partly crystalline, depending on the temperature of heating. In further experiments, some of this material was reheated at various temperatures and for various times in air, vacuum, and oxygen. The phases resulting from these treatments were similar and showed two types of X-ray diffraction lines: a series of 5 sharp lines accurately described by the 110, 211, 220, 321 and 330 reflections of a cubic cell with $a_o = 4.06$ A, and a second series of diffuse lines in a complicated pattern. These two series probably arise from different phases. Several attempts to separate these phases, by boiling in H_2O and leaching with acid had essentially no effect on the diffraction pattern. The sample was then further heated in air at 1100° for 48 hours; this treatment left the five "cubic" lines unchanged, except possibly for sharpening, but caused the appearance of a complex pattern of other sharp lines quite different from those previously observed.

Efforts to obtain the X-ray diffraction pattern of RuO_4 were unsuccessful because of experimental difficulties. Two capillaries filled with powdered material exploded (entrapped liquid N_2) before an X-ray photograph could be obtained. Attempts to place single crystals of RuO_4 into capillary tubes in a dry box were unsuccessful. The high vapor pressure of the material was responsible for the rapid disappearance of these crystals, even at a working temperature of 0-5°C.

The Crystal Structure of $KRuO_4$

Debye-Scherrer patterns of $KRuO_4$ were successfully indexed on the basis of a tetragonal lattice. The pattern shows the structure to be isomorphous with scheelite ($CaWO_4$). The lattice constants were obtained with greatest precision from reflections in the back-reflecting region on a pattern in which NaCl was mixed with the $KRuO_4$ in order to provide calibrating lines. The lattice spacings considered most precise are as follows:

hkl	a_o, Xu	C_o, Xu
440	5597.6	
620	5597.6	
640	5597.0	
0016		12965

Values adopted: $a_o = 5597 \pm 3$ Xu; $C_o = 12,965 \pm 8$ Xu

The pattern shows the following systematic absences: hkl when h + k + l is odd, corresponding to a body-centered lattice; hko when h or k is odd; ool when l is not a multiple of 4. These absences and no others are required by the space group $C_{4h}^6 - I4_1/a$, which is the space group to which scheelite and a number of other isomorphous crystals belong. The symmetry of this space group requires that 4 molecules of $KRuO_4$ be present in the unit cell, with K and Ru occupying the 4-fold special positions (a) and (b).* The 16 oxygen atoms could be in two sets of 8-fold

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

positions (c), (d), or (e), or in general positions (f). The former do not lead to a chemically plausible structure.

Complete specifications of the structure will require the assignment of values to three parameters on the basis of the observed intensities. This assignment is now under way.

 [redacted]

Separation of the Long-Lived Rare Earth Activities in Fission: (G.W. Parker, P.M. Lantz, J.W. Ruch, G.M. Hebert)

Introduction:

Associated with the extensive effort toward collecting and accumulating milligram quantities of the 4y element 61 for general characterization, there has developed a fortunate opportunity to separate and purify reasonable quantities (millicuries) of the long lived Eu^{155} and Sm^{151}. The 2-3y Eu has been previously accurately described by Winsberg[1] but the ~ 20y Sm, it is believed, has been only incompletely reported [2,3].

The history of the application of the ion-exchange technique in this department to the purification of large quantities of element 61 begins with the original fission element separations experiment devised by Tompkins, Khym and Cohn[4,5], from fractions of which Marinsky and Glendenin[6,7] achieved the first chemical purification of this element. The duplication of Marinsky's separation of 61 by repeated fractionation on somewhat inefficiently but successfully operated six foot columns of Amberlite IR-I was accomplished immediately following the former work and has been continued on a semi-production basis during the past two years, accompanied by a general program of physical characterization of the element.

While this report on the occurrence and characterization of these two long-lived rare earths is not presented in the light of a complete study, an attempt has been made to establish the most prominent radiation characteristics within the limits of the degree of purification indicated in the elution curves of Fig. II and III; i.e., to a purity of 1-2 parts per thousand of cross contamination.

For some time, due to the intensity of the interest in element 61, the normally associated long-lived Eu^{155} and Sm^{151} were sacrificed in fractions deleted to avoid high radiation from large quantities of the 57dY. The only previous separation of fission isotopes of these two elements was observed in connection with the preparation of the ~47 hr. 61^{149} for mass study by

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(1) L. Winsberg, CC-2000, Aug., 1944; See also "Nuclei Formed in Fission, Decay Characteristics" etc. (J.A.C.S. 68, 2411-2422 (1946), issued by the Plutonium Project.
(2) L.G. Lewis and R.J. Hayden, C.P. 3295, Oct., 1945.
(3) M.G. Inghram, D.C. Hess and R.J. Hayden, Phys. Rev. 71, 643, 1947.
(4) W.E. Cohn, E.R. Tompkins, J.X. Khym and G.W. Parker, CC-S-2827, June, 1945.
(5) E.R. Tompkins, J.X. Khym and W.E. Cohn, J.A.C.S. 69, Nov., 1947.
(6) J.A. Marinsky and L.E. Glendenin, CC-R-2829, June, 1945.
(7) J.A. Marinsky and L.E. Glendenin, J.A.C.S. 69, Nov., 1947.

[redacted]

 [redacted]

Inghram[8]. It is recognized that some adjacent rare earths respond much less to the fractionating power of the ion-exchange citrate-elution-method[9]. Such a pair is undoubtedly these two elements for it can readily be seen, for example in Fig. IIA, that an enormous separation exists between Samarium and element 61, while one observes only a bare break in the activity peaks between Eu and Sm in Fig. II. Perhaps a better and more consistent separation of these two elements has been possible by the particular steam heated column method previously reported by Ketelle[10].

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(8) Inghram, Hess and Hayden, Loc. Cit.
(9,10) G.E. Boyd and B.H. Ketelle, JACS 69, Nov., 1947.

Experimental:

Gross Rare Earth Separations

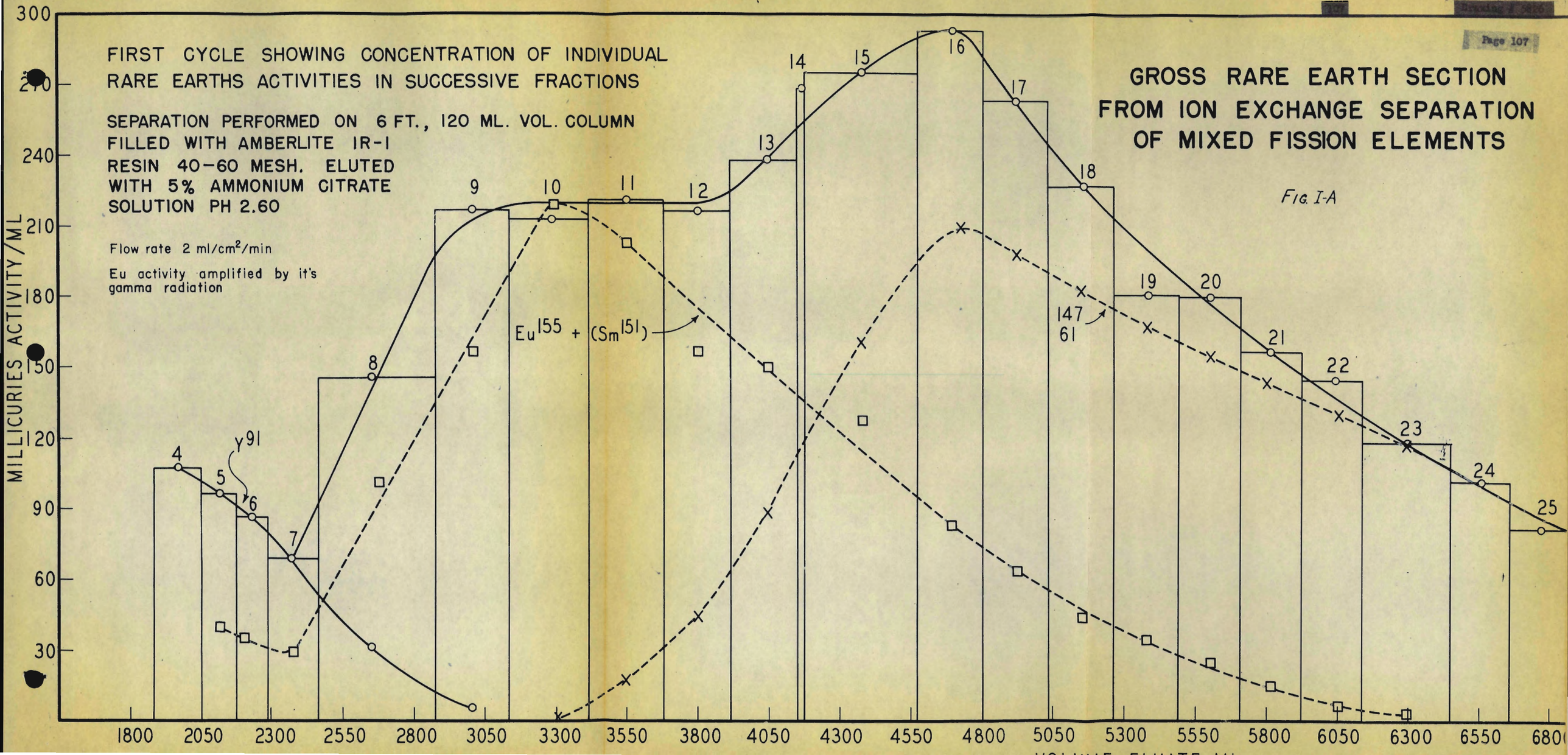
In the average procedure existing for the separation of fission rare earths, a solvent extracted aqueous-residue is used containing the entire fission mixture. From the "Gross Separation Column" a recognizable spread is obtained in the rare earths section between the successive aliquots such as is indicated by the calculated-component curves of Fig. I. This initial separation is currently being performed on an IR-I or Dowex 50 column 6-feet x 1.5 cm and with 4.75% citric acid-NH_4OH solution of pH $\sim$ 2.6 for the former column to 2.9 for the latter. The Dowex 50 column is slower but more efficient and is useful in handling larger quantities of cations whether of fission or foreign material. IR-I was used exclusively for a long time for the advantage of speed.

The components illustrated in this initial separation are arranged in the order Y, Eu, Sm and 61. Nd, Pr, Ce, etc., are not recorded because long-lived activities are apparently not present in the first two and the curves do not extend to the region of the appearance of Ce activity. To date no fission produced Gd which should precede yttrium has been reported.

Quality of the Eu-Sm Separation

By selecting an appropriate division in the aliquots containing Eu and Sm; identical column runs were then repeated for the enhancement of their individual purity. Fig. II A&B illustrate roughly an effect of decreased flow rate on the distance between the centers of the respective bands in terms of numbers of cuts. On the 3-day Separation (Fig. II-A), only 3 cuts separate the peaks, while the 6-day (Fig.II-B) run at least twice as many cuts and a significant "saddle" between the curves is observed. Improved separations with finer mesh media or slower elution are obviously possible.

[redacted]


FIRST CYCLE SHOWING CONCENTRATION OF INDIVIDUAL RARE EARTHS ACTIVITIES IN SUCCESSIVE FRACTIONS
SEPARATION PERFORMED ON 6 FT., 120 ML. VOL. COLUMN FILLED WITH AMBERLITE IR-1 RESIN 40-60 MESH. ELUTED WITH 5% AMMONIUM CITRATE SOLUTION PH 2.60
Flow rate 2 ml/cm²/min
Eu activity amplified by it's gamma radiation
GROSS RARE EARTH SECTION FROM ION EXCHANGE SEPARATION OF MIXED FISSION ELEMENTS
FIG. I-A
MILLICURIES ACTIVITY/ML
Y91
Eu155 + (Sm151)
147 61
300
270
240
210
180
150
120
90
60
30
1800
2050
2300
2550
2800
3050
3300
3550
3800
4050
4300
4550
4800
5050
5300
5550
5800
6050
6300
6550
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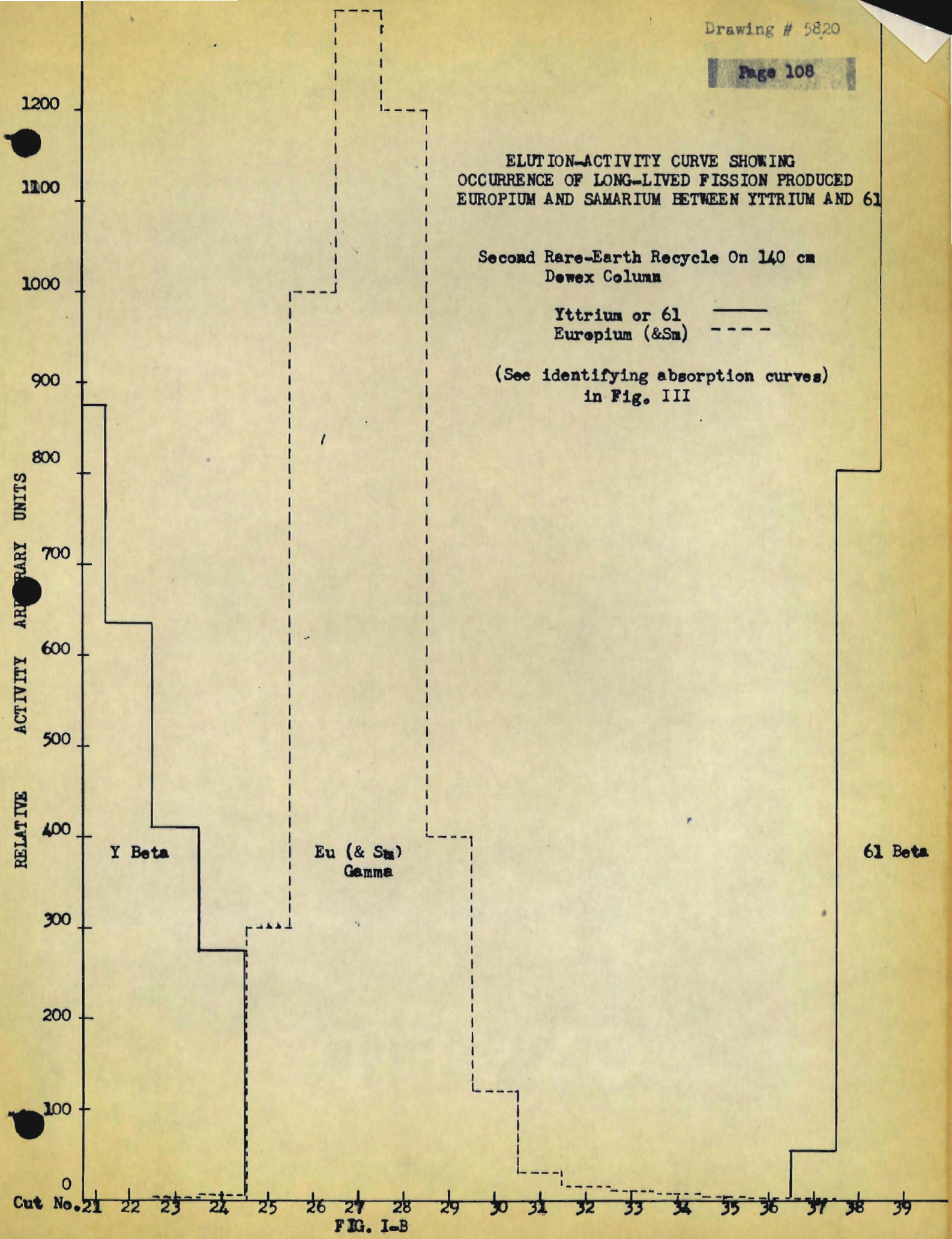

ELUTION-ACTIVITY CURVE SHOWING
OCCURRENCE OF LONG-LIVED FISSION PRODUCED
EUROPIUM AND SAMARIUM BETWEEN YTTRIUM AND 61
Second Rare-Earth Recycle On 140 cm
Dowex Column
Yttrium or 61
Europium (&Sm)
(See identifying absorption curves)
in Fig. III
RELATIVE ACTIVITY ARBITRARY UNITS
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
Y Beta
Eu (& Sm)
Gamma
61 Beta
Cut No. 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39

FIG. I-B

 [redacted]

Radiation Characteristics of 2-3y Eu^{155} and ~20y Sm^{151}
Determined by Absorption (See Fig.IV-4)

	B^-	γ
2-3y Eu^{155}	e^- (~50 Kev) Probable	~50 Kev (Not definite)
	B^- ~ 0.18 Mev*	~ 84 Kev**
		~ 1.2 Mev*** (low yield, probable)

* Previously identified as 220 Kev by Winsberg.
** Previously identified as 84 Kev by Winsberg.
*** May be due to Eu^{152} or Eu^{154} by second order Neutron Activation.

	B^-	γ
~ 20 y Sm^{151}	e^- (not definite)	Probably None
	B^- ~ 60 Kev	

[redacted]

FIG. III

IDENTIFICATION OF RARE-EARTH COMPONENTS IN THE EUROPIUM-SAMARIUM REGION BY ABSORPTION CURVES.

Cuts identified in preceding Fig. # I-B

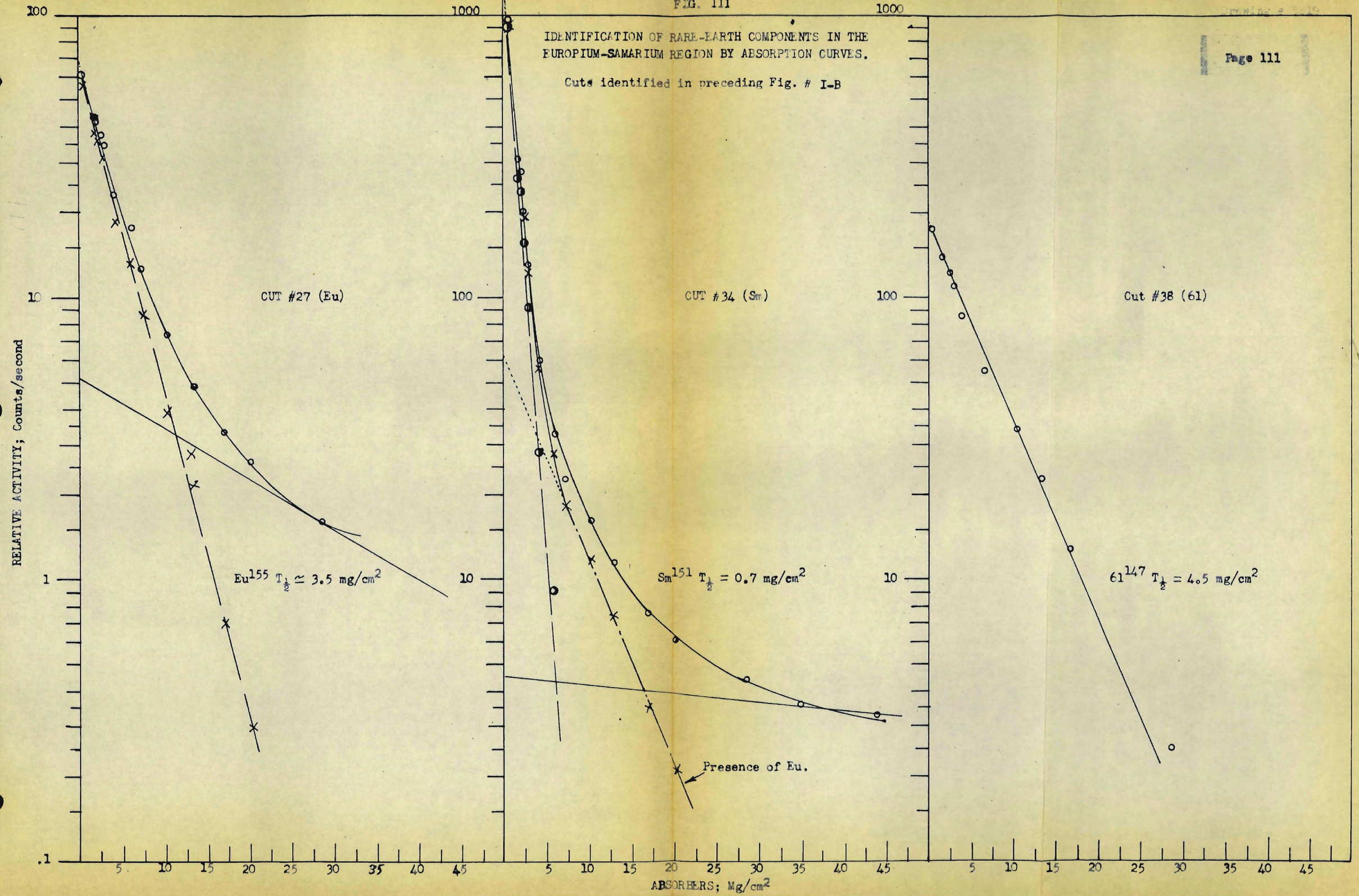


FIG. IV

Drawing # 5821

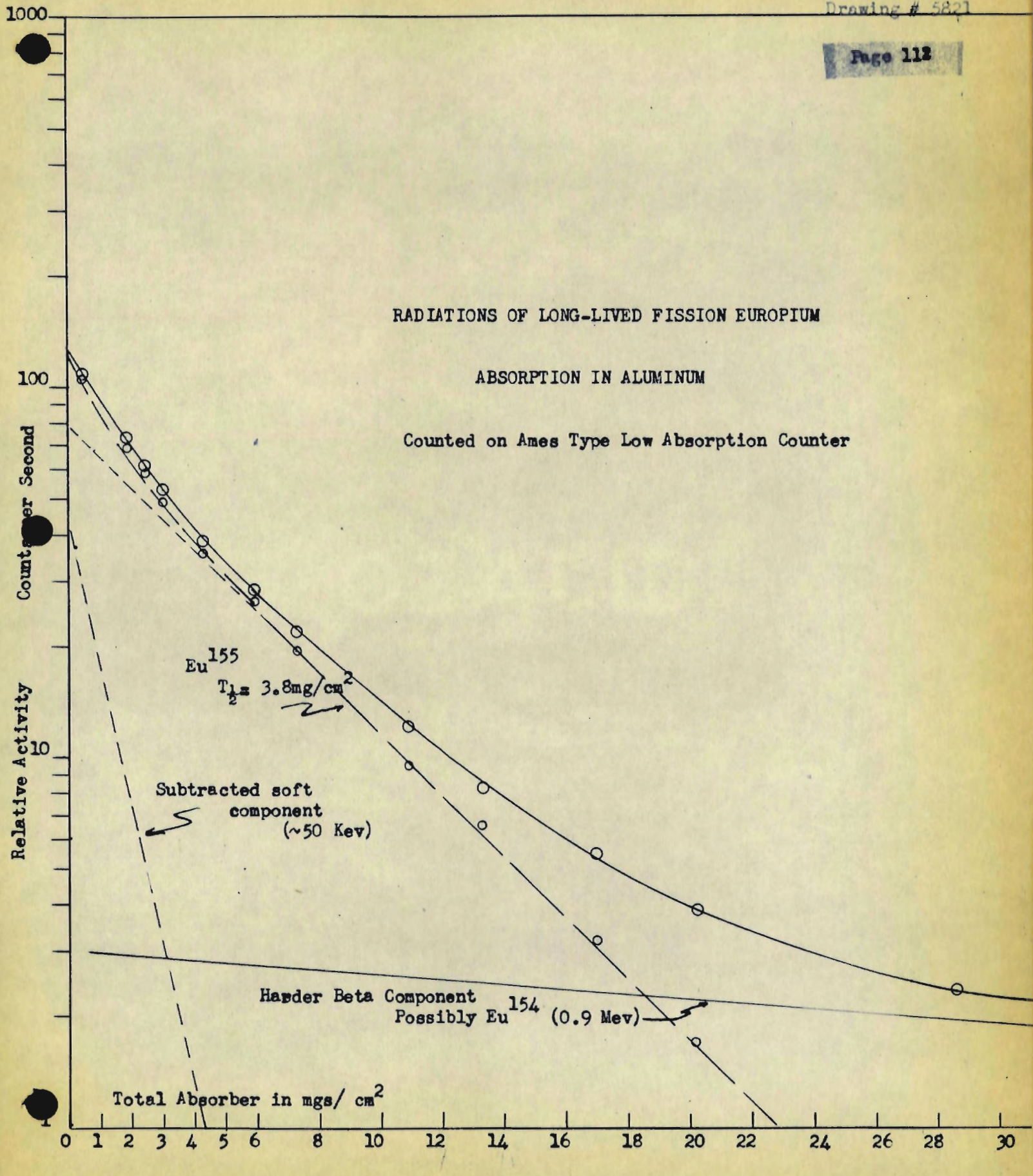
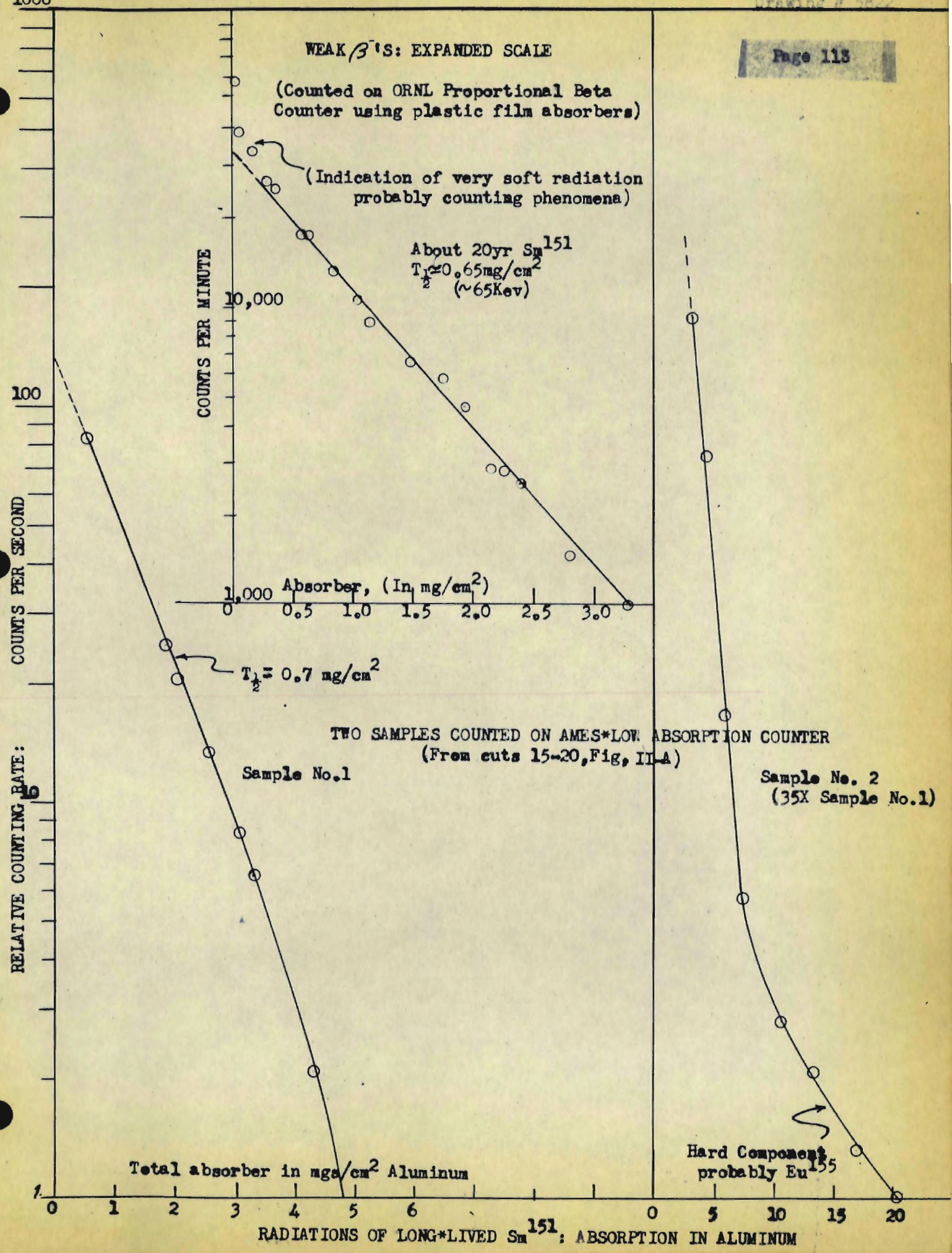


FIG. V

Drawing # 5822



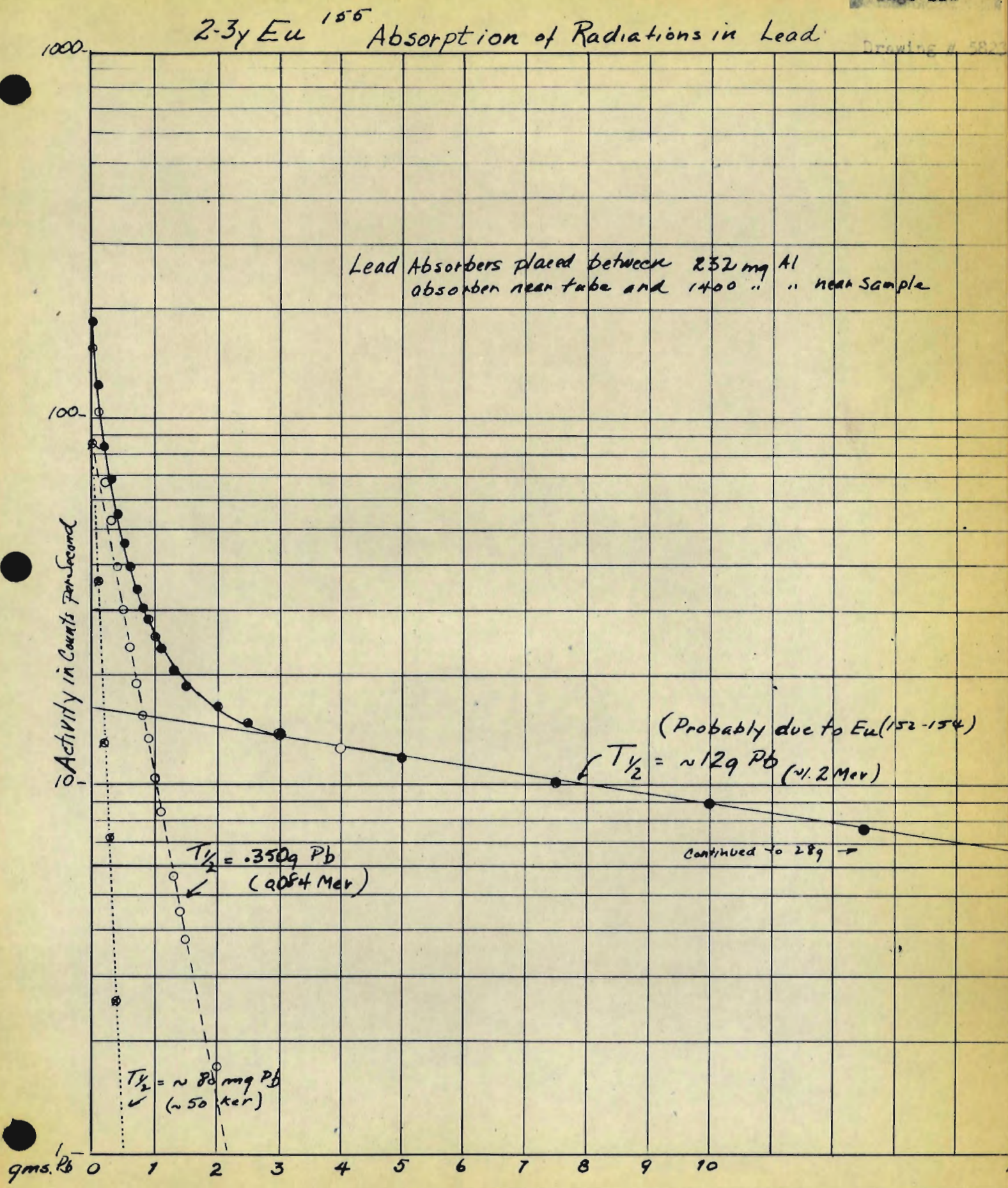

2-3y Eu 155 Absorption of Radiations in Lead
Lead Absorbers placed between 232 mg Al absorber near tube and 1400 " " near sample
Activity in Counts per Second
1000
100
10
1
gms. Pb
0
1
2
3
4
5
6
7
8
9
10
(Probably due to Eu(152-154)
T1/2 = ~12q Pb (~1.2 Mev)
Continued to 28q →
T1/2 = .350q Pb
(.0854 Mev)
T1/2 = ~ 80 mg Pb
(~ 50 kev)

Fig. VI

[redacted]

Production and Measurement of K-Series X-Ray Spectrum of Element 61: (G.W. Parker, P.M. Lantz - with Y-12 Spectrographic Group: L.E. Burkhart, W.F. Peed and F.J. Spitzer.

Introduction:

In an unclassified document Index No. Y 173, May 24, 1948, the Research and Development Division, Isotope Development Department Y-12 Plant; Messrs L.E. Burkhart, W.F. Peed and E.J. Spitzer report in detail the successful completion of a cooperative effort to photograph and measure the K-Series X-Ray emission lines of the radioactive element 61.

In a very excellent photograph made while bombarding about 2 mg of the Ay 61^{147} at 70 Kv; the four major lines were obtained with no evidence of any impurity. After adding about 1 mg each of Nd and Sm as the oxide to the target. A second exposure was taken recording the bracketing lines of the adjacent elements with those of element 61.

The following is an excerpt from p 9 of the report by Burkhart, et al.

Element 61 K-Spectra Lines	Wavelengths XU			
	Measured	Calculated	Possible Interfering Lines	
	323.68	324.27	La	327.26
	319.02	319.60	La	319.66
	282.00	282.99	Nd	285.73
			Td	282.94
			Tb	278.19
			Dy	275.64
	275.03	275.33	Sm	272.50

The group at X-10 are highly indebted to the above authors at Y-12 for their excellent work and intense effort in producing this data.

[redacted]

[redacted]

Effects of Heavy Particles on Water and Aqueous Solutions (A. O. Allen, C. J. Hochanadel, J. A. Ghormley, G. V. Elmore, J. W. Boyle, B. M. Haines, D. M. Richardson). P. A. CX5-20.

1. Study of Back Reaction in Decomposition of Water under Pile Radiation

A number of pile exposures have been made of water containing various amounts of added dissolved hydrogen and hydrogen peroxide. These solutions were sealed in fused silica ampoules with practically no gas volume so that all the gases present were held in solution. The ampoules were exposed in the standard position in Hole 12 of the Clinton Pile for various periods of time and were later analyzed for gas and peroxide content. In this way, results were obtained for the rate of decomposition or formation of water as a function of the concentrations of the various substances involved, and steady-state levels of water decomposition were obtained at different values of excess hydrogen or peroxide. Results in these experiments have been the most consistent of any obtained on water in the pile.

The water was triply distilled in all-silica apparatus. Hydrogen peroxide (Baker and Adamson, reagent grade, 30%) was vacuum distilled in silica apparatus before use. The silica ampoules used were sealed to a silica manifold connected to a silica bulb in which the water or peroxide solution to be used was placed. Hydrogen or helium freed of higher-boiling impurities by passage through a liquid-air trap was bubbled through the solution in the bulb until air was expelled and the solution saturated with the gas at atmospheric pressure. The whole apparatus was then inverted, allowing the gas-saturated solution to flow into the ampoules, which were then sealed off.

The results are given in detail in Table 1. The numbers in the last column headed "$H_2O_2 + 2O_2 - H_2$", should be constant for any series of runs by material balance. Variations in this number indicate either that analysis was faulty or that some side reaction occurred involving impurities or silica. Although considerable deviation from good material balance occurs in some cases, the results in general are regarded as satisfactory.

The outstanding feature of these results is that decomposition of water in the pile is entirely suppressed by adding a relatively small quantity of excess hydrogen. When both hydrogen and hydrogen peroxide are added to the water, the peroxide rapidly drops to zero when the excess hydrogen concentration amounts to 100 micromoles/liter or more (corresponding to a hydrogen pressure of about 10 cm Hg at room temperature). Excess peroxide, however, instead of suppressing the evolution from water, has the opposite effect; the bigger the excess of peroxide the more hydrogen is present at the steady state. Thus hydrogen peroxide plays a double role in the back reaction; it is, of course, a reagent necessary for the back reaction to occur, but it also, like many other solutes, acts as an inhibitor for the back reaction. This is the explanation for the previously observed fact that, starting with pure water, a higher steady-state concentration of hydrogen is observed when a considerable space is available over the water than when the vessel is full. In the former case, most of the hydrogen formed escapes into the gas phase, leaving an excess of peroxide in the solution which inhibits back reaction and causes the hydrogen concentration and thereby its pressure to rise to high levels. Since excess peroxide inhibits the back reaction, a solution containing large peroxide excess would presumably decompose under radiation indefinitely if it were not for the decomposition of peroxide to oxygen which occurs at the same time. The evolution of hydrogen stops when

[redacted]

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Table 1. Reactions in aqueous solutions of hydrogen and hydrogen peroxide exposed in Clinton pile at 25° C.

Batch[a]	Exposure time	Concentrations, micromoles/liter			
		H_2	O_2	H_2O_2	$H_2O_2 + 2O_2 - H_2$
B[b]	0	680	1	775	97
	0	517	4	769	260
	2 min.	710	19	705	33
	2 min.	627	14	717	121
	3 hr.	143	20	173	70
	3 hr.	151	19	161	48
	70 hr.	207	40	204	77
	70 hr.	307	39	202	-27
D1	0	847	4	0	
	10 min.	829	5	0	
	10 min.	828	7	0	
	3 hr.	724	4	0	
	3 hr.	743	4	0	
D2	0	972	4	1190	226
	10 min.	870	1	968	100
	10 min.	937	1	980	45
	3 hr.	395	133	527	398
	3 hr.	403	142	535	416
D3	0	767	10	4720	3973
	10 min.	1220	370	4120	3640
	10 min.	1015	382	3980	3729
	3 hr.	1220	1860	2735	5235
	3 hr.	1910	1750	2665	4255
C	0	780	0	2430	1650
	10 min.	1020	210	1945	1345
	3 hr.	1100	720	1515	1855
	3 hr.	1190	645	1470	1570
E1	0	0	1260	0	2520
	10 min.	204	1360	377	2893
	10 min.	119	1190	380	2641
	3 hr.	913	1110	1496	2603
	3 hr.	948	1085	1470	2692
	6.5 hr.	870	1070	1300	2570
E2[c]	0	20	0	320	280
	10 min.	172	108	280	325
	10 min.	160	97	287	321
	3 hr.	493	105	452	169
	3 hr.	411	112	460	274
	6.5 hr.	352	143	422	356
E3	0	563(?)	4	324	(-231)
	10 min.	395	8	0	-379
	10 min.	402	11	0	-379
	3 hr.	380	4	14	-358
	3 hr.	392	11	13	-356
	6.5 hr.	353	19	0	-315

[redacted]

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Table 1. (Continued)

F1[c]	0	(0)	(0)	0	—
	2 min.	—	—	20	—
	2 min.	10	7	17	12
	4 min.	17	7	13	10
	3 hr.	19	9	13	12
	3 hr.	16	6	17	13
F2	0	773	6	350	-411
	1 min.	687	6	297	-378
	1 min.	—	—	295	—
	2 min.	—	—	227	—
	2 min.	635	10	212	-403
	4 min.	408	7	45	-349
	4 min.	415	22	37	-334
G1[d]	0	742	11	301	-419
	2 min.	740	15	243	-467
	2 min.	733	3	238	-489
	4 min.	693	6	192	-489
	4 min.	642	5	192	-440
	8 min.	501	7	0	-487
	8 min.	535	6	0	-523
	12 min.	487	9	0	-469
	12 min.	436	19	0	-398
	16 min.	477	0	0	-477
	16 min.	425	14	0	-397
G2	0	—	—	282	—
	1 min.	707	6	227	468
	1 min.	682	4	208	466
	2 min.	727	7	142	571
	2 min.	703	1	125	576
H	0	—	—	660	—
	0	823	18	665	122
	10 min.	570	19	435	97
	10 min.	660	21	445	173
	85 min.	51	4	0	43
	85 min.	59	10	0	39

Notes: (a) Ampoules in each batch were filled simultaneously by the same solution.

(b) Hydrogen values in this batch are believed to be low because of incomplete outgassing of samples for analysis after exposure.

(c) Saturated with helium.

(d) Pile operating at 1000 KW. All other runs at normal power, about 3600 KW.

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the peroxide level has been sufficiently reduced by its decomposition to oxygen. On this view, the concentration of hydrogen found at the steady state is regarded as dependent on the concentration of peroxide, but the concentration of oxygen plays merely an incidental role in the picture. Figure 1 shows a plot of the hydrogen concentrations at the steady state versus the peroxide concentration. For the runs with excess hydrogen, the peroxide concentration is zero; the runs with excess peroxide lie on a straight line on this plot.

Figure 2 shows the rate of disappearance of peroxide for experiments with excess hydrogen or with relatively small excess peroxide. Curves A, B, D, E, F and G of Figure 2 were obtained at pile power of about 3600 KW; curve C was obtained at a power of 1000 KW. Curve E was obtained a long time ago in pyrex glass and is put in here for comparison; it seems to fall well in line with the others. In that curve only the sum of hydrogen peroxide and oxygen was determined and is here plotted. For all the other curves (obtained in current work) the amounts of oxygen found by analysis were almost negligible, and the hydrogen peroxide alone is plotted. All solutions initially contained a concentration of 775 micromoles/liter of hydrogen, corresponding to saturation with the gas at atmospheric pressure. The rate decreased less than proportionally to the pile power. The initial rates at normal pile power are plotted in Figure 3 against the initial peroxide concentration. The rate is seen to vary in a regular manner with peroxide concentration and to be a minimum at the point at which the peroxide and hydrogen concentrations are equal. The reaction kinetics here presented should be explainable on the basis of a theory involving the interactions of the free radicals produced by irradiation of water. Such a theory is being worked on, but is not ready for presentation at this time. It may be said that the high rate of disappearance of the peroxide indicated in Figures 2 and 3 proves that the back reaction occurs by a chain mechanism, as had long been suspected; and the straight-line relationship of Figure 1 follows directly if peroxide molecules react readily with OH radicals as well as with H atoms, and all the OH radicals disappear by reaction either with peroxide or with some other impurity.

Water outgassed with helium decomposed less than expected from the experiments in which hydrogen and peroxide were present. This probably indicates that some impurity which slightly inhibits the back reaction was introduced with the hydrogen gas. When water containing only hydrogen was exposed, the hydrogen concentration appeared to decrease slightly, and the peroxide concentration as determined by spectrophotometric iodimetry appeared to be negative. The same phenomenon of apparent negative values of peroxide was always found on long irradiation of solutions containing hydrogen in excess of the added peroxide. The negative values could be ascribed to the presence in the sample of an active reducing agent which reduces some of the iodine unavoidably present in the potassium iodide reagent used for the determination. This reducing agent could result from impurity introduced with the water or the hydrogen gas, or it could conceivably result from reduction of SiO_2. The subject is being investigated further.

2. <u>Decomposition of Water under Pile Radiation in Solutions of Purified Potassium Chloride at Various pH</u>

The quantity of bromide in our purified potassium chloride was determined by activation analysis in the pile. Four 1-g. samples of the pure KCl were

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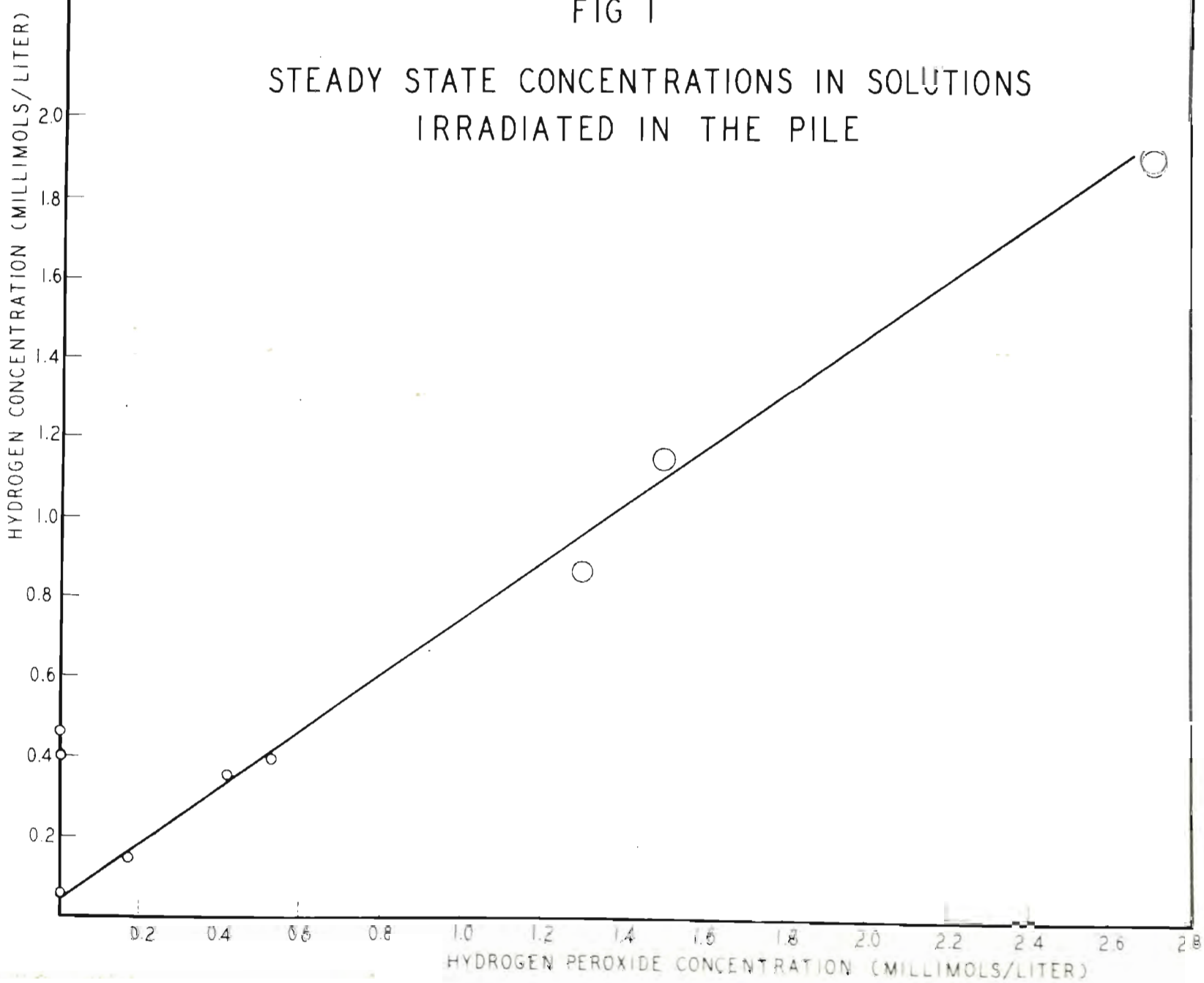
FIG I

STEADY STATE CONCENTRATIONS IN SOLUTIONS IRRADIATED IN THE PILE



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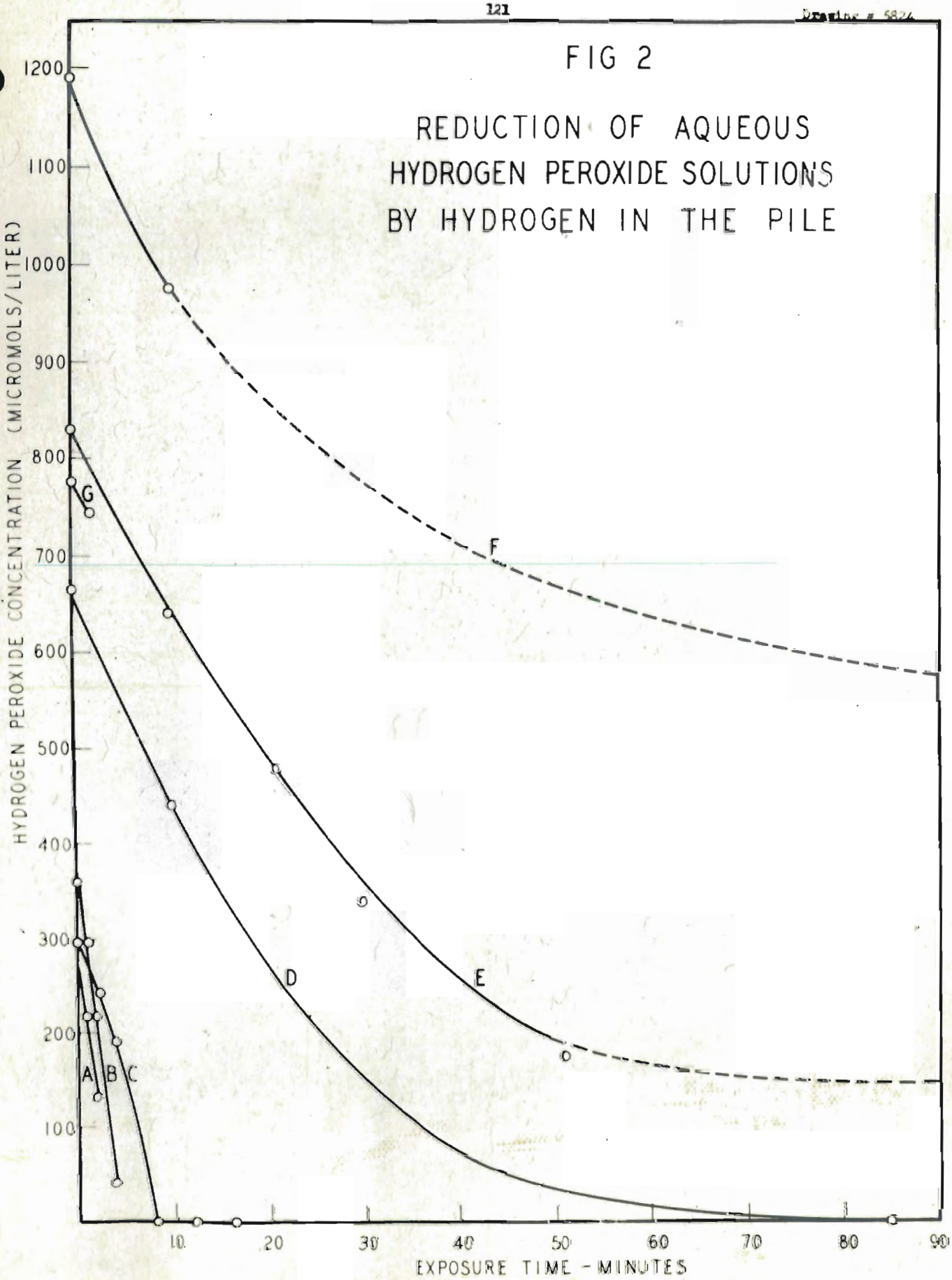
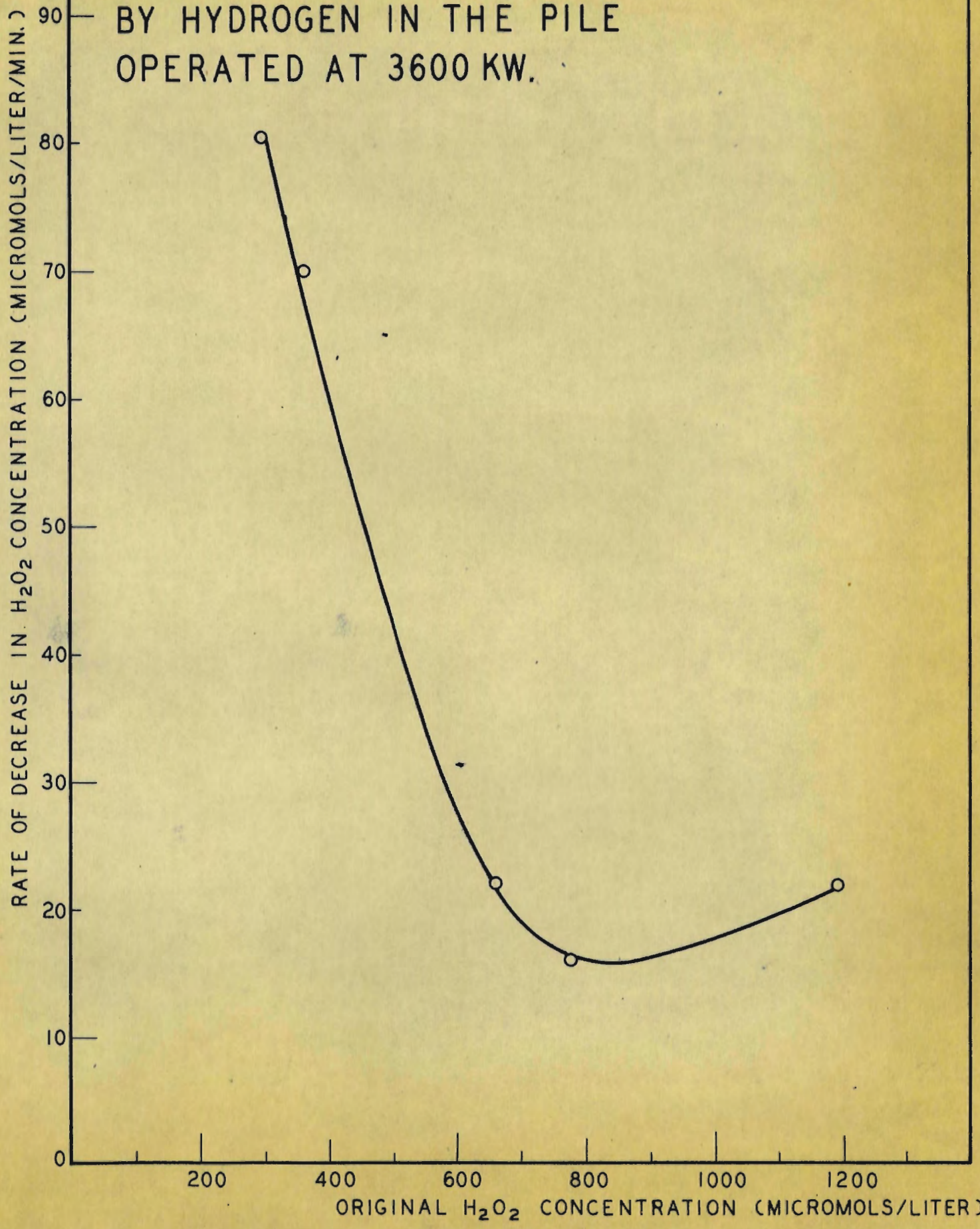


FIG. 3

INITIAL RATE OF PEROXIDE REDUCTION BY HYDROGEN IN THE PILE OPERATED AT 3600 KW.



[redacted]

exposed in the pile for 119 hours. Three of these samples contained small quantities of added potassium bromide. Each sample was dissolved in water, acidified, and carrier KBr and excess $KBrO_3$ added. The resulting bromine was extracted into carbon tetrachloride three times, and the combined extracts then extracted with sodium bisulfite. The bromine was precipitated as silver bromide, mounted and counted. Results are shown in Table 2. The counts per minute here reported are corrected for coincidences and for a background of 17 c/min. All samples showed the proper bromine half-life of 34 hours, and (by absorption) the proper maximum energy of 0.45 Mev expected for active bromine, thus identifying the impurity which was being counted in the sample with no added bromide as being actually bromine.

Table 2. Activation analysis of Br in purified KCl.

Added KBr g/g of KCl	counts/min. (at arbitrary standard time)	counts/min. due to added KBr
0	633	0
3.2×10^{-7}	783	150
3.2×10^{-6}	1963	1330
3.2×10^{-5}	26,020	25,387

Comparison of the added counts produced by the addition of bromide to the chloride sample show that the results are constant within ± 30%; the fluctuation must be due to varying efficiency of recovery of the active bromide in the procedure used. The bromide content of the original KCl was 7.5×10^{-7} mole Br/mole KCl, ± 30%.

A group of solutions containing purified KCl and HCl in various proportions, diluted so that the total chloride ion content was always 0.1 M, was exposed in the pile for 18 hours. The solutions were freed of dissolved air by bubbling with purified helium and were sealed up with negligible gas-phase volume. Gas and peroxide contents after exposure are shown in Table 3 and Figure 4. A regular increase of gas production with decrease in pH is evident. It was apparent that the time allowed was insufficient for the samples at the lower pH's to reach the steady state, and another series was accordingly made with an exposure time of 120 hours. In this series the total chloride ion content was varied in such a way that groups of samples were prepared in which the product of the hydrogen and chloride ion concentrations was constant. It was hoped that the steady-state level of water decomposition would depend only on this product. Results are shown in Table 4 and Figure 5. It is believed that 120 hours allowed sufficient time in all cases so that true steady-state values of the hydrogen concentration were reached. The steady-state level is seen to increase with both chloride and hydrogen ion concentrations, but not in such a simple way that the hydrogen content is always exactly the same for constant values of the ion product. A theoretical explanation of the results is being worked on, and further experiments are planned.

3. Calorimetric Determination of Energy Absorbed by Materials Placed in the Pile

The construction of the calorimeter is essentially complete and the performance of the instrument has been checked outside the pile. The aluminum

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Table 3. Decomposition in solutions of purified KCl and HCl, 0.1 M in total chloride, exposed for 18 hrs. in Clinton pile

pH	Product concns., millimoles/liter			
	CO_2	O_2	H_2	H_2O_2
7	0.035	0.176	0.843	0.395
7	0.030	0.207	0.798	0.367
6	0.094	0.117	0.504	0.380
5	0.074	0.155	0.938	0.550
4	0.116	0.668	2.32	1.19
4	0.061	0.497	1.84	0.885
3	0.048	6.13	17.2	5.40
3	0.00	5.30	16.6	6.20
2	0.170	10.03	29.6	10.60
1	0.00	14.90	21.7	0.200
1	0.00	13.60	38.0	0.037

Table 4. Decomposition in solutions of purified KCl and HCl exposed for 120 hrs. in Clinton pile

pH	Total Cl^- (M)	Product concns., millimoles/liter		
		O_2	H_2	H_2O_2
2.5	0.32	28.6	57.3	10.2
2.5	0.32	27.0	54.3	12.9
3.0	0.32	20.2	40.4	9.94
3.5	0.32	19.4	38.8	9.40
3.5	0.32	14.3	28.7	4.67
2.0[a]	0.10	38.0	81.7	—
2.0	0.10	33.7	68.2	12.5
2.5	0.10	17.4	38.7	11.6
3.0	0.10	3.80	19.9	5.00
3.0	0.10	4.64	21.6	
3.5	0.10	4.66	12.2	1.50
3.5	0.10	4.53	10.2	3.40
2.0	0.032	21.3	45.4	16.9
2.5	0.032	4.16	23.7	12.5
2.5	0.032	3.01	15.6	8.77

[a] 100 hrs. in pile

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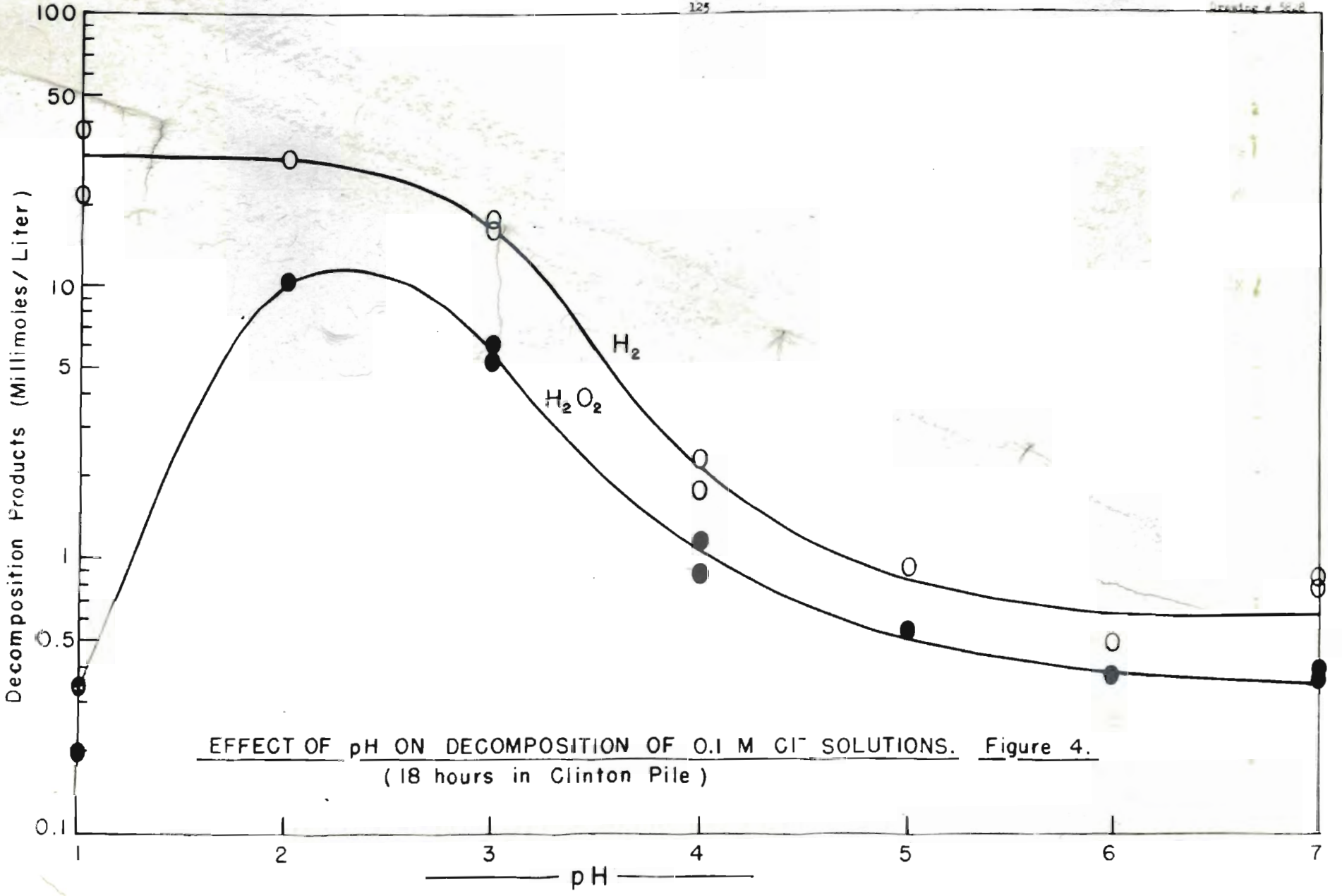
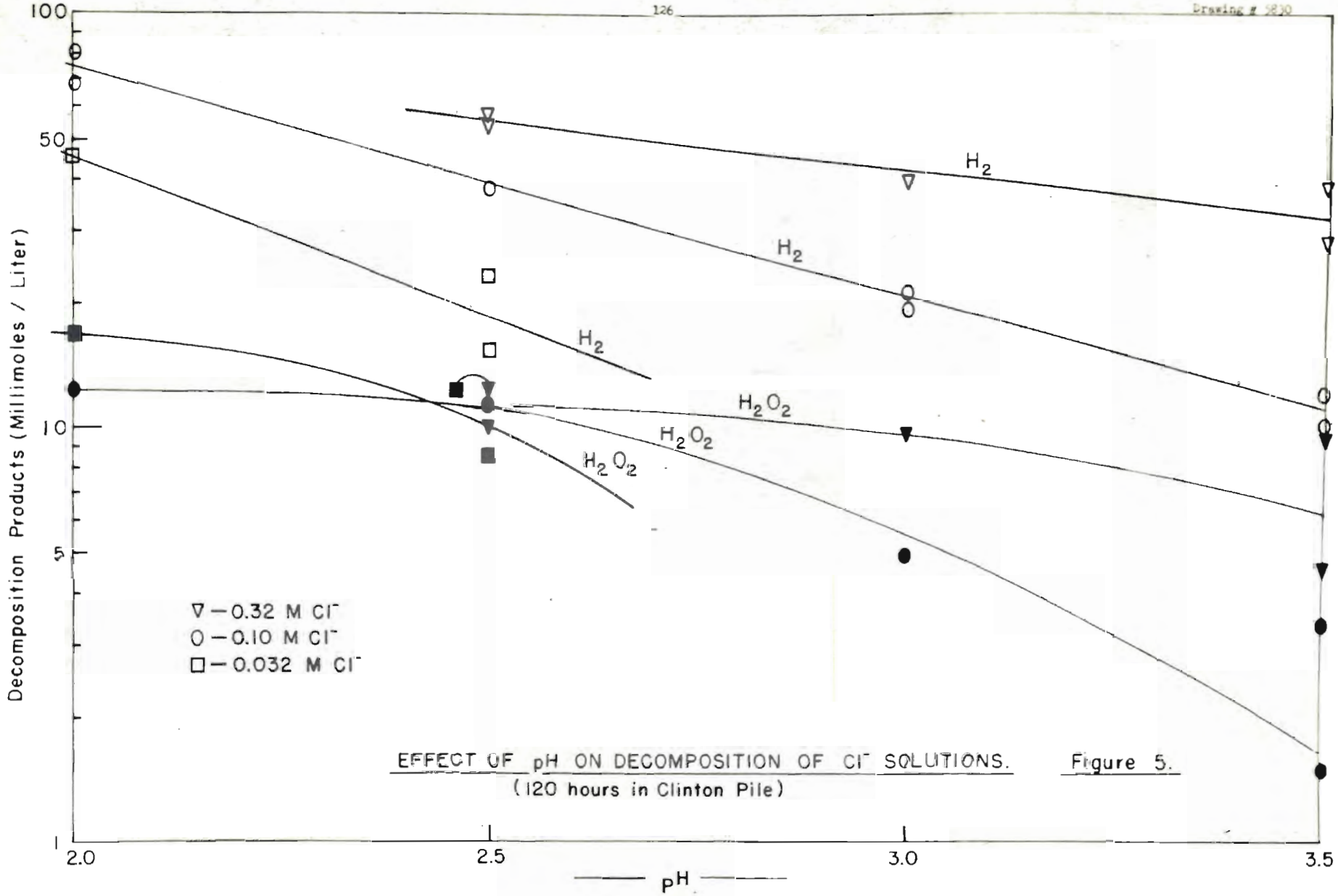


EFFECT OF pH ON DECOMPOSITION OF 0.1 M Cl^- SOLUTIONS. Figure 4.
(18 hours in Clinton Pile)

Drawing # 9830



EFFECT OF pH ON DECOMPOSITION OF Cl^- SOLUTIONS. Figure 5.
(120 hours in Clinton Pile)

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sample cans which are to contain water have to be seasoned by long exposure to water in order to prevent reaction of water with aluminum at a rate which would produce heat rapidly enough to upset the results. This seasoning is nearly finished, and the calorimeter should be placed in the pile very soon.

4. Decomposition of Water Containing Tritium

Previously, pressure drops had been found to occur when ampoules containing tritium water which had reached the steady-state pressure were placed in the pile. The object of such an experiment is to demonstrate that the steady-state level reached as a result of irradiation with slow electrons can be lowered by irradiation with gamma rays. The previous results were regarded as inconclusive because the thermal neutrons present in the pile produce an exothermic n,p reaction on the He^3 which is necessarily present in the gas phase over the tritium water. The resulting fast protons and tritons will cause recombination to water of the hydrogen and oxygen present in the gas phase and the drop in pressure might be ascribed to this reaction. The experiment has now been repeated with the ampoules shielded with cadmium to prevent the n,p reaction from occurring. As a preliminary, it was necessary to demonstrate that a major part of the n,p reaction actually would be cut out by the cadmium shield.

Some He^3 was obtained by diffusion through the walls of fused silica ampoules containing tritium water. Samples of this He were sealed up in two ampoules of identical volume and pressure. The ampoules were placed in Hole 12 of the Clinton pile at a point where the flux was known to be 3.8×10^5 thermal neutrons/sq. cm./sec./watt, and exposed for a total of 1.48×10^5 KWH pile operation. One ampoule was shielded with cadmium, the other unshielded. The ampoules were lined with palladium foils to collect all the tritium atoms which were formed in the n,p reaction. The palladium foils were later heated in a hydrogen atmosphere to give up their tritium, and the resulting gas was placed in an ionization chamber. After each reading the chamber was filled with ordinary hydrogen to the same total pressure (13 cm.) and background readings were obtained which were too small to affect the results significantly. The results are shown in detail in Table 5. It is seen that activations by the n,p reaction were reduced by a factor of 73 when the sample was shielded with cadmium. Thus this reaction possesses no important resonance for neutron energies higher than the cadmium cut-off.

A tritium water ampoule was then filled and allowed to attain a steady-state pressure. It was then placed in the pile, surrounded by water as described in a previous report, and shielded with cadmium and the pressure was seen to drop. Since there is a rise in temperature when a sample is placed in the pile, it was thought that the drop might be due solely to the temperature change. The sample was kept in a bath at 38° and the pressure was found to return to a value close to that found before it had been placed in the pile. The sample was then replaced in the pile surrounded directly by water, the temperature of which was read by a thermocouple and maintained at around 38°; the whole assembly was cadmium shielded. The pressure dropped at a rate of about 5 cm. per day, and was found to rise again after the sample was removed from the pile and replaced in the 38° bath. Figure 6 shows the entire pressure history of the ampoule. Since the rate of pressure drop of one of the samples previously exposed with no cadmium shield was only 10 cm/day (in a considerably higher total pressure of hydrogen and oxygen) it is evident that the observed

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Table 5. Amount of n,p reaction on He^3 in pile, with and without cadmium shielding

No. of atoms He^3 in each ampoule - $4.6 \times 10^{15} \pm 10\%$
Total exposure - 1.48×10^5 KWH; thermal flux 3.8×10^5 n cm^{-2} sec^{-1} $watt^{-1}$

		Ionization chamber readings (amps.)
Cd-shielded sample - 1st extraction from Pd		1.62×10^{-15}
2nd extraction from Pd		0.44×10^{-15}
	Total	2.1×10^{-15}
Background reading (hydrogen only)		1.05×10^{-16}
Unshielded sample - 1st extraction from Pd		1.39×10^{-13}
2nd extraction from Pd		0.15×10^{-13}
	Total	1.54×10^{-13}
Background reading (hydrogen only)		6.2×10^{-16}

Cd ratio = $1.54 \times 10^{-13}/2.1 \times 10^{-15} = 73$

Table 6. Decomposition in Clinton pile of 98.6% H_2SO_4 with and without dissolved UO_2SO_4

Composition of Sample	Sample No.	M.W.H.	cc O_2/g.soln.	cc H_2/g.soln.	cc SO_2/g.soln.
98.6% H_2SO_4	215	4.75	0.0002	0.0024	—
	216	16.5	0.0075	—	—
	217	62.8	0.0029	0.0102	—
	218	249.	0.011	0.026	—
	220	249.	0.020	0.072	—
	213	345.	0.022	0.054	—
98.6% H_2SO_4 5 g/L U 25/28 = 1/2950	239	244	0.125	0.045	(0.157)
	237	432	0.190	0.128	(0.148)
98.6% H_2SO_4 5 g/L U 25/28 = 1/137.97	222	64.1	—	0.044	
	224	69.3	0.148	0.045	(0.164)
	223	275.	0.522	0.155	—
	225	343.	0.606	0.252	—
	226	446.	0.744	0.328	(1.133)
98.6% H_2SO_4 5 g/L U 25/28 = 5.061/1	230	4.00	1.25	0.145	2.32
	231	7.52	2.19	0.282	4.2
	232	15.0	4.35	0.57	7.96

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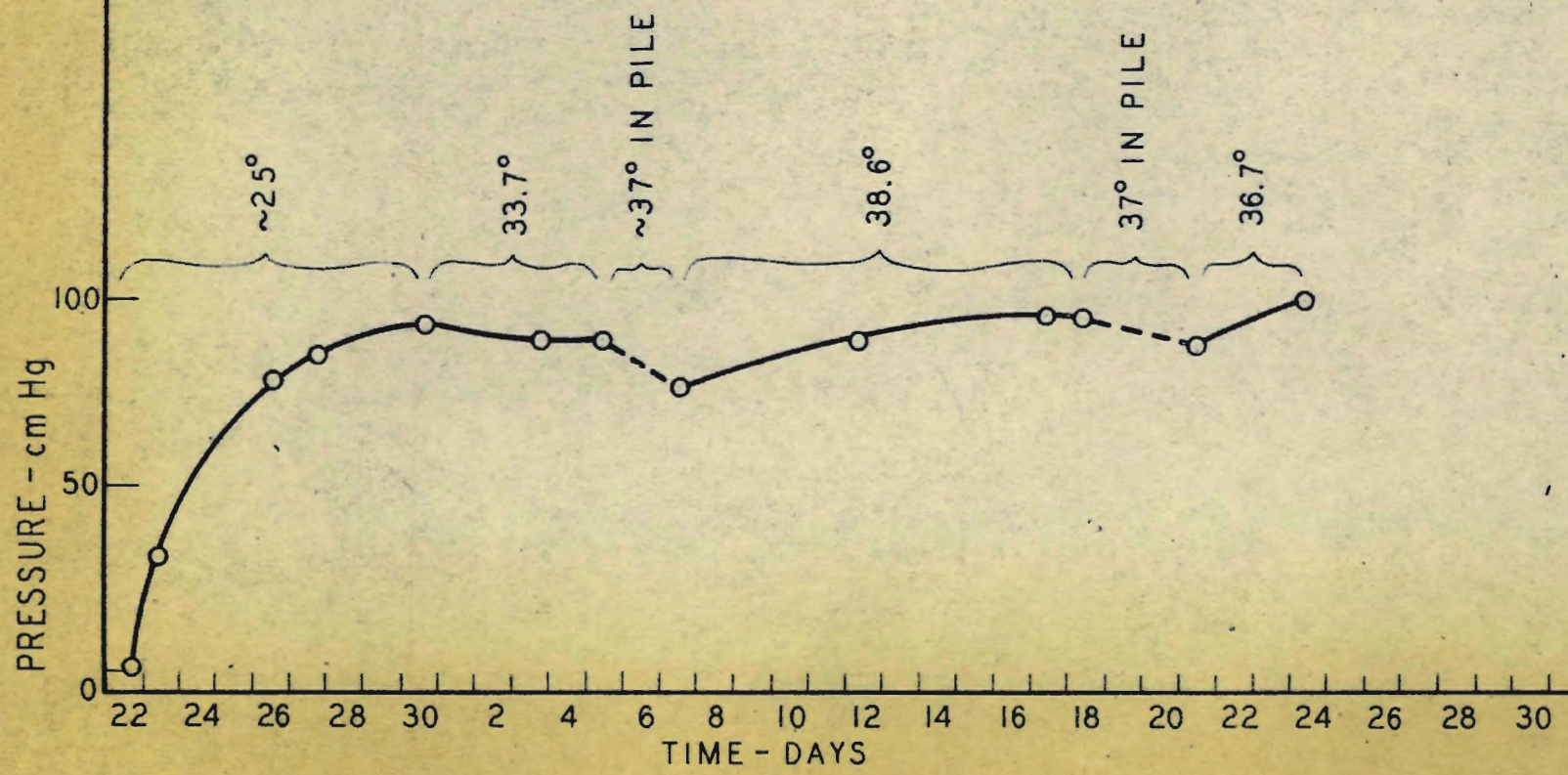
Drawing # 5799

FIG. 6
PRESSURE PRODUCED IN AMPOULE
CONTAINING TRITIUM WATER



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pressure drop here cannot be ascribed to back reaction in the gas produced by effects of thermal neutrons. This is regarded as a fairly good demonstration that fast electrons give a lower steady-state decomposition level of water than do slow electrons under the same conditions.

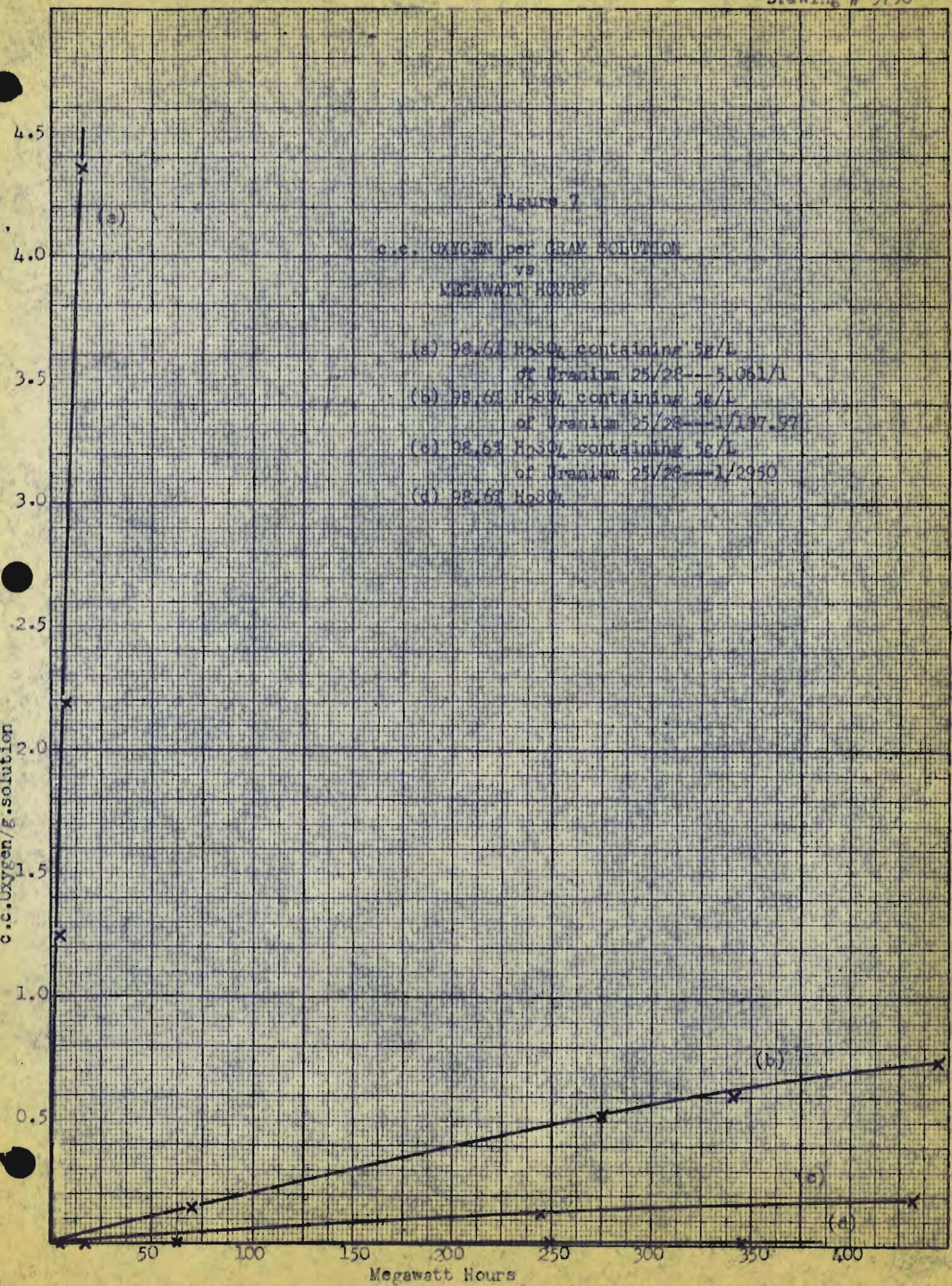
5. Decomposition in the Pile of Pure Sulfuric Acid, with and without Dissolved Uranyl Sulfate

Previous work had shown that pure sulfuric acid shows relatively little decomposition under pile radiation. It was thought that the gas evolution which is so pronounced when aqueous solutions of uranium compounds are allowed to undergo fission might be greatly reduced by dissolving the uranium in pure sulfuric acid instead of water, and that such a solution might accordingly be valuable as a medium for homogeneous reactors. In the present experiments gas produced from 98.6% sulfuric acid and from solutions of uranyl sulfate exposed in the Clinton pile has been measured and analyzed. To separate the chemical effects of the uranyl sulfate from the effects which might occur peculiar to fission recoils, uranium was used having three different isotopic compositions: normal (25/28 = 1/137.97); depleted (25/28 = 1/2950); enriched (25/28 = 5.061/1). Results are shown in Table 6.

The gases from the pure acid consisted entirely of hydrogen and oxygen. All the uranium solutions, however, gave considerable sulfur dioxide as well as hydrogen. The sulfur dioxide is difficult to collect for analysis because of its high solubility, and the values given in parentheses in the table are regarded as low. The actual amount of sulfur dioxide + hydrogen produced is thought to be chemically equivalent to the oxygen formed. The best measure of total decomposition is given by the quantity of oxygen formed, which is plotted in Figure 7 for the various solutions as a function of pile exposure. It should be noted that the amount of energy expended in the solution for a given exposure is practically the same for the pure acid and the depleted uranium, but is greater for the normal and enriched uranium samples because of the fissions occurring. The hydrogen produced is about the same for depleted uranium solution as for the pure acid, but the depleted uranium solutions show large additional amounts of sulfur dioxide and oxygen. Thus, the presence of uranium in solution sensitizes a decomposition of the acid to sulfur dioxide and oxygen, or inhibits the recombination of these gases. This purely chemical effect results in the evolution of large quantities of these gases when the energy imparted to the solution is large, as is the case with the enriched sample. In fact, the total gas production per fission in the enriched sample is greater in sulfuric acid solution than it is in aqueous solution. The hope that sulfuric acid might have some use in homogeneous reactors thus appears to be unfounded.

The curves of oxygen evolution versus exposure dose are not linear for the depleted and normal solutions, but show a decrease in the rate of oxygen evolution with increasing exposure time. This suggests that a back reaction enters in as the concentrations of dissolved oxygen and sulfur dioxide build up in the solutions. In the enriched solution, where essentially all the energy comes from fission, the rate of oxygen evolution is 0.29 cc/g. soln./megawatt-hr. From the fission energy in the normal solution one would therefore expect a yield of 0.29 x 6.061/5.061 x 1/139 = 0.0025 cc./g. soln./Mwh. The initial rate of production of oxygen in the normal solution, as obtained from the initial slope of the curve in Figure 7 was only 0.0024 cc/g. soln./Mwh. One would expect a higher rate since the depleted solution, where no fissions are occurring, evolves oxygen initially at a rate of about 0.0009 cc/g. soln./Mwh. Pile radiation seems to produce more back reaction than decomposition when fission radiation is accompanying it.

Drawing # 5798



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A Simplified Equation of State Applicable to Surface Films. (S. Ross, C. H. Secoy)

The work on a simplified equation of state applicable to surface films on solid and liquid substrates, which was briefly reported in the previous quarterly report, has been carried further forward and a complete report (ORNL-39) has been issued and is available. It does not, therefore, seem appropriate to report that portion of this quarter's work a second time.

A Comparison of Two Theories of Multilayer Adsorption (S. Ross)

During the past quarter, a new theory of multilayer adsorption has been investigated, especially to discover if it would offer any improvement on the now generally used B.E.T. theory, either as a better description of experimental observations or to provide a more secure value of specific surface areas of solids adsorbents.

The new theory, recently published by G. F. Hüttig[1], results in the following equation for an adsorption isotherm:

$$\frac{V}{Vm} = \left[\frac{C\ p/po}{1 + C\ p/po}\right]\left[1 + p/po\right]$$

To test this equation one plots the function $\frac{p}{V}(1 + p/po)$ against p and draws the best straight line through the experimental points. The slope of the line is equal to $\frac{1}{Vm}$ and the intercept on the ordinate axis is po/C Vm. It has been found that for low temperature ethane adsorption isotherms on NaCl crystals and on pulverized NaCl crystals, Equation 1 describes the experimental data far more precisely than the B.E.T. equation. Further tests of Equation 1 were made using data already in the published literature for room temperature adsorption of methanol and ethanol on SiO_2 and TiO_2, and again Equation 1 proved superior to the B.E.T. equation.

A comparison is tabulated in Table I of the constant C and the specific surface of the adsorbent, Σ, in cm^2/gm. as they are obtained by Equation I and by the B.E.T. theory. It can be seen that the values of the specific surface of the adsorbent are not very different by the two methods, but the constant C in some cases may vary by a factor of 2 or 3 when compared by each method.

The theoretical implications of these results are of considerable interest, especially because of the practical importance of gas adsorption on solids both for certain purposes on the project as well as for commercial undertakings elsewhere. These implications require more space for their discussion than can be claimed here with propriety. A full-size report is in preparation.

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(1) G. F. Huttig, Monatsh. 78, 177 (1948). Equation 1 is here expressed in a form utilizing the same constants as the B.E.T. theory, and not as published by Huttig. The proof of this form of the equation is too long for inclusion in this place.

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Table I

Comparison of Two Theories of Multilayer Adsorption

Isotherm	C Hüttig	C BET	Σ cm^2/gm Hüttig	Σ cm^2gm BET
C_2H_6 on NaCl crystals at 90°K.	70.4	58.0	2300	2260
C_2H_6 on pulverized NaCl at 90°K.	42.0	137	1020	915
CH_3OH on rock crystal SiO_2, at 298.5°K.	143	137	541	529
C_2H_5OH on rock crystal, SiO_2, at 298.5°K.	79.0	92.1	625	586
CH_3OH on glassy quartz, SiO_2 at 298.5°K.	78.0	77.1	451	449
C_2H_5OH on glassy quartz, SiO_2, at 298.5°K.	54.7	75.1	486	412
CH_3OH on rutile, TiO_2, at 298.5°K.	91.0	220	434	385
C_2H_5OH on rutile, TiO_2, at 298.5°K.	54.7	58.8	313	296

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

Silica tubing of a modified size (2 mm. bore, 4 mm. wall thickness) was received late in the quarter and nineteen tubes have been made up containing uranyl sulfate solutions varying in concentration from 5 to 60% uranyl sulfate. The temperature at which separation into two liquid phases occurs has been determined for nine of these. The results are given in Table I. The designation liquid salt refers to the liquid phase composed of uranyl sulfate saturated with water and the designation aqueous refers to the phase composed of water saturated with uranyl sulfate.

TABLE I

Percent UO_2SO_4	Temperature of Phase Separation	Separating Phase
5.86	310.1 °C.	Liquid Salt
12.30	299.9	" "
20.40	295.8	" "
31.65	295.5	Aqueous
40.72	297.5	"
48.06	302.3	"
55.45	308.2	"
58.64	312.5	"
60.87	324.9	"

The new data is shown graphically in Figure I and the temperature-composition diagram for the system, insofar as it has been determined, is shown in Figure II. The curve lmn represents the new data. The rest of the diagram has been presented previously (CNL-18; MonN-311). Concerning the application of the phase rule to this diagram, it must be remembered that the system as studied is a condensed system. That is to say, the pressure on the system is at all times greater than the vapor pressure of the solution thus preventing the existence of a vapor phase. Therefore, pressure is eliminated as a degree of freedom and for such a system the phase rule may be written $F = C - P + 1$. Since there are two components involved, this becomes $F = 3 - P$. Three phases, the maximum number possible, can exist in equilibrium only at an invariant point. There are two such points on the diagram, Point A at which the coexisting phases are ice, $UO_2SO_4 \cdot 3H_2O$, and saturated solution, and Point B at which the phases are $UO_2SO_4 \cdot 3H_2O$; $UO_2SO_4 \cdot 1H_2O$; and saturated solution. The only area in the diagram which permits two degrees of freedom is the area marked "solution". All other areas represent two phase regions in which the temperature fixes the composition of both phases. Thus at 310° and for any over-all composition between l and n the composition of the two phases is fixed at l and n respectively.

There remain two regions which require further investigation, namely, concentrations of less than 5% UO_2SO_4 above 310°, and concentrations between 60 and 74% UO_2SO_4 above 290°. Concerning the first of these, it is known that the curve lmn reaches the water axis below 374.4°, since the aqueous phase undergoes critical transformation at precisely this temperature and this is the critical

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temperature of pure water. Probably this end of the curve cannot be followed to its intersection with the water axis since phase separation will become increasingly more difficult to observe as the concentration of salt decreases.

The other end of the lmn curve may or may not intersect the solid phase solubility curve, BC. Furthermore, one or more solid phase transition points should occur at some higher temperature. At least the transition from $UO_2SO_4 \cdot 1H_2O$ to UO_2SO_4 is certain. If curve lmn and curve BC intersect, the transition may occur before or after the intersection, probably before in view of the trend of the curves. The height to which these curves may be followed will be limited by either of two factors, failure of the tubes to withstand the pressure, or decomposition of the uranyl sulfate. No evidence of decomposition of the salt has been observed so far except in four cases. In each of these four a small amount of black oxide was formed in the tube during the sealing-off process, and the amount of oxide seemed to increase during the run. It may be that UO_3 or U_3O_8 has a catalytic effect on the decomposition of uranyl sulfate. The results in these cases are not included in the data. No evidence of precipitation of hydrated oxide due to hydrolysis has been observed.

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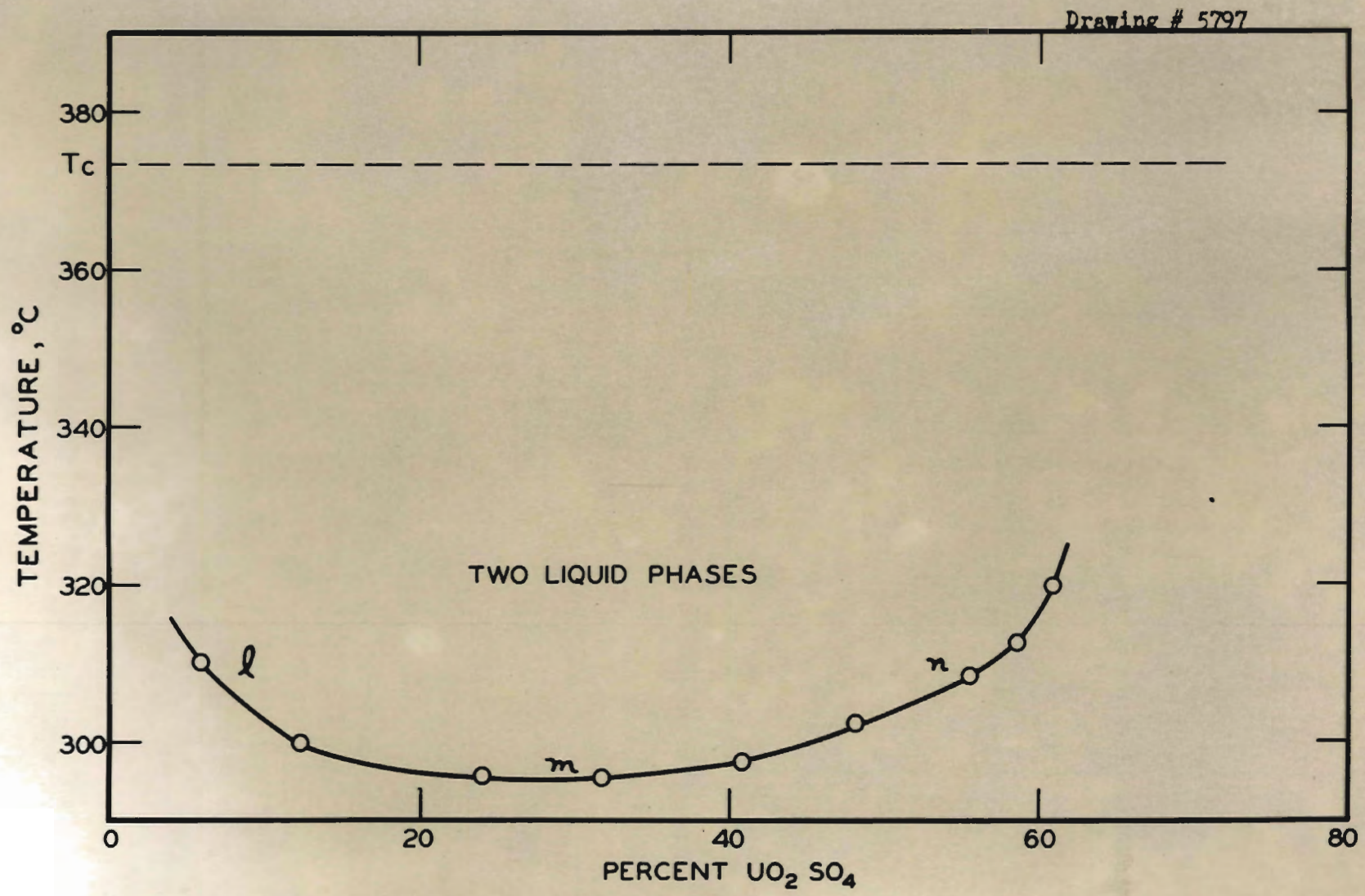

FIG. I

TWO LIQUID PHASE REGION FOR THE SYSTEM URANYL SULPHATE-WATER

Drawing # 5796

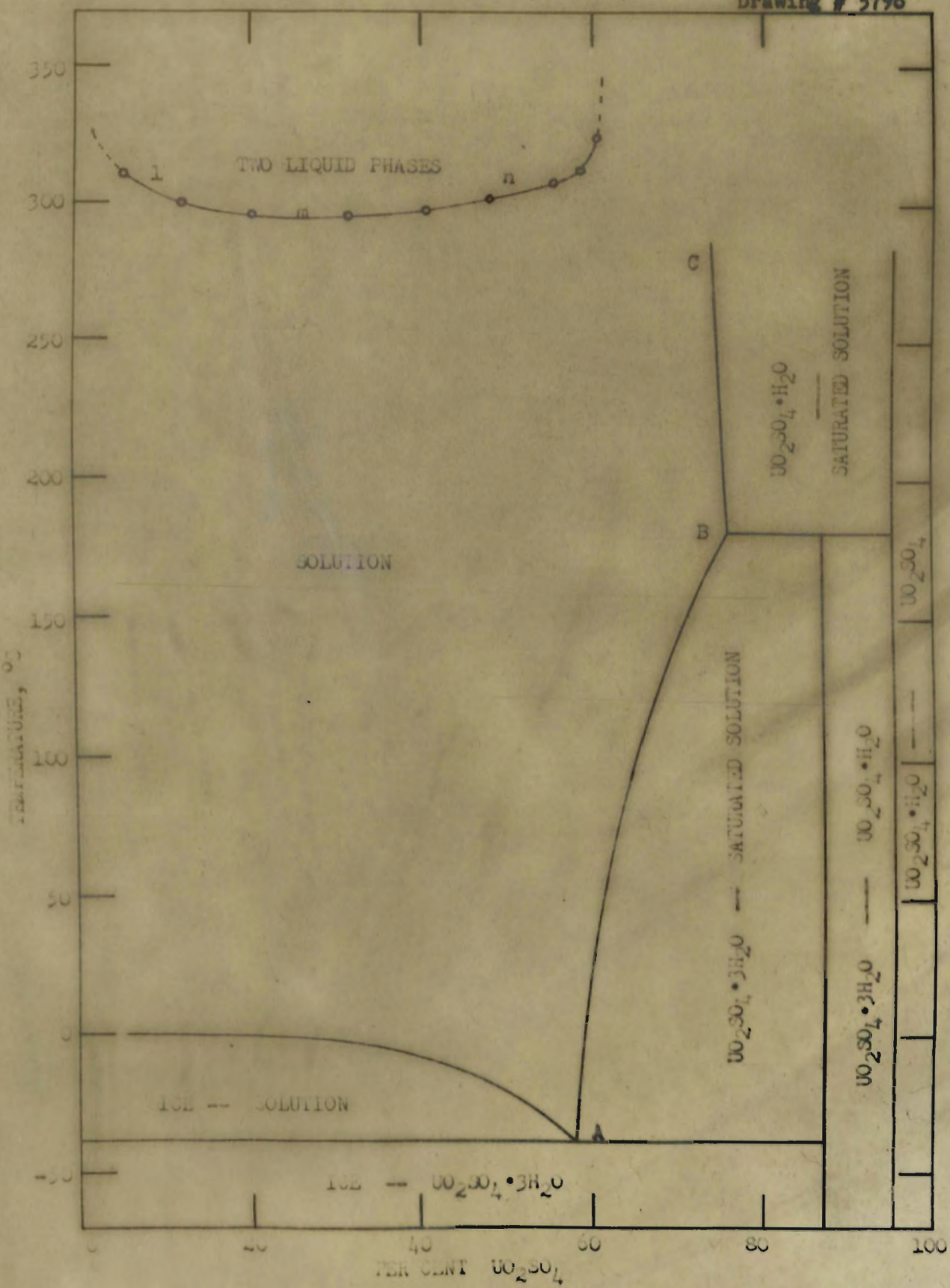

FIGURE 11. — PHASE DIAGRAM FOR THE SYSTEM URANYL SULFATE - WATER

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

In order to get more fissions per cloud chamber expansion, a larger neutron beam was needed. The graphite stringer and shield plug assembly in the pile was replaced with one having a larger hole. The chamber was refilled using 816-Cl_2 (a chloro fluoro dimethylcyclohexane) and several hundred pictures made. The number of fissions now averages well over two per picture. The beam is so intense that a substantial increase in fog background is noted. The picture quality has been poor and considerable effort was spent in trying to refine the lighting, photography and general operating conditions.

Equipment additions include an exposure counter and a new stroboscopic light. The exposure counter is in the camera field of view and gives a numbered and dated record of each picture made. The new stroboscopic light is similar to the old design with essential changes being improved electrical connections, method of mounting and reflector. A new, higher voltage, sweep field power supply is near completion.

A few tests were made to improve fog background by placing bismuth in the neutron beam to absorb some of the gamma energy. The method shows promise and will be continued after improvements in lighting and photography are complete.

In past work Eastman Super XX film processed in X-ray developer has been used. The film is very fast but poor in resolution and contrast. Some of the orthochromatic emulsions have been reported to be relatively fast when used with stroboscopic lights. For this reason test pictures were made with several different emulsions. Each film was used with f settings from 2.8 to 11 and developed in Eastman D-11. The films tried, listed in order of increasing speed, are DuPont motion picture fine grain release positive, DuPont motion picture sound recording (both orthochromatic), Eastman Plus X, Eastman shell bursting panchromatic, and Eastman Super XX. Unfortunately the full capabilities of the ortho emulsions cannot be utilized since the filters used on the strobo lights do not pass light in a moderate portion of the films sensitive region. The ortho films tried were too slow for general use. New films to be tried include Eastman linagraph ortho and pan.

In all the above work the strobo lights were beamed into the chamber in a direction normal to the neutron beam. The light has to be scattered 90° from the fog droplets to get to either camera lens. A series of pictures was made by beaming the light in along the direction the neutron beam takes. During the test, uranium alphas were photographed, and the neutron beam was sealed off. Only one light was used. The light had to scatter 70° to get to one camera lens and 110° to get to the other. The improvement in picture quality was quite remarkable. The stero halfs that involved 70° scattering showed great improvement over the old lighting method. The other half of the stero pairs involving 110° scattering showed slight improvement. The two lights will be mounted in this new position relative to the camera optics so that either lens will see light scattered off droplets through 70°. The camera optics cannot be rotated due to an overhead obstruction. Thus the lighting optics will be changed. Thin surface coated mirrors inclined at 45° will be placed in front of each chamber lighting port. The lights will mount over the neutron beam and will look down into the inclined mirrors. The neutron beam will pass through the mirrors. Upon completion of these changes the tests run on various photographic emulsions will be repeated.

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Calorimetry of Radioactivity (G. Jenks, F. H. Sweeton)

Determination of average energy of tritium decay

In previous reports (CNL-37), it has been indicated that the β-calorimeter (MonC-410) had become unreliable for determining energies of the order of 10^{-4} watts or less. The characteristics of the calorimeter have been reinvestigated using improved Dewars which were silvered and degassed following the procedure of Scott, Cook and Brickwedde, (Bur. Standards J. Research 7, 935-43 (1931)). The reproducibility of the calorimeter using these Dewars was found to be ± 1.5% at energies of the order of 3.6×10^{-5} watts, a precision which was satisfactory.

Using the calorimeter in this form, the rate of heat production of a sample of tritium water has been measured. In the following table the data obtained with the tritium sample are shown together with the calibration data.

Set #1

Date	Calibration: Heat input watts	Calibration: Rate (Arbitrary Units)	T_2O sample Rate (Arbitrary Units)
April 14	19.67×10^{-5}	1.038	
April 14	3.600×10^{-5}	0.212	
April 15	3.607×10^{-5}	0.207	
April 16			0.208
April 26			0.208
April 27	3.611×10^{-5}	0.214	
April 28			0.205
April 30			0.204

Average rate 0.211 ± .003 at 3.60×10^{-5} watts

Av. rate for sample 0.206 ± .002 equivalent to 3.52×10^{-5} watts ± 1.5%

Set #2

May 5	3.592×10^{-5}	0.196	
May 6	3.586×10^{-5}	0.195	
May 7			0.190

3.51×10^{-5} watts

Discussion

The first set of data tabulated above were taken with the liquid nitrogen in the intermediate Dewar at a fixed level. It was felt that the reproducibility could be improved somewhat by raising that level and the second set were obtained under the altered operating conditions. The estimated error is the total spread of the data.

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The disintegration rate of the above sample of tritium had been determined by J. Ghormley to be 4.05×10^{10} dis./sec., five months prior to the energy measurements. His method, which was described briefly in the quarterly report, Mon-432, P. 112, made use of the fairly rapid diffusion rate of helium through quartz. The sample was first allowed to stand at constant temperature until the equilibrium pressure of the tritium decay product, He^3, had been built up within the ampoule. Then the rate at which He^3 appeared in a soft glass container in which the ampoule was sealed was measured at intervals over a period of several weeks to assure that the rate was constant. Results consistent to better than 1% were obtained by this method. Mr. Ghormley estimates his error to be ± 1%.

Correcting for the decay of the sample using a half-life of 12 years determined by Novick (Phys. Rev. 72, 972 (1947), the disintegration rate at the time of the calorimetric measurement was 3.95×10^{10} dis./sec. The average energy per disintegration is then

$$\frac{3.52 \times 10^{-5}}{3.95 \times 10^{10} \times 1.589 \times 10^{-13}} = 5.58 \pm .17 \text{ KV}$$

The estimated overall error for the average energy is ± 3%.

It is possible that the above value is further in error due to the storage of energy in the ice making up the calorimeter sample. However, it was expected that if energy were stored in the ice, it would reach a saturation value rather quickly. The runs were usually started approximately three hours after the sample was frozen, and no trend in the rate during the five hour runs was observed. We intend to further investigate the possibility with the higher activity sample now being analyzed with the gas density balance.

Preparation of a Quantitative Sample of Tritium for Calorimetric Use

The gas density balance to be used to determine the isotope ratio of a tritium-hydrogen mixture is ready for use. The tungsten points used in place of a knife edge are now sealed directly to the balance through graded seals, eliminating the cement previously used. The balance bulb has been replaced because the original one contained condensable moisture which could affect the balance reproducibility. Electrostatic effects which made the balance very erratic at first have been eliminated for all practical purpose by using shields and sources of ionizing radiation. The sensitivity of the balance has been increased so that a change of hydrogen pressure of 1.0 mm of Hg results in a balance deflection of 0.3 mm. The reproducibility of the balance is about 0.35% which is equivalent to a precision of 0.7% in determining the amount of tritium in a 50-50 mixture of hydrogen and tritium.

Work has continued on the glass system to be used to control the tritium mixture. A Pirani gauge has been installed. Cold traps have been added to keep mercury vapor out of the balance case and out of the palladium-filled ampoule in which the sample will be absorbed for later use in the β-calorimeter. The volumes of the essential parts of the system have been determined. Several valves that have developed a tendency to leak have been replaced.

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Analytical Chemistry

Electroseparation of Radiosilver from Palladium (J. C. Griess, L. B. Rogers)

This study has just been completed, and the results are being submitted for publication as a project report. In brief, neutron-bombarded palladium is used as the source of Ag^{111} of high specific activity. The silver is deposited from a cyanide solution without prior addition of dead silver or another carrier element.

Preparation of Silver-Free Palladium Metal (D. P. Krause)

For studies dealing with the electrodeposition behavior of traces of silver, it was necessary either to know the amount of silver present in the palladium before neutron-bombardment or to reduce it to a negligibly small (but unknown) amount. Although Cyrus Feldman of the spectrographic laboratory was able to detect silver in the palladium, attempts to prepare standards for quantitative analysis were unsuccessful. In that connection, a brief examination was made of the possibility of preparing standards by electrolytic codeposition of silver and palladium on graphite and aluminum electrodes. Because the results were poor, the idea was abandoned in favor of reducing the silver content to a negligible value.

Palladium metal was purified in 50 mg. lots by the following procedure: After dissolution of the metal in a nitric-sulfuric acid mixture, the solution was made 1.0 M. in sodium hydroxide and 0.1 M. in cyanide. An electrolysis for 15 hours then removed 90% or more of the silver. (See preceding section by Griess.) Acidification with sulfuric acid followed by warming of the remaining solution precipitated palladium cyanide which was washed with triply-distilled water before being dissolved in hot fuming sulfuric acid.

The final step consisted of precipitation of palladium metal by means of formaldehyde added after the solution had been cooled and diluted with triply-distilled water. The resulting metal was spectrographically-free (less than about 5 ppm.) from silver. Substitution of single and double precipitations by alpha furildioxime (1) for the formaldehyde step did not always succeed in removing all of the silver so it was abandoned.

Studies of the Electrodeposition of Traces of Silver (D. P. Krause, L. B. Rogers)

Using palladium which had been purified by the above method, it was possible to prepare Ag^{111} of high specific activity using the method outlined by Griess in an earlier section of the present report. The silver activity could be dissolved in a solution of any composition by imposing a potential of +1.5 V. on the electrode. In this way 150 - 400 c/m/100 λ of Ag^{111} were added to 0.1 M. potassium nitrate solutions of pH 4.00 prepared with triply-distilled water.

Portions of such stock solution were used in determining the percentage of silver deposited on a platinum cathode at various potentials (2). It was necessary to use wax-coated (ceresine) glass to minimize sorption in all of these

(1) Reed, S. A., Private communication.
(2) Ehrlinger, D. B., and Rogers, L. B., in MonN-311, p. 197, MonN-370, p. 163.

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experiments so that a sum of the activity on the cathode and that remaining in solution represented 90% or more of the original activity.

The results of Ehrlinger (2) which indicated a shift of the deposition curve to more positive potentials were duplicated. For example, "tracer" silver was almost completely plated out at a potential nearly 0.2 V. more positive than the analogous potential for a 10^{-3} M. solution. The curves for different batches of tracer were constant within ± 0.025 V., and a ten-fold dilution of the tracer produced a curve falling in the same region of potential. These experiments indicate that the simple form of the Nernst-type equation cannot be used to describe the behavior of tracer silver. Because tests have shown that the Nernst equation does hold at concentrations close to 10^{-6} M., experiments are now in progress to determine the concentration at which marked deviations appear.

Polarography with Solid Electrodes (H. H. Miller, L. B. Rogers)

It has been shown that a small stationary platinum electrode will give a reproducible polarographic wave using automatic recording (1)(2). A rotating electrode has also been used in the same way by several investigators. The experiments described below as well as others to be carried out in the future were designed to compare the results obtained by both methods.

The rotating electrode was essentially that described by Laitinen and Kolthoff (3). A 25 gauge platinum wire was held in a brass shaft with a set screw. After the lower portion of the shaft had been coated several times with ceresine wax, 1 mm. at the tip of the platinum was scraped with a razor blade to expose the metal. The electrode was rotated by a synchronous motor at 600 r.p.m.

Silver ion was studied in a 0.1 M. potassium nitrate solution containing 0.01% gelatine and nitric acid to give a pH of 4.0. The solutions were deaerated with nitrogen before use (1). Potentials were measured against a saturated calomel electrode.

In general, the results were similar to those found for cadmium (2). However, using a 5.0×10^{-4} M. solution of silver, a slight variation in the deposition potential resulted from a change in rate of polarization.

Table I.

Deposition Potentials for 5.0×10^{-4} M. Silver

Rate of Polar. mv/sec.	Deposition potential vs. S.C.E.
1.55	+0.32
	0.31
3.10	+0.29
	0.29
	0.28
4.65	+0.29
	0.29

(1) Rogers, L. B., et al., MonC-236, November 1947.
(2) Skobets, E. M., and Kacherova, S.A., Zavodskaya Lab., 13, 133 (1947).
(3) Kolthoff, I. M., and Lingane, J. J., "Polarography" Interscience Publishers Inc., New York, 1941.

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However, these variations border on the limit of error with which the deposition potential can be determined.

These tests produced another startling and more clear-cut result: Namely, the appearance of maxima in the curves obtained with the two faster rates of polarization. The fact that a distinct inflection occurred near the top of the silver wave before the maximum began indicates that the maximum is probably the result of a second reaction, possibly the evolution of hydrogen or the reduction of oxygen. The characteristic hydrogen wave did not appear until several tenths of a volt later.

A test was made of the Nernst equation which predicts that the halfwave potential should shift by -0.06 V. for a ten-fold dilution. Assuming that the values for a 5.0×10^{-4} M. solution are correct, the equation holds quite well.

Table II.

Shift in Halfwave Potential with Dilution

Silver Molarity	$E_{1/2}$ vs. S.C.E. Experimental	Calculated
5.0×10^{-4}	+0.31 +0.31	+0.31
5.0×10^{-5}	+0.24 +0.25	+0.25
5.0×10^{-6}	+0.17 +0.16	+0.19

The discrepancy in the 5.0×10^{-6} M solution may result from the fact that the reduction wave is only slightly larger than the residual current.

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Polarographic Analysis of Radioactive Cobalt Solutions (P. F. Thomason)

The radioactive isotope production group has required an ionic analysis of their products in order to calculate specific activities. As these products are necessarily quite radioactive and also limited in quantity, methods are required that are capable of giving accurate results with microliter volumes of solutions. Polarographic and colorimetric methods have been used successfully for this purpose.

Lingane and Laitenin (1) found a well-defined wave of cobaltous cobalt in a supporting electrolyte of pyridine and pyridinium chloride with 0.01% gelatin as a maximim suppressor. Ten microliters of a cobalt solution measuring 750 mr/ml were diluted to 10 ml. with 0.1 M. pyridine containing 0.1 M. pyridinium chloride and 0.01% gelatin. This solution was analyzed with a Heyrovsky Model XII Polarograph using a dropping mercury electrode (2). The height of the curve was measured and the concentration of the cobalt was found from a calibration curve Figure 1 made with standard cobalt solutions electrolyzed under the same conditions.

The cobalt half-wave potential is -1.07 volts versus the saturated calomel electrode and is followed by a wave for pyridinium chloride at -1.37 volts. However, the cobalt wave is well-defined and can be easily measured.

The concentration of the radioactive cobalt solutions have varied from 0.04 M. to 0.60 M.

Determination of Tantalum with Alizarin (W. H. Davenport, P. F. Thomason)

The radioisotope product of tantalum in a solution of 4% potassium hydroxide has been analyzed colorimetrically with sodium alizarin monosulfonate (3). The following procedure has been found adequate:

An aliquot containing 100 - 600 micrograms of the basic tantalum solution is pipetted into a 25 ml. volumetric flask. It is diluted to 10 ml. with distilled water and 1 ml. of a 0.2% sodium alizarin sulfonate solution is added. The solution is allowed to stand a hour. Concentrated hydrochloric acid is added dropwise until the purple basic color is completely dispelled and 5 drops of acid is added in excess. The solution is allowed to stand for 15 minutes, then diluted to the mark, and mixed thoroughly. The lake is read versus a reagent blank at a wave length of 320 mμ in a Beckman spectrophotometer using 1 cm. path length cells. The concentration of the tantalum is obtained from a calibration curve, Figure 2, made with a standard tantalum solution.

Interference from other cations known to form lakes with alizarin was not checked as a spectrographic analysis of the tantalum oxide bombarding material showed it to be exceptionally free of impurities.

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

Radioactive ruthenium solutions have been analyzed colorimetrically with thiourea as recommended by Sandell (4). Ruthenium in a 4 N. hydrochloric acid solution gives an intense blue color when heated with thiourea. The spectral

(1) Lingane, J. J., and Kerlinger, H. Ind. Eng. Chem., Anal. Ed., 13, 77 (1941).
(2) Lingane, J. J., Laitinen, H. A., Ind. Eng. Chem., Anal. Ed., 11, 504 (1939).
(3) Yoe, J. H., and Sarver, L. A., Organic Analytical Reagents, John Wiley and Sons, Inc., New York (1941) p. 210.
(4) Sandell, E. B., Colorimetric Determination of Traces of Metals, Interscience Publishers, Inc., New York, N. Y. (1944) p. 388.

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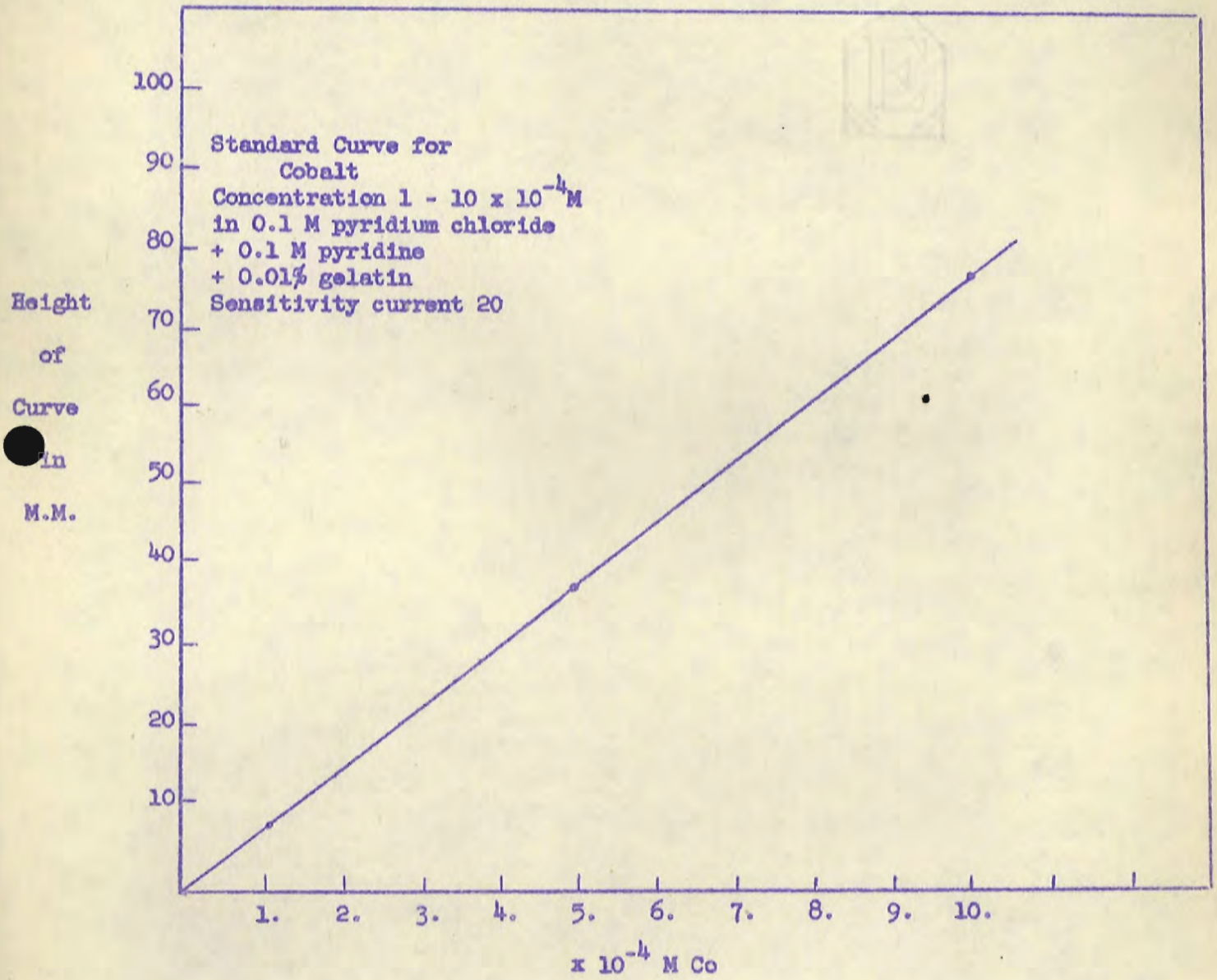

Figure 1.

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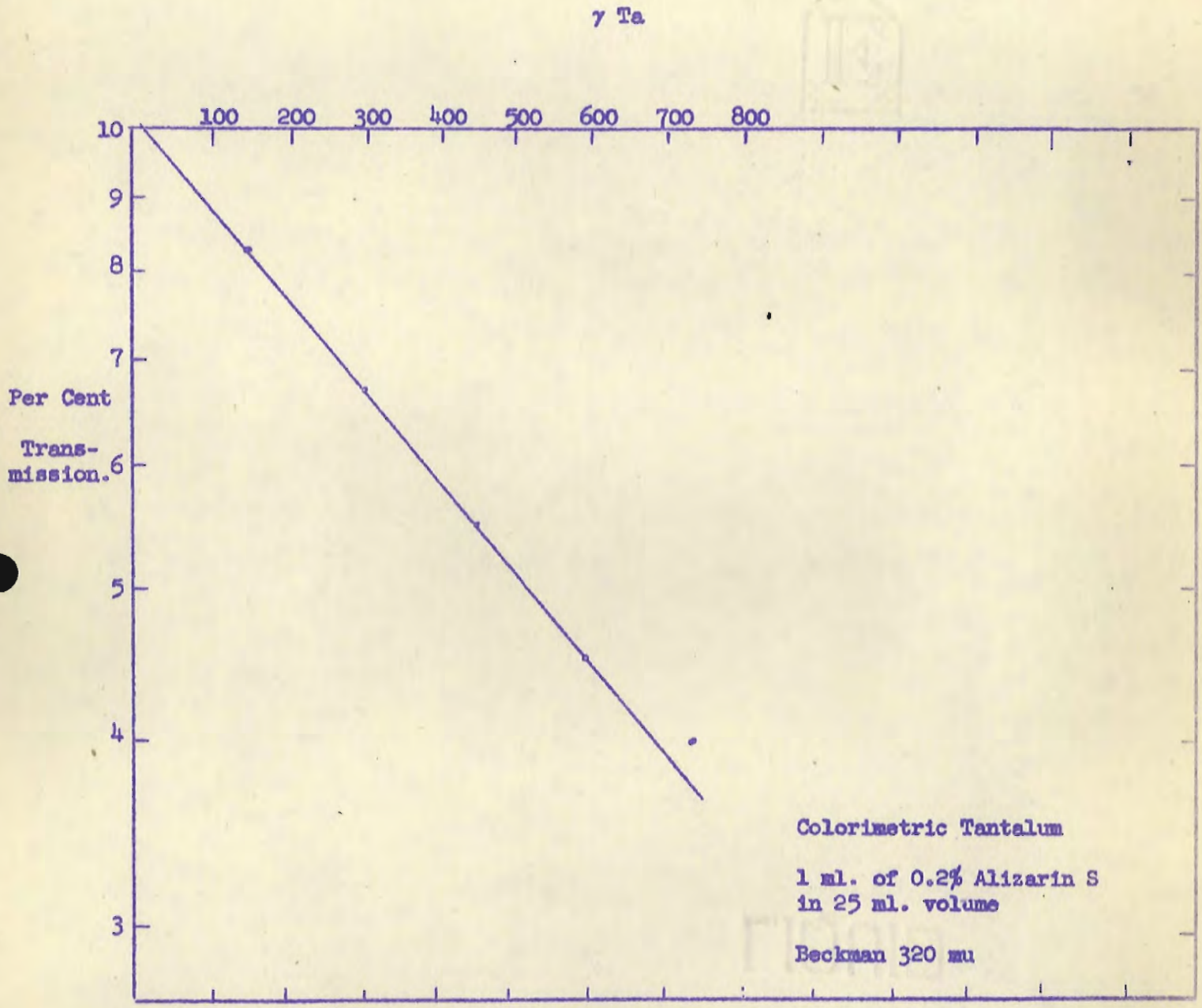

Figure 2.

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transmission curve of this solution shows a maximum absorption at 635 mμ wavelength. Five to twenty-five micrograms of ruthenium in 4 N. HCl are heated in a water bath with 1 ml. of 5% aqueous thiourea solution for 10 minutes, cooled to room temperature, and diluted to 10 ml. volume with distilled water. The transmittancy of this solution is determined in a Coleman spectrophotometer at 635 mμ. The concentration of ruthenium is obtained from a standard calibration curve.

A standard ruthenium solution was made by dissolving the mixed chlorides in distilled water to obtain approximately 20 mg/ml of ruthenium. Five ml. aliquots of this solution diluted to 100 ml. with 4% HCl were analyzed gravimetrically by reducing the ruthenium to the metal with powdered magnesium and weighing. Dilutions of this standardized solution were used to obtain a calibration curve.

Dissolving Gold and Silver Alloys by Electrolysis (F. J. Miller, P. F. Thomason)

An analytical method will be required for the determination of gold and silver in an alloy to be used for migration studies by the metallurgy group. Attempts to dissolve a synthetic alloy containing 50% Au and 50% Ag with aqua regia failed due to the formation of a coating of Ag Cl on the surface of the metal protecting it from further action of the acid. Parting the metals with nitric acid requires at least 75% silver for the complete solution of silver.

It has been known for a long time that gold and silver are soluble in dilute potassium cyanide and has been made the basis for their extraction from ores (1).

It was found a rapid dissolution of the alloy could be accomplished by electrolyzing the metal in 5% potassium cyanide solution using carbon electrodes. Air is passed through the solution during the electrolysis for thorough stirring and according to Elsner (2) aids in the dissolution of the gold in accordance with the equation:

$$4\ Au + 8KCN + O_2 + 2H_2O \rightarrow 4K\ Au(CN)_2 + 4\ KOH$$

Standard analytical methods for gold and silver can be used after the alloy is in solution.

Conductometric Titration of Aluminum with Sodium Fluoride (F. J. Miller, P. F. Thomason)

Colorimetric aluminum methods are subject to many interferences and have not been completely satisfactory for the "25" recovery process analytical group. The rapid volumetric method (3) has not given the accuracy desired. Therefore, it was considered worthwhile to investigate the possibility of using the reverse of the Harms and Jander conductometric method (4) for the determination of the fluoride ion with aluminum chloride.

Preliminary work has indicated it is possible to titrate conductometrically 200 micrograms of aluminum with a standard sodium fluoride solution using an Industrial Model RC conductivity bridge with 6 mm^2 platinum electrodes in a 15 ml. titration cell.

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(1) Roe, J. H., U. S. Pat. No. 61866, (1867).
(2) Elsner, L., Journ. prakt. chem., (1), 37, 441 (1846).
(3) Snyder, L. J., Ind. and Eng. Chem. Anal. Ed., 17, 37 (1945).
(4) Harms, J., and Jander, G., Z. Electrochem., 42, 315 (1936).

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The effect of temperature, time, and solubility of the sodium, aluminum fluoride complex will be studied. Also the interference of other cations in the process solutions will have to be known.

Determination of 2-Hexylpyridine in Hexone (P. F. Thomason)

2-Hexylpyridine is one of the complexing agents for decontamination of uranium tested by the "25" recovery development group (1). It was necessary to know the concentration of this reagent in the hexone following the extraction process. A direct titration with a standard acid was not feasible as the hexone had adsorbed acid from the aqueous feed solution. A colorimetric procedure as recommended by Feigl (2) for tertiary ring bases did not prove satisfactory for the determination of 2-hexylpyridine.

By steam distilling the hexone samples, made alkaline with sodium hydroxide, it was possible to determine as low as 0.1% 2-hexylpyridine in hexone. The distillate was made homogeneous with methyl alcohol and titrated to a methyl orange end-point with a standard acid. This method proved to be adequate for most purposes.

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

The usual procedure in this laboratory for determining nitrogen in nitrates is by the Devarda method (3). However, while this method is accurate, it is also time-consuming and requires trained personnel. As the production analytical group needed a fast control method for the fission iodine production, several colorimetric methods were studied.

The intense color produced by the reaction of brucine with nitrates in the presence of sulfuric acid (4) seemed to be quite stable and suitable for a control method. The phenoldisulfonic acid method (5) while sensitive is subject to many interferences. The reagent 2-naphthol-6,8-disulfonic acid (6) was also tested and gave a very sensitive reaction but was not superior to the simple brucine procedure.

Nitrites are also determined with brucine by oxidizing to nitrates with potassium permanganate. The color development is carried out in a 50 ml. volumetric flask with 2 - 10 micrograms of nitrate nitrogen and 0.2 ml. of 5% solution of brucine in chloroform in the presence of 35 ml. of concentrated sulfuric acid. The solution is diluted to volume and allowed to stand until the orange, red color changes to a stable sulfur yellow. The solution is read in a Coleman spectrophotometer at 380 mμ wave length any time within eight hours and the nitrate concentration is obtained from a standard calibration curve.

Volumetric Determination of Uranium in Alloys Using Ferric Sulfate as the Titrant (E. K. Hanig, P. F. Thomason)

Uranium in aluminum alloys submitted by Engineering Materials, Technical Division, Section IV has been determined by a ceric sulfate volumetric procedure which requires a time-consuming mercury cathode step to remove iron interference. As the number of samples increased a faster method was desired.

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(1) Monthly report, Technical Division Dection I, April 20, 1948.
(2) F. Feigl, Qualitative Analysis by Spot Tests, Elsevier Publishing Co., New York (1946).
(3) A. Devarda, Chem. Ztg. 16, 1952 (1892).
(4) Haase, L.W., Chem. Ztg. 50, 372 (1926).
(5) Chamot, E.M., and Pratt, D. S., J. Am. Chem. Soc. 31, 922-8 (1909).
(6) Nixon, I. G., Chem. News, 126, 261-2 (1923).

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The potentiometric titration of reduced uranium with ferric sulfate (1) offers a method that can be used directly after dissolving the alloy in hydrochloric acid. A great saving in time is also obtained by dissolving in hydrochloric acid instead of sulfuric acid as previously required.

The dissolved alloy in 7.5% acid solution is run through a Jones reductor together with approximately 100 mg. of chromium sulfate. The chromium aids in the titration by increasing the inflection of the first equivalence point to 100 - 150 millivolts. This inflection is taken as the point where the uranium +3 has been oxidized to the +4 state. The titration is continued until the second inflection of 40 - 60 millivolts is obtained which indicates the uranium has been oxidized to the +6 state. The volume of standard ferric sulfate consumed between the two inflection points is the amount required to oxidize the uranium present. The titration is carried out at 90° - 95° C. using a Leeds Northrup galvanometer to measure the potential between platinum and calomel electrodes. The platinum electrode is made of 3 or 4 coils 1" in diameter of No. 24 platinum wire and should be flamed periodically and kept in cleaning solution when not in use.

A number of alloys were run by both methods for comparison. The following results were obtained:

Alloy No.	% Uranium By Ceric Sulfate Mtd.	% Uranium By Ferric Sulfate Mtd.	Relative per cent Difference of Ferric Sulfate Mtd.
287A	14.82	14.94	+0.8%
288A	17.83	17.77	-0.3%
288B	17.83	17.88	+0.3%
288C	17.85	17.91	+0.3%
2	39.75	39.82	+0.2%

The ferric sulfate method seems to be satisfactory as the desired accuracy and precision is 0.5%. The accuracy of the ceric sulfate method has been checked by Bureau of Standards MS-T U_3O_8. The ferric sulfate method will also be checked against this standard and also synthetic alloys.

Remote Control Apparatus (H. L. Hemphill, F. F. Thomason)

(a) Measurement of Microliter Volumes of Salt Solutions with an Electronic Capacity Relay.

The measurement of microliter volumes of highly radioactive solutions for analytical purposes is a difficult problem. A number of pipettors have been made that are capable of close control of the solution in the micro pipette, however, the problem of visibility has increased with the distance at which one is forced to work. Periscopes and other visual aids to determine the height of the liquid

(1) Nessle, G. J., Grimes, W. R., Potentiometric Titration of Uranium with Ferric Sulfate, C-4.381.10, August 22, 1946.

[redacted]

in the pipette have been only partially successful. It was suggested by M. T. Kelley that possibly an electronic capacity relay might be used as an indicator for the height of the liquid column. This device would permit the measurement of salt solutions behind barricades with zero visibility as a milliammeter indicating the height of the solution could be placed at any distance from the pipettor.

Miss Martha Smith and Mr. M. Oppegaard of the Instrument Department designed and built a capacity relay (1) in two units. The detection unit, consisting of an oscillator in which the amptitude of oscillation is markedly changed by very small changes of capacity, was installed on the base of a remote control pipettor. The indicating unit which includes the milliammeter was connected to the detection unit by a long cable that permits any convenient placement.

Micro pipettes are painted with parallel stripes of silver conducting paint which are connected to the detection unit. When a salt solution is drawn up into this pipette the capacity between the striped electrodes is changed in proportion to the amount of solution. This capacity change is indicated by the milliammeter thus allowing the operator to determine the height of the liquid column without actually seeing the pipette.

Preliminary tests with this device have been very satisfactory and should find many useful applications.

(b) Improved Hand Micro Pipette Control.

The mortality rate of the glass syringe type micro pipette control has been extremely high due to breakage and failure of the pipette socket. A simple hand control (drawing No. 277346) has been made with a 12" stainless steel tubing connected to a pistol grip lucite handle. A small piston in the handle operated by the thumb controls the liquid level in the pipette. This control is positive in action and permits safer sampling of radioactive solutions than with the conventional glass syringe.

(c) Simplified Remote Pipette Control.

This pipette control (drawing no. CD-256) is an adaptation of the regular pantagraph sampler. It has fewer working parts and is easier and more economical to make as the precise machining of the original pantagraph has been reduced. All of the desirable qualities of the original have been retained in this control.

[redacted]

The Decay Scheme of Columbium ^{95} (W. S. Lyon, J. E. Hudgens)

Summary

The thin lens beta ray spectrometer described by Peacock (1) and by Deutsch et al (2) has been used to study the radiation and mode of decay of columbium^{95}. These results indicate that the 35 day columbium^{95} isotope decays by the emission of beta particles, photons and conversion electrons. The beta spectrum has a maximum energy of 0.145 ± 0.01 mev. A partially converted gamma ray was observed at 0.755 ± .02 mev. This isotope has an isomer which decays by the emission of an almost completely converted 0.217 ± 0.02 mev. gamma ray. Preliminary results indicate that the half-life of this isomer is 84 hours.

Introduction

Nedzel (3) in 1944 assigned to the 35 day columbium 95 isotope a beta spectrum having a maximum energy at 0.154 mev. and a 0.77 mev. gamma ray. This author also observed a conversion electron of 0.224 mev. energy and was uncertain of its origin. A 180° spectrometer was used in obtaining these values. Wilkinson and Rall (4) reported a value of 0.75 mev. for the 35 day columbium gamma ray. Levinger (4) investigated the 0.2 mev. conversion line of columbium and concluded that it arose from a short lived columbium isomer which decays by the emission of a 0.24 mev. totally converted gamma ray to the 35 day columbium isotope.

Experimental

A sample containing one millicurie of 35 day and the 84 hour columbium^{95} activities and a trace of 65 day zirconium^{95} activity was purified by adjusting the hydrochloric acid concentration to approximately 10 M. and equilibrating this solution with four successive aliquots of a 0.5 M. TTA benzene solution. Columbium was then precipitated as columbium oxide by adding 0.5 milligrams of columbium carrier and heating in the presence of nitric acid. This precipitate was washed thoroughly with distilled water and transferred to a Formvar polystyrene film (~50 micrograms per sq. cm.). After the precipitate was completely dried the film was mounted as the source in the thin lens beta ray spectrometer.

The counts per minute observed at each momentum interval for the beta spectrum versus the coil current in amperes is plotted in Figure 1. These data were corrected for absorption in the window of the Geiger-Muller thin window counting tube (2.2 milligrams per cm.^{2}) using the range values given by Glendenin (6) for each energy. The dotted line shown in this figure was obtained by extrapolating the kurie plot (Figure 2) back to low values of E and re-calculating the $\frac{N}{I}$ vs. I curve from this line.

In the data shown in Figure 3, the K photo electron peak which occurs at 6.34 amperes originates from the conversion of the 0.755 mev. gamma ray of the 35 day isomer and the peak which occurs at 2.65 amperes arises from the almost complete conversion of the 0.217 mev. gamma ray of the 84 hour columbium isomer.

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(1) Peacock, W. C., MonN-311, p. 94 (1947).
(2) Deutsch, M., Elliott, L. G., and Evans, R. D., Rev. Sci. Inst. 15, 179 (1944).
(3) Nedzel, V.A., CC-2283, Oct. 1944, CD-1954, July 1944 PPR Vol. 9B 7.15.7 (1946).
(4) Wilkinson, R. G., and Rall, W., CP-2590 Feb. 1945.
(5) Levinger, J. S., CC-2775, March 1945. PPR Vol. 9B, 7.15.11 (1946).
(6) Glendenin, L. E., Nucleonics 1, 12 (1948).

[redacted]

[redacted]

The same preparation used in obtaining the data in Figure 1 was used for the determination of the conversion electron lines.

The gamma ray energies and an estimation of the completeness of the conversion of the gamma rays of the 84 hour isomer were obtained by observing the photo electrons which are formed by the interaction of the gamma rays with a uranium and a lead radiator. A preparation containing approximately 80 millicuries of columbium beta activity was purified as described above and used as the source in the spectrometer. A uranium foil was used as a radiator and the sample was contained in a holder of sufficient thickness to completely absorb the beta rays and the conversion electrons. The data obtained using this arrangement are shown in Figure 4 where the counts per minute per unit momentum versus the coil current in amperes is plotted. The solid line in this figure was obtained by subtracting the compton electron background from the total curve.

The half-life of the 84 hour columbium^{95} isomer was determined by integrating under several $\frac{N}{I}$ vs. I curves of the 0.217 mev. conversion electrons obtained at different times and plotting these values. A more refined experiment designed to more accurately establish the half-life will be performed in the near future.

The ratio of the conversion electron to the continuous beta spectrum of the 35 day columbium isomer was obtained by determining the relative areas under the dotted $\frac{N}{I}$ vs. I curves of the beta spectrum and the conversion electron peak. This ratio was 2.42×10^{-3}. The ratio of the number of 35 day columbium atoms to the number of 84 hour columbium atoms formed by decay of zirconium^{95} (the branching ratio) was determined by correcting the relative areas under $\frac{N}{I}$ vs. I curves for the continuous beta spectrum and the 0.217 mev. conversion electron for decay between the counting time and the time the separation from the zirconium parent was performed. This branching ratio was 1.38×10^{-2}.

The Beta Spectra of Strontium^{90} and Yttrium^{90}. (W. S. Lyon, J. E. Hudgens)

Introduction

The determination of the energy of the beta spectra of strontium^{90} and yttrium^{90} is complicated by the large concentration of strontium^{89} usually present in samples of uranium which have been allowed to cool for relatively short periods of time after a bombardment with neutrons. Since the yttrium^{90} can be isolated by using chemical separations, the energy of its beta spectrum is more accurately known than that of strontium^{90}. Steward, Lawson and Cork (1) in 1937 separated yttrium^{90} from a deuteron bombarded strontium cyclotron target and by using the cloud chamber observed the effect of a magnetic field on the beta tracks. These authors found a maximum energy of 2.6 mev. for the yttrium^{90} beta spectrum. Coryell and Ballou (2) by means of absorption curves obtained a maximum energy for the yttrium^{90} spectrum of 2.5 mev. Nedzel (3) analyzed the radiation of strontium^{89} and yttrium^{90} in a 180° beta ray spectrometer and found a maximum energy

(1) Steward, D.W., Lawson, J. L., and Cork, J. M., Phys. Rev. 52, 901 (1937).
(2) Coryell, C. D., and Ballou, N. E., CC-529, March 1943.
(3) Nedzel, V. A., CC-2283, October, 1944.

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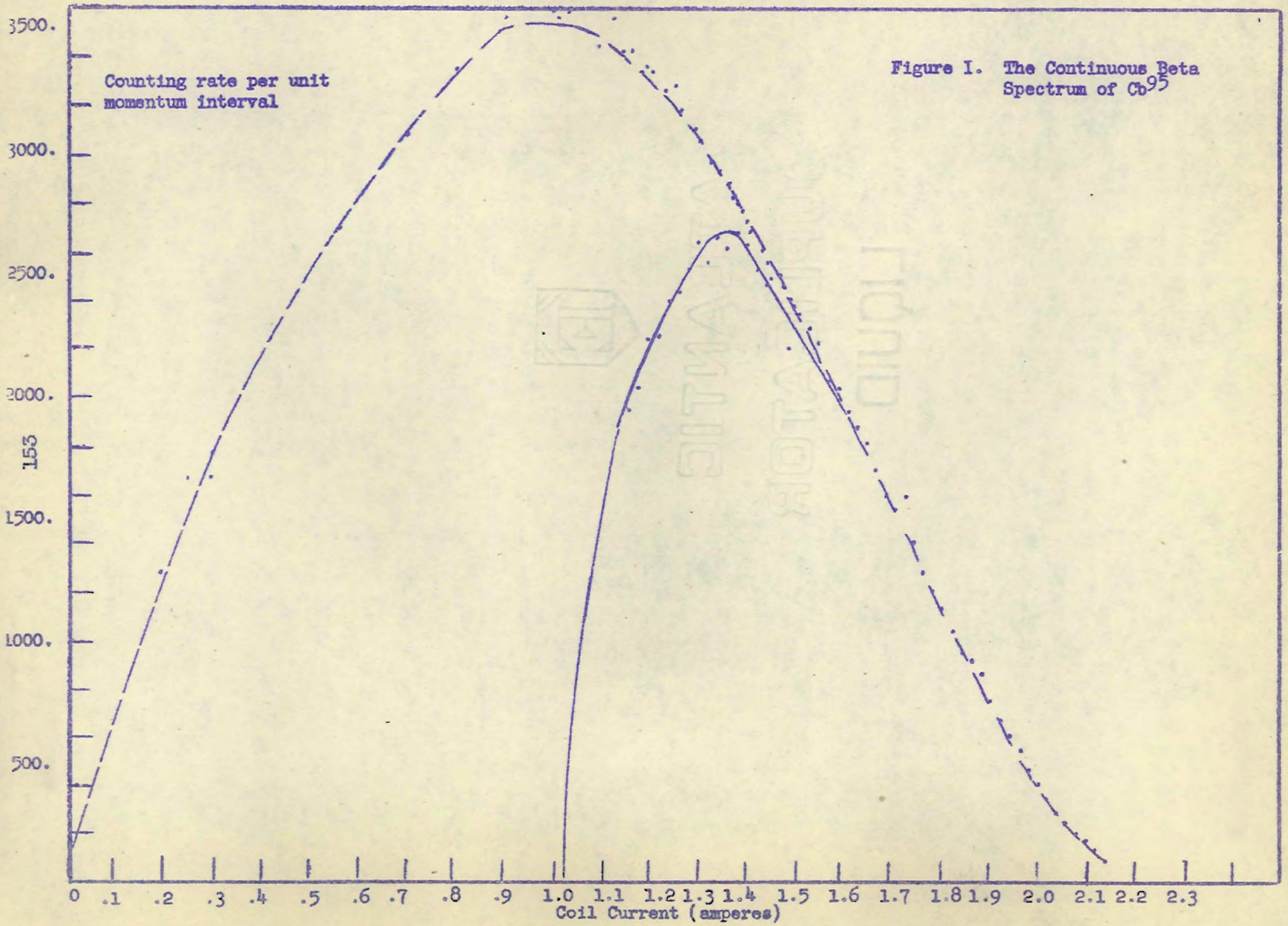

Figure I. The Continuous Beta Spectrum of Cb^{95}

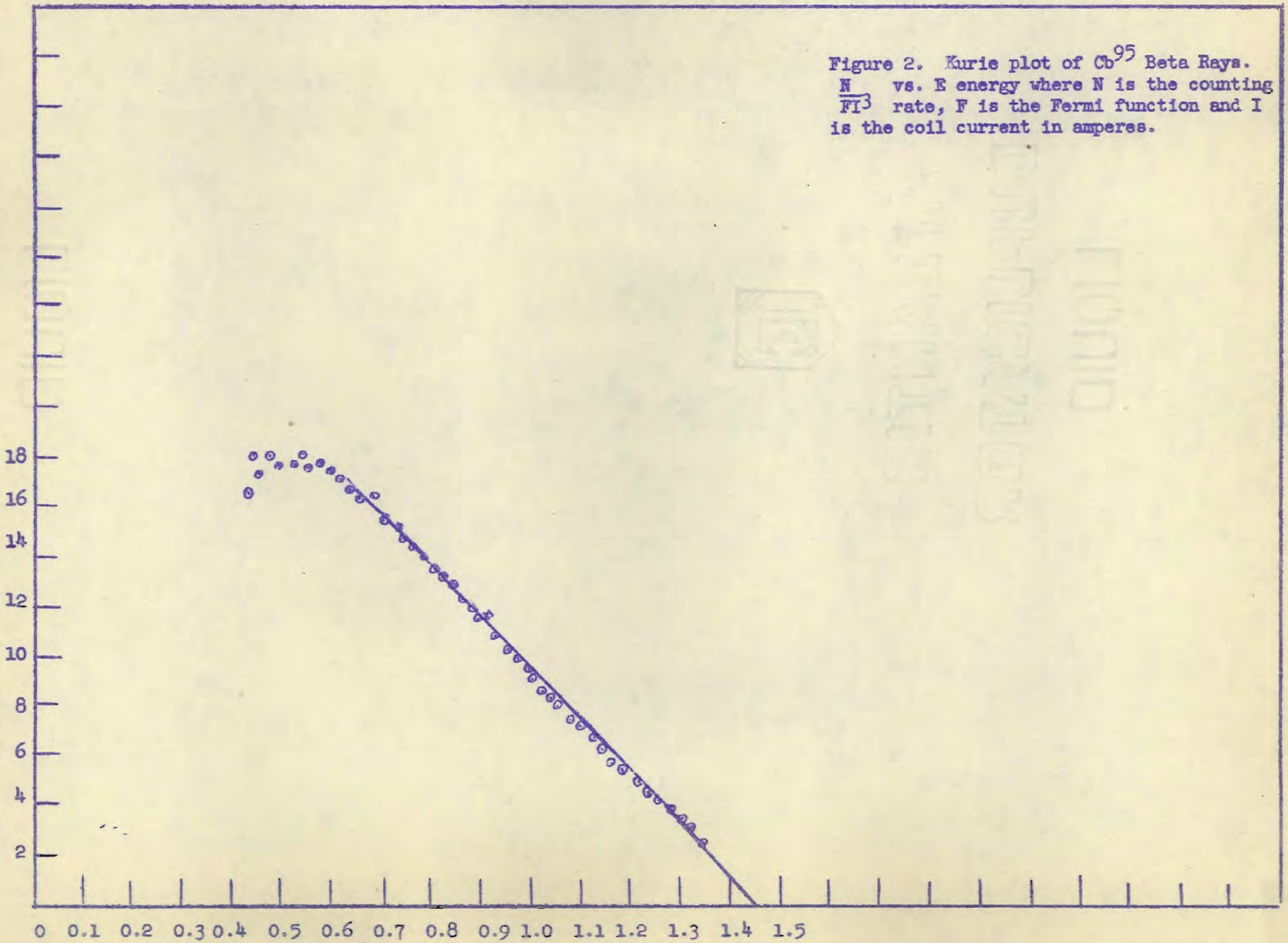

Figure 2. Kurie plot of Cb^{95} Beta Rays. $\frac{N}{FI^3}$ vs. E energy where N is the counting rate, F is the Fermi function and I is the coil current in amperes.

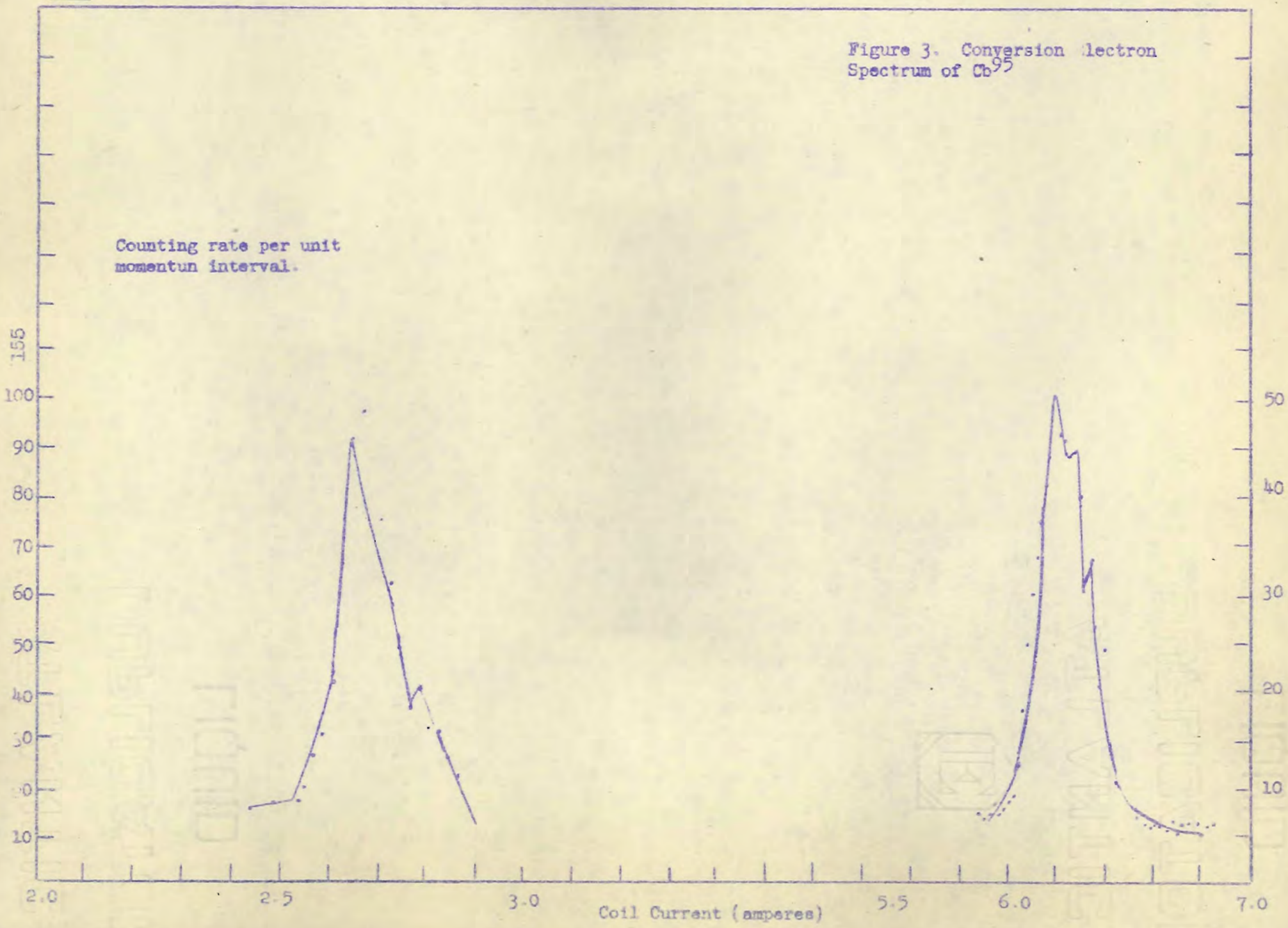

Figure 3. Conversion lectron Spectrum of Cb^{95}

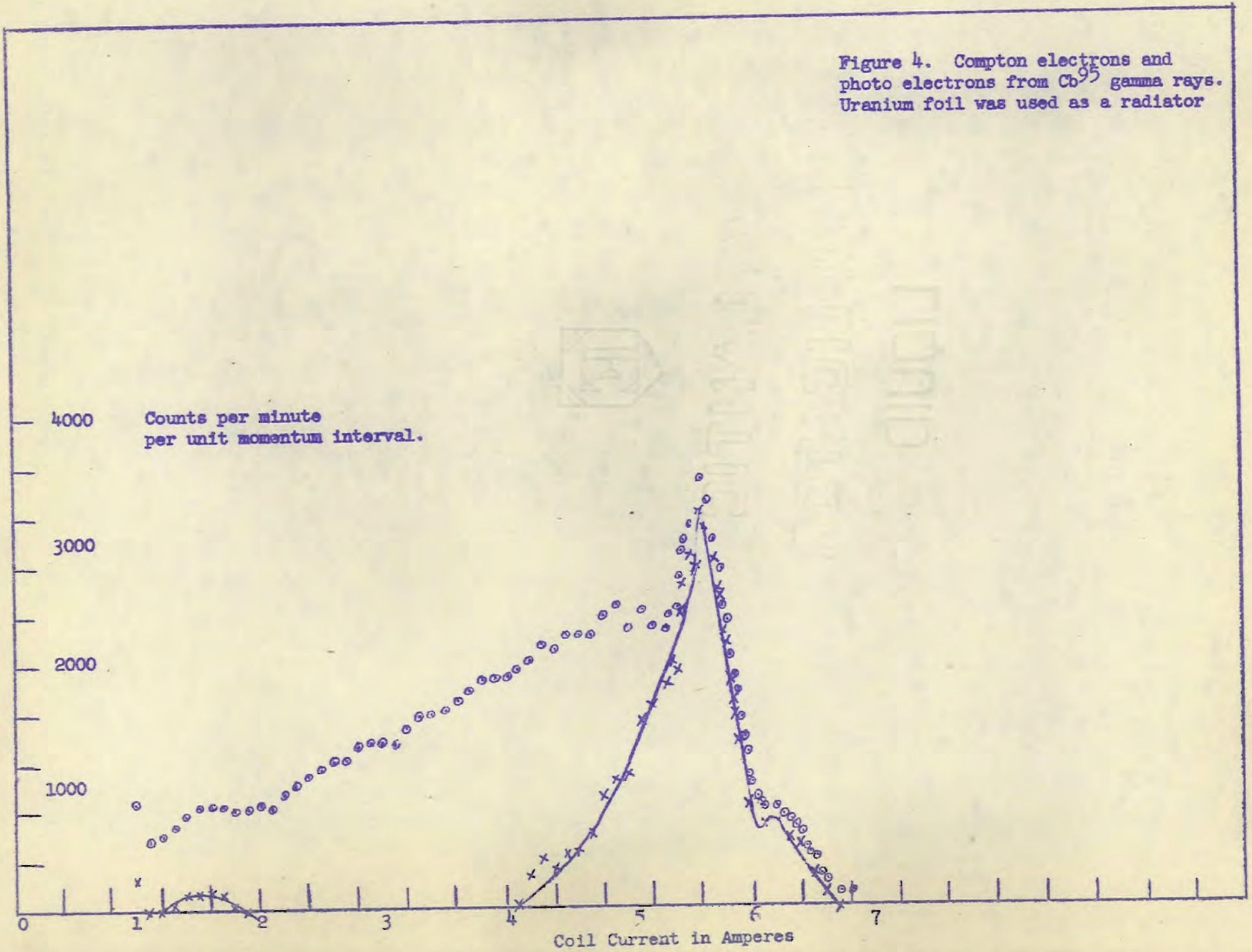

Figure 4. Compton electrons and photo electrons from Cb^{95} gamma rays. Uranium foil was used as a radiator

[redacted]

of 2.2 mev. for the yttrium^{90} beta particle. Glendenin and Coryell (1) by absorption methods derived a value of 0.65 mev. for the maximum energy of the strontium^{90} beta spectrum. None of these authors found gamma rays associated with the strontium^{90} or with the yttrium^{90} beta decay.

Experimental

A sample purified by the radioisotope group at Oak Ridge National Laboratory and containing very pure Sr^{90} and Y^{90} in equilibrium was evaporated on a Formvar polystyrene film (approximately 50 micrograms per sq. cm.), and this film mounted as the source in the thin lens beta ray spectrometer. A plot of the counts per minute per unit momentum interval vs. the coil current in amperes is shown in Figure 1. The kurie plot of this data in which the $\sqrt{\frac{N}{FI^3}}$ where N is the counting rate; F is the Fermi function, and I is the coil current in amperes, is plotted against energy in mev. is shown in Figure 2. Three straight line components may be extracted from this curve. The continuous beta spectrum assigned to 60 hour yttrium^{90} has a maximum energy of 2.40 ± .10 mev. The beta group which has an end point at 0.54 ± .05 mev. is assigned to strontium^{90}. A third beta group with a maximum energy of 0.95 mev. must be due to contamination since in crude experiments no gamma radiation which could explain the difference between the energy state formed by the emission of the 0.95 mev. beta radiation, and that which would be formed by the emission of either a 0.54 mev. or 2.44 mev. beta radiation was found. The $\frac{N}{I}$ vs. I curve calculated by extrapolation of the best straight lines of the kurie plot to low energy values for each of the beta spectra are also shown in Figure 1. The relative areas under the curve of the 0.54 mev. beta spectrum and that for the 2.40 mev. beta spectrum are approximately equal. This is further evidence for the mass assignments given above. Since the beta decay observed for these isotopes is forbidden, the Fermi function does not accurately describe the distribution observed for the beta spectra, and the interpretation of the data is in part intuitive.

E. Wyatt (2) in an independent measurement of the energy of strontium^{90} beta spectrum by the use of a feather analysis obtained the value of 0.55 mev. in good agreement with our results.

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

The study of a radiochemical method for plutonium based on solvent extraction with a TTA benzene solution has continued during this report period. The prin ipal effort has been expended in the determination of equilibrium constants for extraction, the study of oxidation and reduction reactions capable of forming plutonium^{+4} quantitatively in the presence of different solution compositions and in testing the method on pilot plant solutions.

The Equilibrium Constant for the Extraction of Plutonium

The equilibrium expression for the chelation reaction of plutonium^{+4} may be written: (3)

$$K_{pu^{+4}} = \frac{(PuT^4)(H^+)_A}{(Pu^{+4})_A(HT)^4_B}$$

(1) Glendenin, L. E., and Coryell, C. D., CC-1112, December, 1943.
(2) Wyatt, E. I., Private communication.
(3) Thomas, J. R., and Crandall, H. W., CN-3733, December, 1946.

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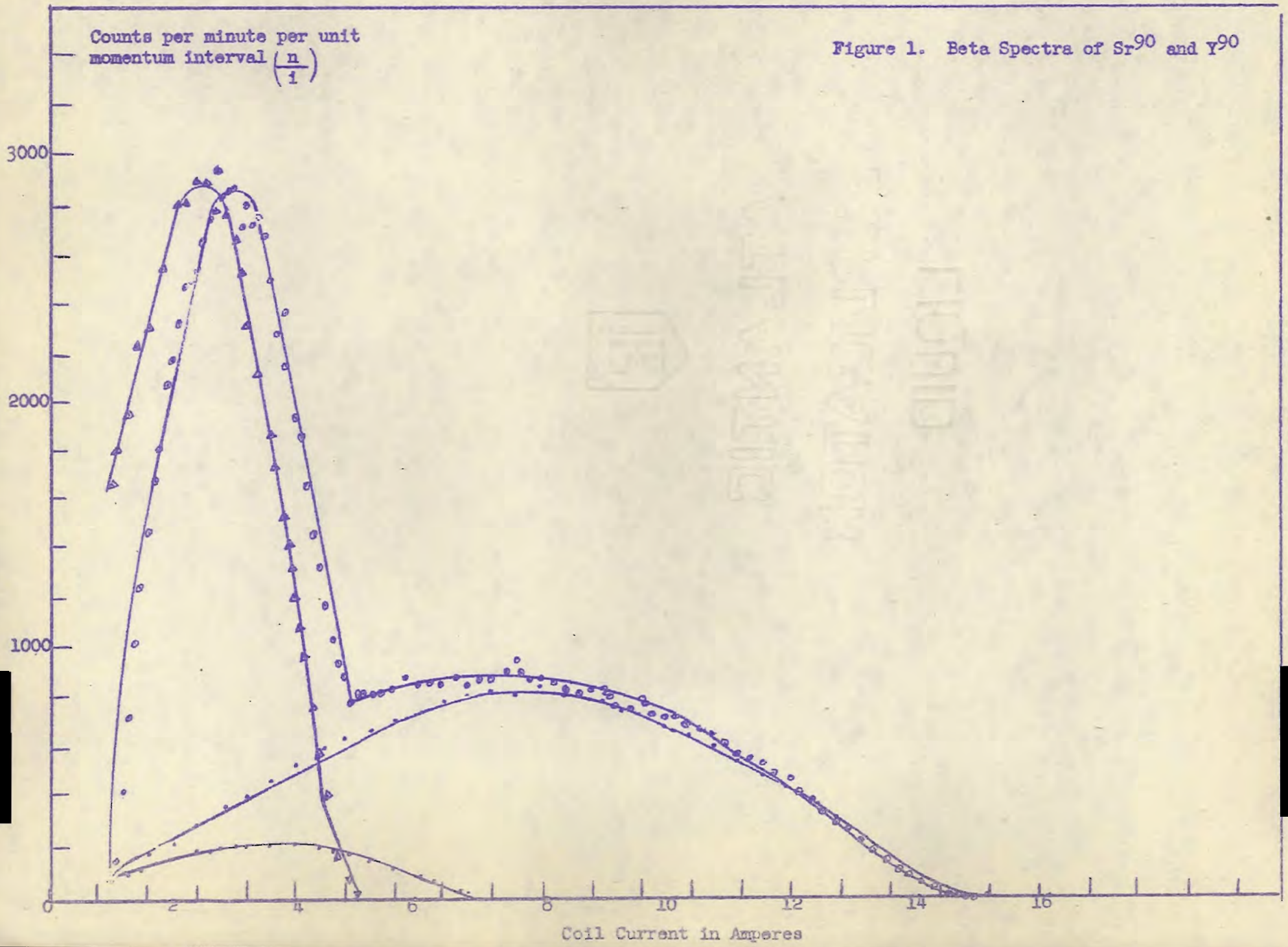

Figure 1. Beta Spectra of Sr^{90} and Y^{90}

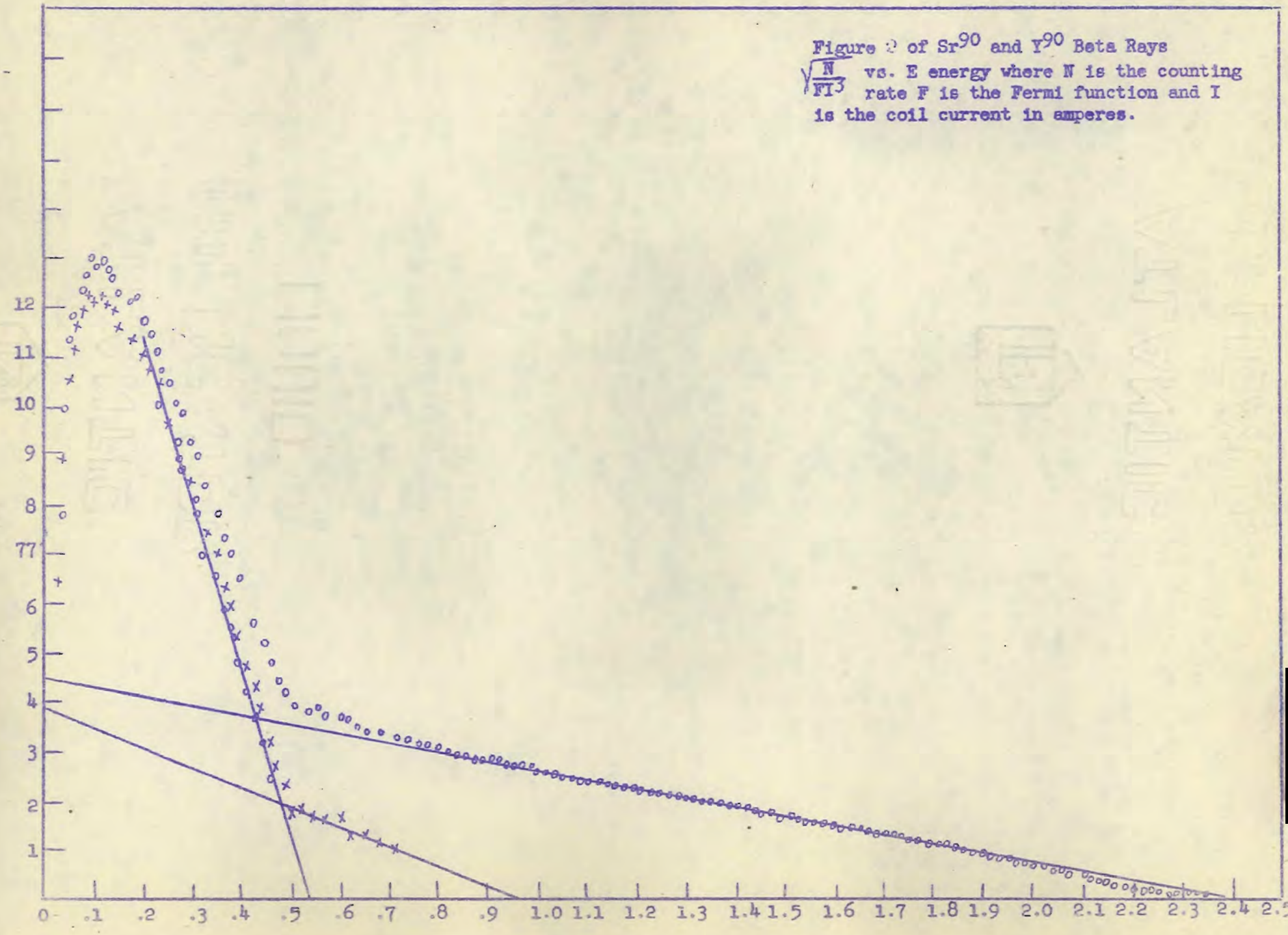

Figure 2 of Sr^{90} and Y^{90} Beta Rays $\sqrt{\frac{N}{FI^3}}$ vs. E energy where N is the counting rate F is the Fermi function and I is the coil current in amperes.

where the $_B$ and $_A$ refer to the benzene and to the aqueous phases respectively, and HT refers to Thenoyl trifluoro acetyl acetone (TTA). The procedure used for the determination of the constant was to mix equal volumes of a 0.5 M. TTA benzene solution and a 1 M. nitric acid solution of plutonium^{+4} tracer for a time sufficient to assure the attainment of equilibrium. After separating the organic phase from the aqueous phase the alpha activity in each of the phases was determined. The pH of the aqueous phase was also measured. The average value obtained for the constant was 1×10^{-3}. This value is not a true thermodynamic equilibrium constant since the ionic strengths were not considered, however it may be regarded as an apparent equilibrium constant for these conditions.

Oxidation and Reduction Studies

The samples to be submitted for analysis in the heterogeneous pile program may contain plutonium in any one of its several oxidation states and for this reason, it is desirable to reduce the plutonium quantitatively to the +3 valence state before attempting to oxidize to the intermediate +4 state. Several reagents, which seemed to offer promise of accomplishing this reduction have been studied. In the determination of the quantity of plutonium reduced, an aliquot of plutonium^{+4} tracer was mixed with the reducing agent being tested, sufficient nitric acid was added to make this solution 1 Molar and five minutes were allowed for the reduction. The solution was then equilibrated with an equal volume of 0.5 M. TTA benzene solution for two minutes. The results of this experiment are shown in Table I.

Table I

The Reduction of Pu^{+4} by Different Reducing Reagents.

Reducing Reagent	Concentration of Reducing Reagent in the Aqueous Phase	Percent Pu Reduced After 5 Minutes
H_2O_2	6%	27.1
$NH_3OH \cdot Cl$	0.2 M	100.
$N_2H_2 \cdot SO_4$	0.02 M	33.6
$FeCl_2$	0.02 M	100
HCl	0.12 M	
1.6% H_2SO_4	1.6%	25.1

Since ferric iron is readily extracted by TTA benzene solutions, hydroxylamine hydrochloride was selected as the most effective reducing reagent for incorporation in the procedure.

Several experiments were performed in which plutonium^{+3} was reduced with hydroxylamine hydrochloride and then re-oxidized to plutonium^{+4} with sodium nitrite. In each case the re-oxidation was found to be nearly instantaneous and was quantitative.

Since many of the process solutions will contain uranium, several experiments have been performed to determine the quantity of uranium which is

[redacted]

extracted under the conditions of the procedure. In these experiments, the nitric acid concentration of a synthetic solution containing uranium was adjusted to 1 M. and an extraction with an equal volume of a 0.5 M. TTA benzene solution performed. The TTA benzene solution was then equilibrated with a solution 0.5 M. in hydrofluoric acid. An average of 0.1% of the uranium added to the synthetic solution was carried through these separations.

The solvent extraction procedure is now being tested on process solutions. After completion of these tests, work on this problem will be terminated.

[redacted]

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Diffraction and Microscopy

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

Electron and Photomicrographs of Powders, etc.

(a) Beryllium Oxide. A sample of refractory grade fused superfine beryllium oxide was examined for the Clifton Products Company. Practically all the mass of the material is in the range 10 ± 7 microns. There are a few particles larger than 25 microns, and a larger number (but a negligible mass) between ½ and 3 microns. Most of the particles are plate-like in shape (C.F. 48-4-179).

The material is, therefore, intermediate in size between the fluorescent grade and the ground fused refractory grade.

Another sample from a large batch of fluorescent grade BeO heated above 2700°F by Clifton Products was examined for W. W. Galbreath (Power Pile Division-48-5-344). This sample resembled very closely the A,1,c and A,2,c samples as reproduced in CNL-37, p. 149.

(b) Palladium Iodiode. A sample of colloidal palladium iodide was examined by electron diffraction for A. R. Brosi. The results could be interpreted as representing a body-centred cubic lattice with a = 10.1 Angstroms. From somewhat similar material M. Bredig has obtained 2 different patterns, which are each different from the above. (C.F. 48-3-402).

(c) Natural U_3O_8. A sample of U_3O_8 examined for L. Hunter consisted of aggregates of ellipsoidal particles ½ to 1 micron in diameter (C.F. 48-4-11).

(d) Dowex Resins. Several samples of fractionated Dowex 50 resin have been examined for J. Savolainen and B. H. Ketelle (C.F. 48-5-346). See Fig. 1.

A recent sample of this resin (#49172M) consists entirely of light brown particles in contrast to the wide range of brownish tints observed in previous samples.

Corrosion Studies.

(a) Films on Aluminum. In a continuation of work described in previous quarterly reports, pits which appeared on some samples of 2 S aluminum heated at 165°C in a weak dichromate solution have been examined metallographically. It is obvious from

[redacted]

the overhanging edges that, once the protective film is broken down, the underlying metal corrodes more rapidly.

The material in the pits was examined with x-rays by M. A. Bredig and the pattern obtained resembles that of boehmite.

(b) Microphotographs of Corrosion Test Specimens of Al, Zr, Ti, Cb. Microphotographs of these metals have been taken for J. E. Perry before and after exposure to 30% hydrogen peroxide at 350°C for 61 hours (C.F. 48-5-345). As can be seen in Fig. 2 all of the materials have been attacked more or less severely.

(c) Microphotographs of Corrosion Test Specimens of Stainless Steel Welds. Microphotographs have been taken for J. Olsen. In this case rather brilliant colours developed in certain areas during the test and Kodachrome transparencies have been made to record the results.

(d) Electron Diffraction Pattern of Beryllium Corrosion Product. A sample of beryllium exposed to a dilute solution of hydrogen peroxide at 90°C for 2 weeks was examined by electron diffraction for J. E. Draley (Metallurgy Division). A broad line pattern, indicating small crystals, was obtained, but the material could not be identified (C.F. 48-4-10). It did not appear to be either BeO, or $Be(OH)_2$, for which diffraction data were available.

Preparation of Evaporated Films.

Since the evaporator, which was designed chiefly for making silica replicas for electron microscopy, has been assembled, there has been a considerable demand for the evaporation of various materials. The examples given below are typical, and several similar, and a few more complex, problems are still pending.

(a) Coating Al Tube for Photomultiplier Type Counter -- for E. P. Blizzard. Since it was desired to have the photomultiplier tube about 1 meter from the crystal it was necessary to put an aluminum film on the inside of a 2" tube of this length.

(b) Aluminum Absorbers -- for M. Feldman. It is difficult to procure a satisfactory range of aluminum foils in the very thin sizes, but they can be made by evaporation.

(c) Evaporated Gold Films on Mica for Counter Windows -- for C. Borkowski. A rather thin film of gold (0.05 mgm. per sq. cm.) was sufficient to markedly reduce the electrical resistance of the mica.

[redacted]

Crud.

In a continuation of the study of crud in the solvent extraction process, a sample of material settled from C. P. aluminum nitrate was examined for J. Gost (C.F. 48-5-339). Most of the material consists of aggregates of very small primary particles, which are about 100 A in diameter. Since no definite pattern was obtained when the sample was examined by electron diffraction, the material must be amorphous in nature.

Nucleic Acid.

An unsuccessful attempt was made to take electron micrographs of nucleic acid fibres for E. Volkin (Biology Division) (C.F, 48-4-178). Inability to dispurse the material properly appeared to be the main cause of failure.

K-25 Work.

About 2/3 of the time has been spent on work for K-25 which is not discussed here because of security reasons.

Misc. Photography, Metallographic Polishing, Apparatus Design, Instrument Maintenance, etc.

During the period a considerable number of slides have been made for use at the ACS meeting and the Brookhaven Information Meeting.

A few metal samples have been metallographically polished for various people.

A certain amount of time has been spent on minor apparatus improvements.

About a week has been spent on electron microscope maintenance in an attempt to eliminate a troublesome image shift. Some improvement has been obtained but the remaining components of the shift are erratic, and therefore it is difficult to locate their source.

[redacted]

Figure 1

Dowex 50 Resin

5000 x

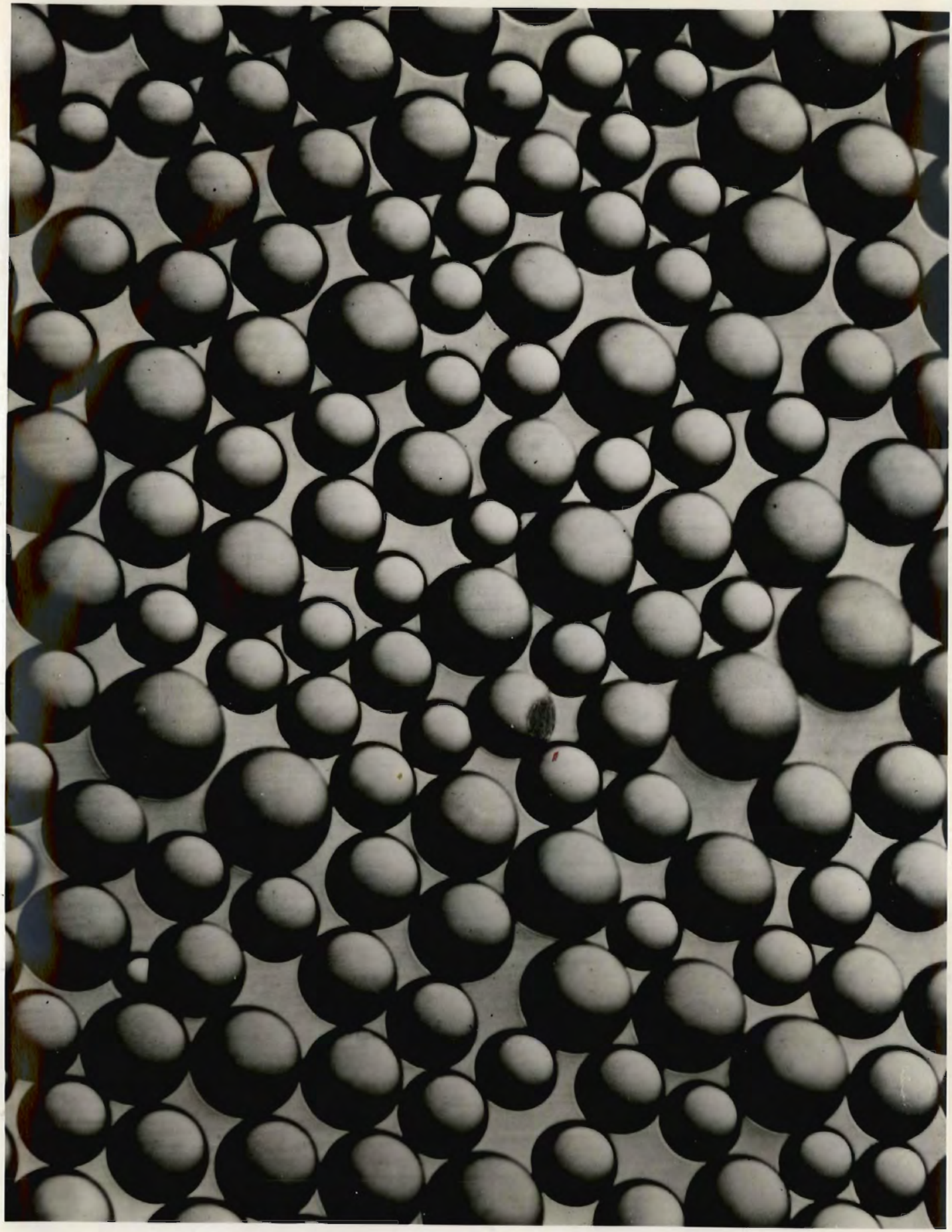
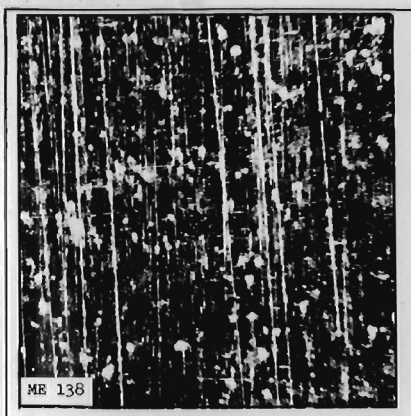


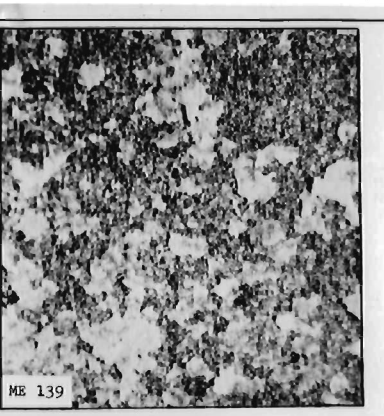
Figure 2

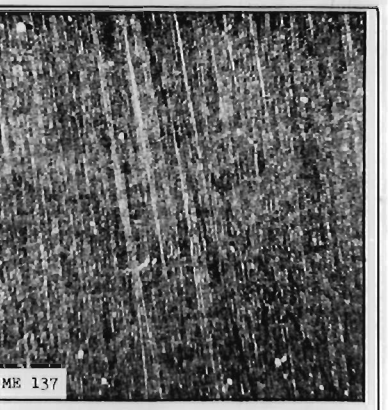
Record Macrographs of Metals Used in Corrosion Tests

$\frac{1}{2}$ reduction



Zirconium - new
U. S. Bureau of Mines
25x

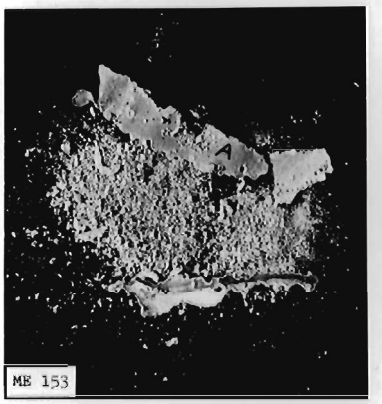




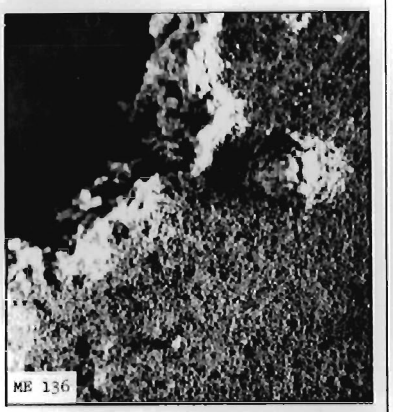
Zirconium - new
Foote Metals Company
25x

Zirconium after test run - Foote Metals Company
Approx. 2x Above-macrograph of area circled 25x

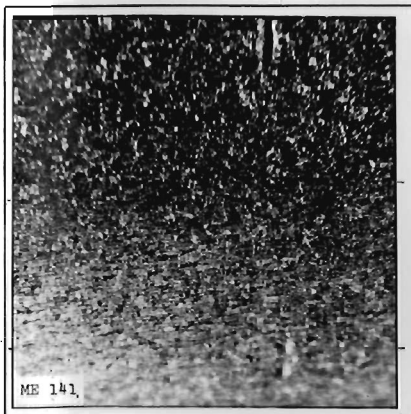
Aluminum - new



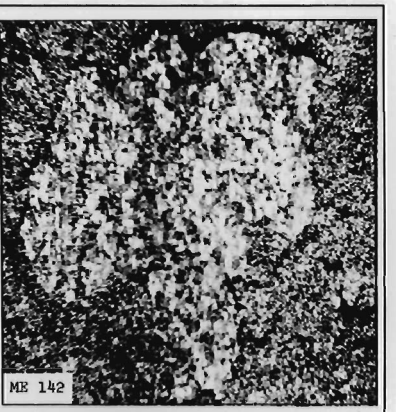
Aluminum after test run
Approx. 2x



Aluminum - showing edge and
surface of A-ME 153 25x



Columbium - new
Approx. 25x



Columbium after test run showing
typical surface attack 25x

CONDITIONS OF TEST

30% H_2O_2

Temp 350°C

Time 61 Hrs.

MACROGRAPHS BY T. WILLMARTH

Record Macrographs of Metals Used in Corrosion Tests

Explanation of photographs:

Fig. 3: Black glaze on surface of BeO pellet (Fe-7, XR-218), heated 1 hour at 2100°C, supported on graphite, contains high concentration of new BeO phase, or phases.

Fig. 4: Black blisters on surface of BeO briquette, heated one hour at 2100°C, on graphite support.

Fig. 5: Rounded, reacted (right), and sharp unreacted (left) edges of BeO briquettes, heat-treated at 2100° and 1800°C, respectively. (Melting point of pure BeO: 2550°C).

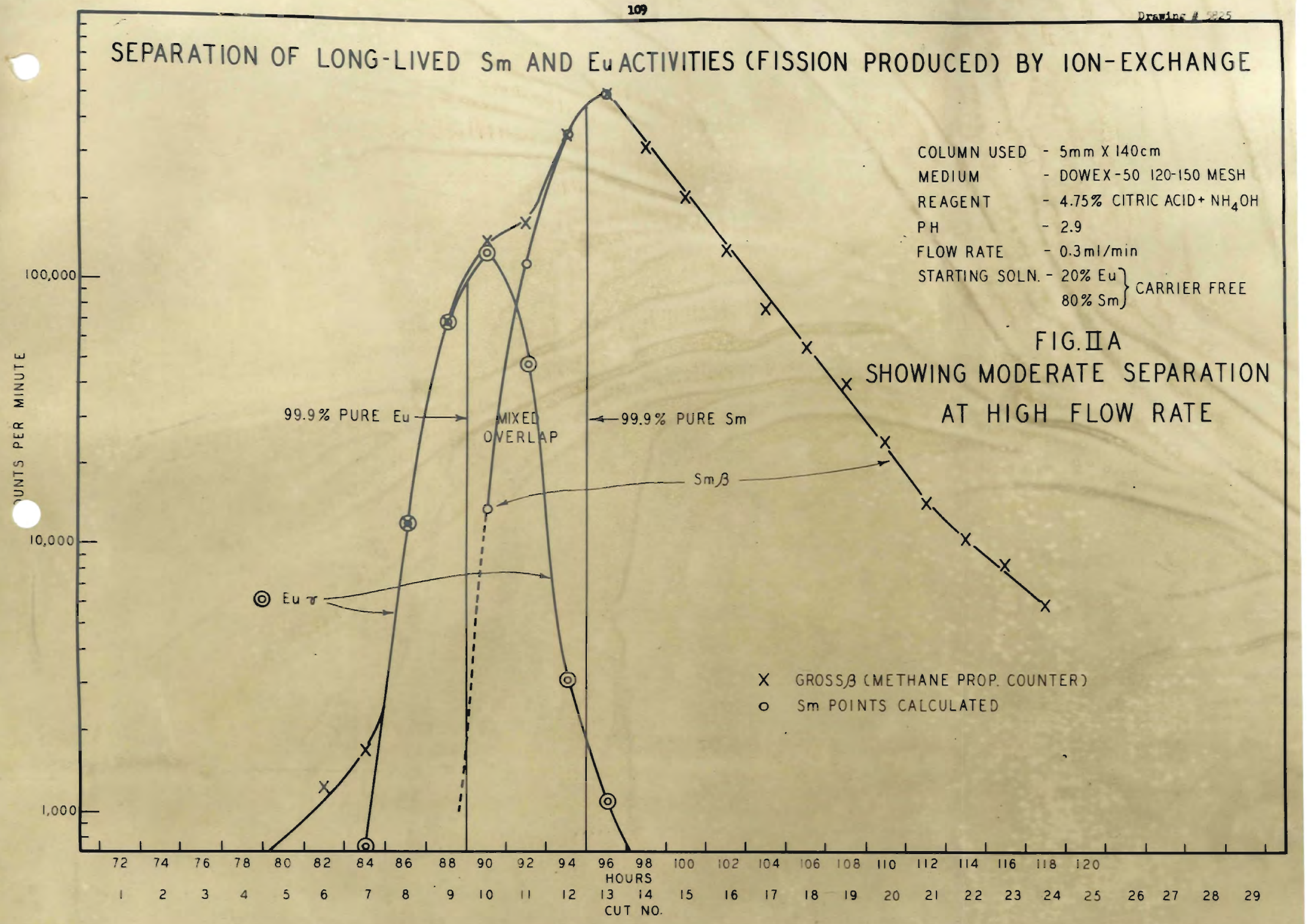
Fig. 6: Cross section (fracture) through BeO briquette (G-6, XR-178), dark-grey, containing at least 50% of new BeO phase, or phases, besides common hexagonal phase and traces of graphite.

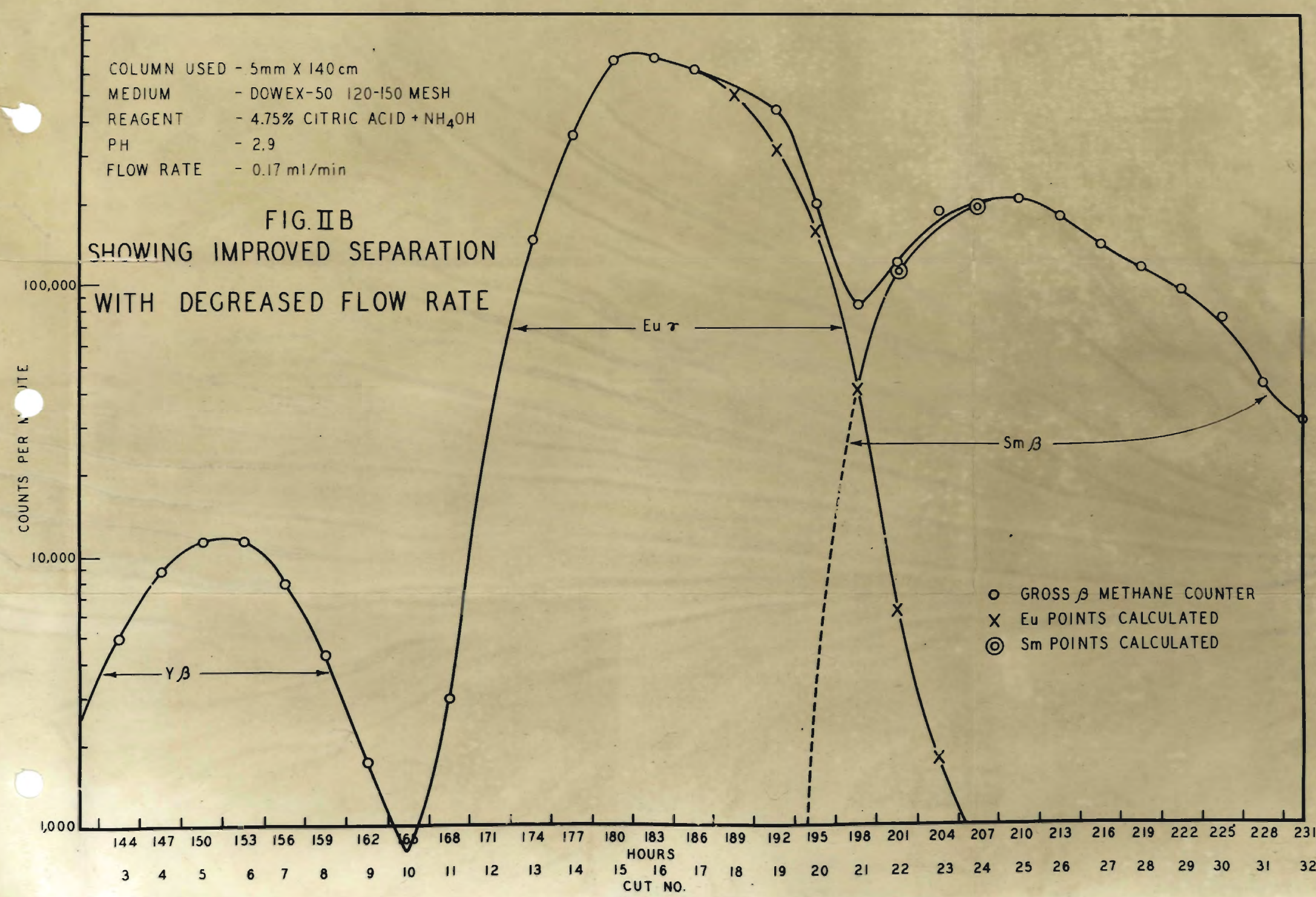
Fig. 7: Thin, black surface skin (glaze), same as in Fig. 3, in cross section view.

Briquettes obtained from W. W. Galbreath, Jr.
Macrographs by Ted Willmarth.

Figures 3,4,5,6 - approx. 2.5 x
Figure 7 - approx. 15 x

Drawing # 5825





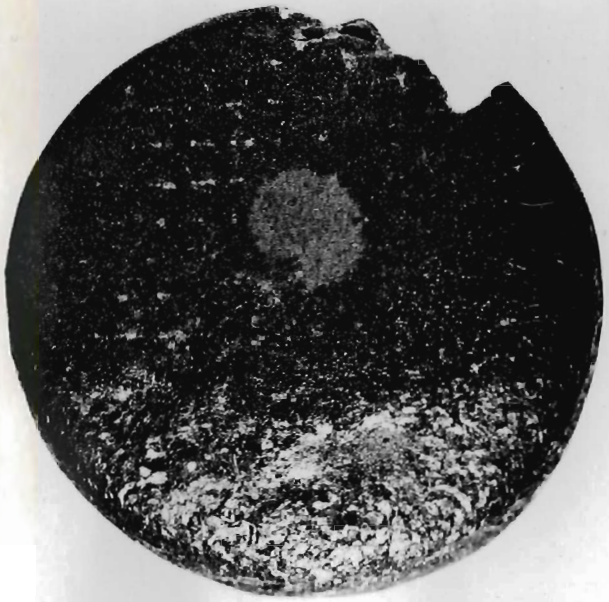


Fig. 3

Fig. 4

Fig. 5

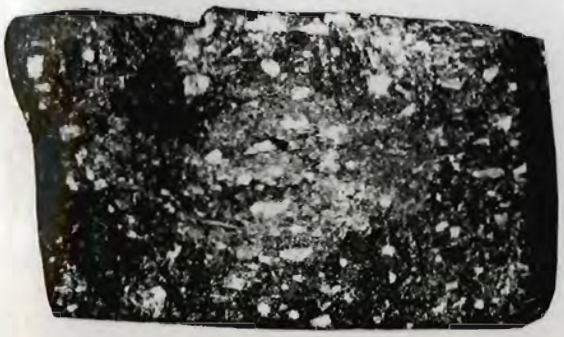
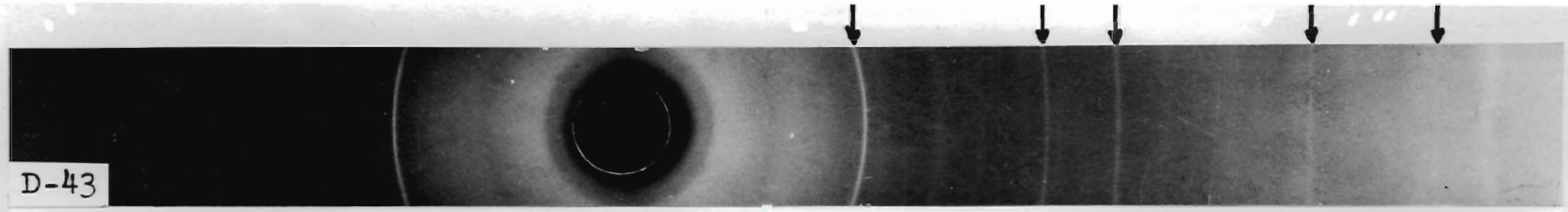
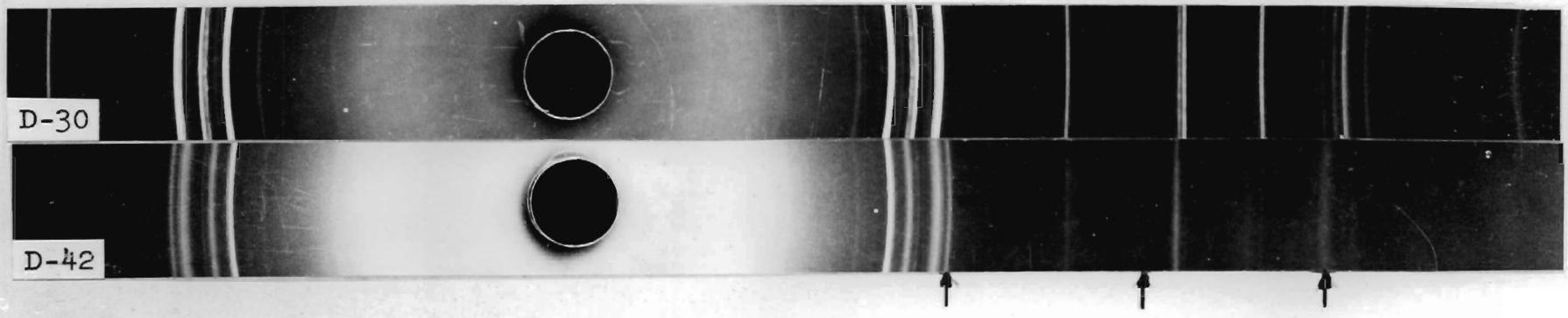


Fig. 6

Fig. 7



Film D-43. Black product of heating barium ruthenate to 450°C. Weak, broad lines ascribed to colloidal phase of unknown composition. Five sharp lines(arrows) tentatively ascribed to a cubic phase, possibly of RuO_2.



Film D-30. BeO briquette G-6, XR-178, pulverized. Estimate is: not more than 50% of common, hexagonal, form, and 50%, or more, of new BeO phase (or phases). Traces of graphite.

Film D-42. BeO from black surface of briquette Fe-7, XR-218. Estimate: not more than 10% of common, hexagonal, form, 10% metallic iron (added) (arrows) traces of graphite; all other lines, including strongest one, are those of new BeO phase (or phases).

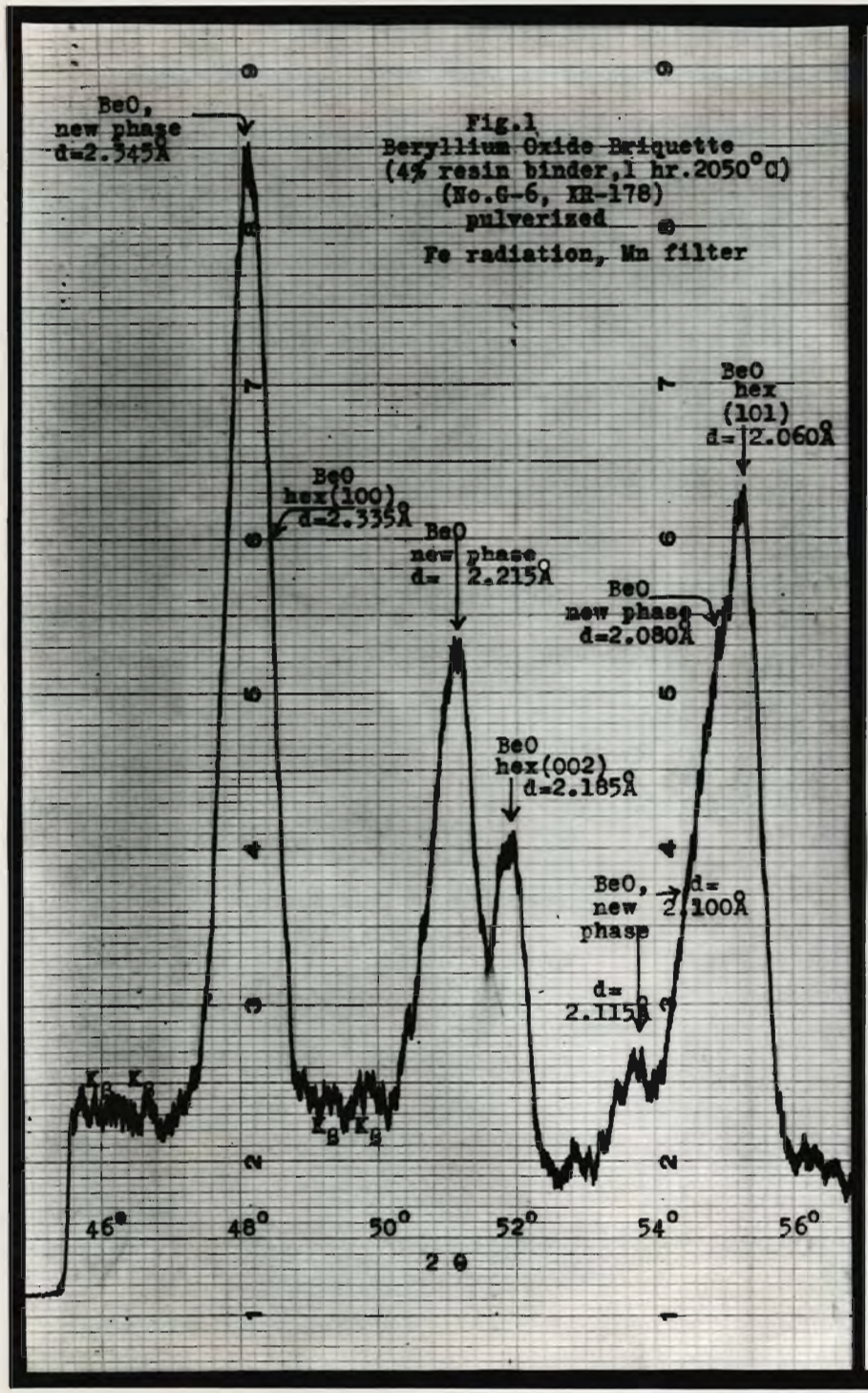


Fig.1
Beryllium Oxide Briquette
(4% resin binder, 1 hr. 2050°C)
(No.G-6, XR-178)
pulverized
Fe radiation, Mn filter

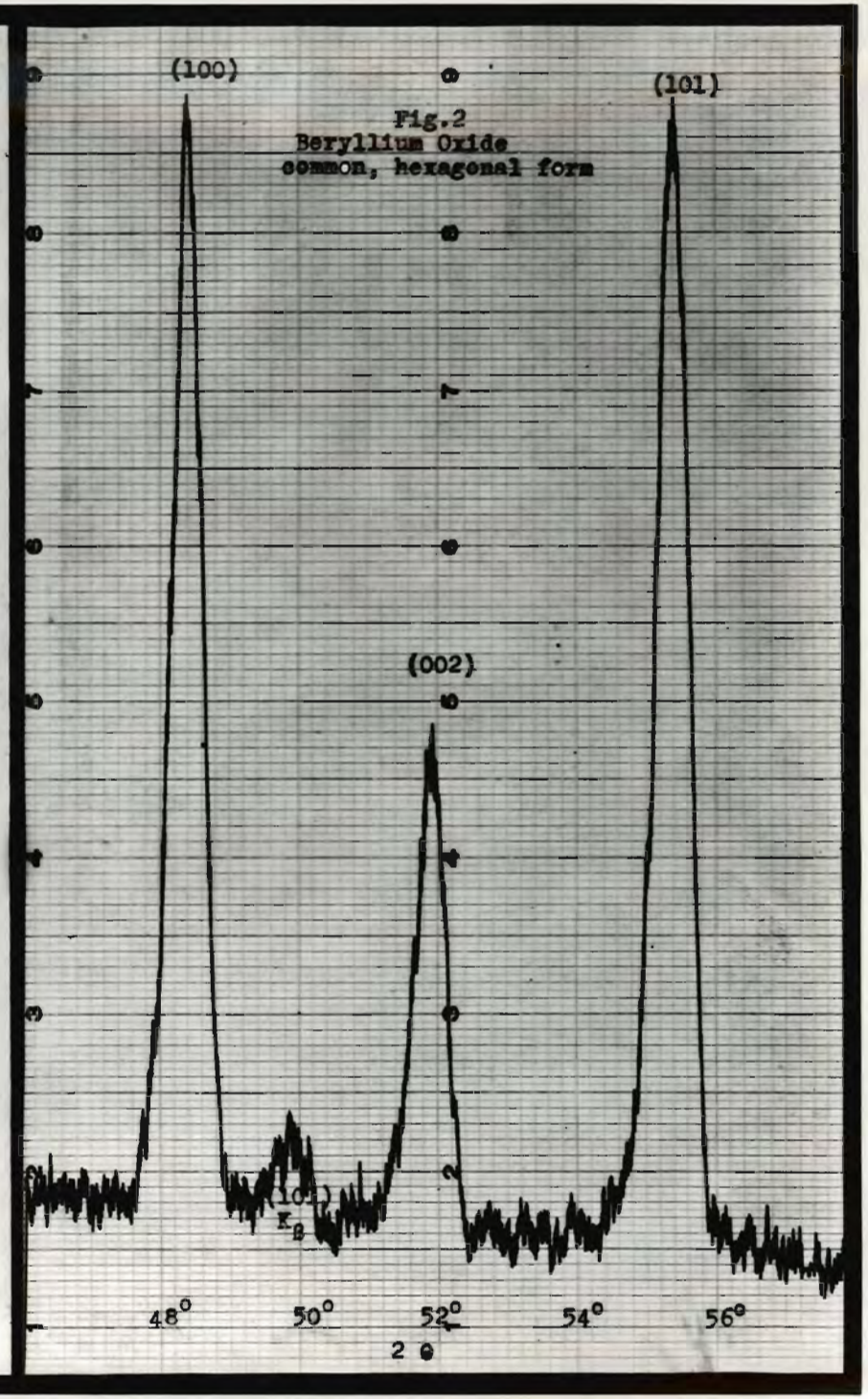


Fig.2
Beryllium Oxide
common, hexagonal form

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X-Ray Diffraction
(M. A. Bredig)

High-Temperature Vacuum Chamber for X-Ray Spectrometer

The apparatus was received from the machine shop. Efforts to eliminate a number of leaks are being made. It may be necessary to have at least some parts of the apparatus rebuilt and to use more satisfactory material than aluminum which was employed in the present model. The problem of windows of sufficient transparency for x-rays combined with mechanical stability also still needs further attention.

Crystal Structures of Beryllium Oxide

In the preceding quarterly report, the occurence of a new crystal phase in high-fired beryllium oxide was described. Present experimental work has largely been directed towards determining the conditions under which this new phase forms. W. W. Galbreath Jr., of the Power Pile Division co-operated by having a number of preparations made in a high-temperature, carbon tube furnace at the Morris Electrotechnical Laboratories of the U. S. Bureau of Mines. Success has not been attained as yet beyond the observation that beryllium oxide briquettes (dimensions: 2" x 1" x 1/2") fired at or below 1900°C, did not show the new phase while those fired at or above 2000°C did contain varying amounts thereof. These were sometimes limited to a thin surface skin of high concentration, and sometimes distributed throughout the briquette. While it seems most likely that the formation, in this beryllium oxide of comparatively high purity, of a new phase, different in crystal structure from the common hexagonal one, is connected with the introduction of small amounts of impurities during the process of firing , the particular substance responsible for the effect has not as yet been identified, and efforts are continuing to determine its nature and origin.

As to the atomic structure of the new phase, the data obtained with the more recent preparations suggest that an alternate interpretation to that of a cubic crystal lattice suggested in the previous report, is possible. In the x-ray pattern discussed previously the lines of the common hexagonal form were still very prominent. Besides 3 or 4 weak additional lines which then were attributed to the possible presence of an impurity (graphite was, f.i., identified also), three reflections of strong or intermediate intensity had given a perfect agreement with an assumed cubic lattice. With a constant of $a_0 = 3.83$ Å , such a polymorphous form of BeO would be entirely analogous to that of zinc sulfide. However, from

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a small amount of powder collected in the process of rubbing two high-fired briquettes against each other, whose dark-gray, glossy appearance indicated a surface reaction with either the supporting graphite crucible or the furnace atmosphere, an x-ray (film D-42) pattern was obtained in which the lines of the common hexagonal form had almost disappeared. (See Table 1, and the reproduction of film D-42). The three lines which have been interpreted as the (111), (220) and (113) reflections of a cubic-face centered structure of the zinc sulfide type are prominent in this film. However, the strongest line of the pattern was not one of them, but one corresponding to a lattice spacing of 2.345 Å, that is almost identical with that of the second strongest line ((10.0); d = 2.335) of hexagonal BeO. That this latter phase was not present in the specimen in more than minor quantities, of the order of 10%, is proven by the weakness of its strongest reflection, (101), d = 2.060 Å. In addition, lines that were very weak in previous preparations, appeared now with somewhat greater intensity, and a few weak new lines also became measurable, that were not detected in specimens containing larger amounts of the hexagonal phase. Careful examination of a number of film and spectrometer records of various specimens shows that at least the stronger ones of these lines are present, whenever the 3 reflections ascribed to a cubic phase are strong. Especially the presence of the strongest line of film D-42, with the spacing of 2.345 Å, in patterns where its presence is easily concealed to more superficial observation because of its closeness to the (10.0) reflection of the hexagonal phase, could be established by precise measurements of both line-positions and line widths. Even in film D-30, reproduced in the last report, it is now possible to detect the presence of this strong line in close vicinity of, or almost coincidence with the hexagonal (10.0) reflection. Film D-30 is representative of the material of briquette No. G-6, XR-178, as a whole. Therefore, the possibility of ascribing the non-cubic lines of film D-42 to the crystal phase of a substance different from BeO and present in the surface of the briquette only can be ruled out. Actually, this briquette, apparently consisting of rather pure BeO, according to spectrographic and carbon analysis (traces only of Fe, Si, Ae and Mg; 0.2% C) must on the basis of film D-30 and the spectrometer chart (this report, Figure 1) be assumed to average not more than 50% of the common hexagonal form, and to contain at least 50% of the new crystal phase (or phases?) of beryllium oxide, as characterized by the pattern of film D-42.

It may be noted here that the spacings of the non-hexagonal lines in pattern D-42 of the surface abrasion product, which are also of decreased sharpness, are larger by 0.5 to 1% than those in film D-30, representing an average of a briquette. The reason is considered to be the higher amount of impurity assumed to be present in solid solution in the surface specimen of film D-42. Assuming a maximum possible difference of 20% in the lattice dimensions of the solute from that of the solvent in this solid solution, one obtains, as the amount dissolved, $\frac{0.6 \times 100}{20} = 3$ mol % of an impurity present in the surface skin, and approximately half this figure in the average of briquette G-6. These figures seem not unreasonable.

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Another observation may turn out to be of some interest in the process of elucidating the nature of the new beryllium oxide phase (or phases): A high degree of orientation of crystallites was observed in most of the briquettes, with the (00.2) plane of the hexagonal lattice oriented preferentially parallel to all surfaces. While it is somewhat difficult, though not impossible, to understand the mechanism of this type of preferred orientation, it is noteworthy that the other phase, or phases, seem to follow a related mode of orientation: Whenever the intensity ratio of the hexagonal (00.2) reflection was high when compared with those of the (10.0) and (10.1) reflections in randomly oriented powders, the reflection d = 2.215 Å also was of very much increased intensity, f.i. in comparison with that of d = 2.345 Å. This most likely indicates a kinetic, or "genetic", relationship between the hexagonal and the new cubic, or pseudo-hexagonal phase of BeO similar to that observed in other substances.

In view of the observations and measurements described here, one is faced with the necessity of choosing between two possible interpretations: First, two new crystal phases of beryllia may have been observed here to occur together with the common hexagonal modification, one of which would be the cubic structure, a_o = 3.83 Å, as derived from three prominent x-ray diffraction lines which fit the indices (111), (220) and (311) of a zinc sulfide type lattice accurately. The second of the new phases, represented by the very strong line d = 2.345 Å and a set of at least half a dozen weaker lines would be of lower symmetry.

The other possible and perhaps more plausible interpretation involves abandoning altogether the assumption of a cubic structure in these briquettes, and ascribing all x-ray reflections different from those of the hexagonal modification to one new crystal phase of beryllia of a symmetry lower than cubic or hexagonal, and probably pseudo-hexagonal.

A third possibility namely to interpret the major new lines as those of a solid solution of an impurity in beryllia, having the common hexagonal, though slightly expanded structure of pure BeO, may be suggested by a certain similarity of the x-ray patterns. It may be ruled out however for the following reason: A (10.2) reflection, with an expected spacing of d = 1.615 Å, calculated from the spacings d = 2.345 Å and 2.230 Å, if assumed as (10.0) and (00.2), respectively, of the hypothetical expanded hexagonal lattice is definitely missing in the x-ray pattern, while the corresponding reflection in pure BeO is a comparatively strong line.

Perhaps, the good fit of the "cubic" lines, and also some very slight differences in their "spottiness", when compared with the other lines of film D-30 (preceding report), cannot be considered sufficient evidence for a choice between the first two interpretations in favor of the first one. It is true, also, that a preliminary examination, with the polarizing microscope, of finely pulverized material from a high-fired briquette, did not reveal the presence of an optically isotopic crystal phase. A microscopic study of a thin section which is underway is hoped to help clarify this point.

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TABLE 1

Powder X-Ray Pattern (D-42) of High-Fired Beryllium Oxide

(sample from surface of briquette made with the addition of 10% metallic iron and 4% durite resin binder)

No Fe-7, XR-218

Intensity	Spacing exper. Å	Spacing calc. Å	Substance	Crystal Form	Indices hkl
VW	3.385	3.400	C	graphite	00.2
VS	2.345	-	BeO	new	
W	2.330	2.332	BeO	hex	10.0
S	2.230	2.225	BeO	new	*)
VW	2.185	2.185	BeO	hex	00.2
VW	2.115	-	BeO	new	
W	2.100	-	BeO	new	
S	2.080	-	BeO	new	
W	2.060	2.058	BeO	hex	10.1
S	2.030	2.020	Fe	α	110
W	1.600	1.595	BeO	new	
VW	1.575	-	BeO	new	
VVW	1.430	1.430	Fe	α	200
S	1.365	1.365	BeO	new	**)
VW	1.350	1.347	BeO	hex	11.0
W	1.247	-	BeO	new	
W	1.240	1.235	BeO	hex	10.3
VVW	1.175	-	BeO	new	
W	1.160	1.165	Fe	α	211
W	1.155	1.160	BeO	new	***)
VVW	1.140	1.145	BeO	hex	11.2
VVW	1.127	1.126	BeO	hex	20.1
VVW	1.120	-	BeO	new	

*) **) ***) These three lines might also be interpreted as those of a separate cubic phase, a_o = 3.860 Å, indices (111), (220) and (113), of beryllium oxide. Their calculated spacings refer to this structure.

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The results obtained thus far may then be summarized as follows:

a) A large percentage of beryllium oxide after being heated to or above 2000°C, is found, probably under the influence as yet of unidentified impurities, to assume a crystal structure different from the common hexagonal one.

b) As an alternative to a previous suggestion involving a cubic face-centered, zinc sulfide type structure, the assignment, to one new crystal phase of BeO of all new x-ray lines observed, would lead to a structure of lower symmetry, the nature of which remains to be determined.

c) The occurrence of the new phase (or phases) seems to be connected with a marked depression of the melting point. This may have a bearing on technological considerations in connection with the use of high-fired beryllia.

On the Possibility of a Cubic Structure of Ruthenium Dioxide Occuring in Calcined Barium Ruthenate.

M. D. Silverman who submitted preparations of barium ruthenate to which various heat treatments had been given is reporting on this work in another section of this report. Here, therefore, only a few points somewhat hypothetical in nature may be brought out in some detail, which the present rather scanty data suggest.

a) The black substance obtained, when reddish brown $BaRuO_4 \cdot H_2O$ is heated to temperatures at which the water and most of one atom of oxygen are given off, yields an x-ray diffraction pattern in which two sets of lines are readily distinguished (see reproduction of film D-43). One set consists of 5 very sharp lines, very prominent in the pattern, showing a "normal" decrease in intensity from very strong to very weak with increasing Bragg angle. The other set comprises a somewhat larger number of weak or very weak, and broad, reflections, indicating a rather small crystallite size which increases slowly with increasing temperature. These two sets of x-ray diffraction lines may be assumed to represent two different phases, one well crystallized, the other colloidal.

b) On prolonged heating, at 1100°C, the first set, of sharp lines, is preserved, while the second one is changed into a new set of a large number of sharp reflections of intermediate intensity, indicating the transformation of the colloidal substance into a well crystallized, third phase.

c) While structures have not as yet been derived for the two latter ones of these three phases, Table 2 intends to show for the five sharp reflections the excellent agreement of experimental lattice spacings with the assumption of a cubic body-centered structure.

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TABLE 2

X-Ray Pattern of Hypothetical Body-Centered Cubic Phase (RuO_2) in Calcined Barium Ruthenate Film D-44

Intensity	Bragg Angle for CuK_α θ°	Indices hkl	Lattice constant $a_o = \frac{0.770}{\sin\theta}\sqrt{h^2+k^2+l^2}$ Å
very strong	15.60	110	4.054
medium	27.70	112	4.060
medium	32.50	220	4.055
weak	45.30	123	4.056
very weak	53.75	330	4.052
			mean: 4.055 ± 0.002 Å

a_o corrected (for $d_{calcite}$ = 3.036 Å): 4.067 ± 0.002 Å

The lattice constant a_o = 4.067 Å is quite similar to that of $BaTiO_3$ (3.97 Å, perovskite structure), with which a compound of the composition Ba Ru O_3 might be expected to be isotypic. However, the intensities observed, and in particular, the absence of the (200) reflection permits one to rule out the presence of a barium ruthenite phase of perovskite structure. It also seems impossible to reconcile any other atomic arrangements for a compound Ba RuO_3 with the dimensions of the unit cell given and the x-ray intensities observed.

A few preliminary structure factor computations suggest as a possibility the assignment of the recorded 5 x-ray lines to a hypothetical, cubic, form of ruthenium dioxide, possibly stabilized by barium oxide, and different from the common, rutile type, tetragonal form, although similar to it in regard to its deep black color. In placing two Ru^{+4} ions at the locations 000 and 1/2 1/2 1/2, and the oxygen ions at 111/444, 1/4 3/4 3/4, 3/4 3/4 1/4, and 3/4 1/4 3/4, one obtains an intensity ratio of approximately 10:1 for the reflections (110):(200). This may, or may not, be considered in poor agreement with the experimental data, in view of the fact that the (200) reflection has not been observed at all. Above all, this structure would involve a change from the octrahedral coordination of 6 oxygen ions around a Ru^{+4} ion, such as in the common rutile type structure of RuO_2, to a fourfold, tetrahedral coordination in an anti-cuprite (Cu_2O) type structure. At present, germanium seems to be the only element known to occur in both a rutile structure (6 fold coordination) and a structure (quartz type) with 4 fold coordination. In considering the chances of ruthenium also occuring in both coordinations, it is found that the radius ratio of the Ru^{+4} and O^{2-} ions seems to approach if not actually reach the lower limit for the range of the 6-fold coordination, at 0.41, below which 4 fold coordination becomes the energetically more stable structure: We consider, as an approximation, the ratio $\frac{d_{Ru-O} - r_O}{r_O} = 0.41$ in which d_{Ru-O} = 1.97 Å is the approximate distance between Ru^{+4} and O^{2-} in tetragonal

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RuO_2 (Strukturbericht) and r_0 is 1.40 Å. It is seen that the ratio comes indeed close to the limiting one for 6-fold coordination. This situation is further illuminated by the rather small distance between two oxygen ions, of only 2.4 Å, in tetragonal RuO_2 (and, for that matter, in several other compounds of the rutile type). A tendency towards a conversion, under suitable conditions of temperature and degree of purity, to smaller, less "crowded" coordination, may thus be indicated. If we further consider that in rutile type GeO_2 the corresponding "radius" ratio is only 0.35, and that in spite of this fact GeO_2 occurs in both the 6-fold and 4-fold coordinations as mentioned above, we may conclude that substances in the border range can assume structures of both types of coordination. Since Ru^{+4} must be considerable larger than Ge^{+4}, it is only reasonable that RuO_2 would not take on quartz structure, but instead, under suitable conditions an apparently new, anti-cuprite, type of XO_2 structure, tentatively proposed here, and presumably intermediate between the quartz and rutile structures, as far as "radius" ratio and polarizability of the ions are concerned. The latter factor probably plays a significant roll in the case of Ru^{+4} which is not of noble gas type electronic configuration, but in which 4 electrons remain attached to a shell of Krypton configuration. Ru^{+4}, as contrasted to more rigid ions such as Ti^{4+}, may thus be one of those cations whose partial penetration by, and polarizability in the field of comparatively small negative ions may contribute decisively to the forces involved in the binding. It is possible to imagine that tetrahedral symmetry may result in such a case.

The question of the possible occurrence of tetrahedral coordination of oxygen around Ru^{+4} appears to be of sufficient interest for a general understanding of the chemistry of this element, and in particular the acid-base behavior of the dioxide to warrant further experimental investigation of the relationships discussed in the foregoing.

Miscellaneous X-Ray Diffraction Work

a) Determination of the Form of Carbon Present in Cobalt Metal. Powder x-ray patterns of cobalt metal from Eimer and Amend Company, submitted by C. P. Stanford of the Physics Division, and containing 2% carbon, did not show the lines of any of the two carbides of cobalt known. However, a broad diffraction ring of comparatively high intensity at $\theta = 6.4°$ (Fe K_α radiation) and 3 very weak diffraction lines with spacings d = 5.12, 4.68, and 4.32 Å, are present on the film, beside the x-ray lines of hexagonal cobalt and weak ones of its cubic modification. The substance producing the lines and the amorphous ring have not been identified, but it seems an almost inescapable conclusion that they must represent heretofore unknown almost amorphous compound of carbon and cobalt. It is believed that only a combination with cobalt would enable the 2% carbon present to produce as strong a diffraction effect as that observed.

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b) Corrosion Films on Beryllium Metal and Stainless Steel. Attempts to obtain diffraction effects from the surface film of corroded metal pieces of beryllium and stainless steel, submitted by J. E. Draley, Metallurgical Division, and A. S. Olsen, Technical Division, respectively, failed due to the insufficient thickness of such films. The samples were referred to examination by electron diffraction. Three weak lines obtained in one case of a comparatively thick deposit on stainless steel were tentatively ascribed to adsorbed sodium bichromate which was a constituent of the corroding solution.

c) A Precision Measurement of Two Cobalt-Iron Alloys, submitted by S. Siegel, yielded the values 2.849 ± 0.001 Å and 2.847 ± 0.001 Å for the lattice constants of the alloy FeCo, cooled slowly from 760° (ordered lattice) and cooled fast in the form of a casting (disordered), respectively, in good agreement with values of the literature.

d) Several dozen samples of elements and compounds submitted by C. G. Shull in connection with neutron diffraction studies were checked for phase purity.

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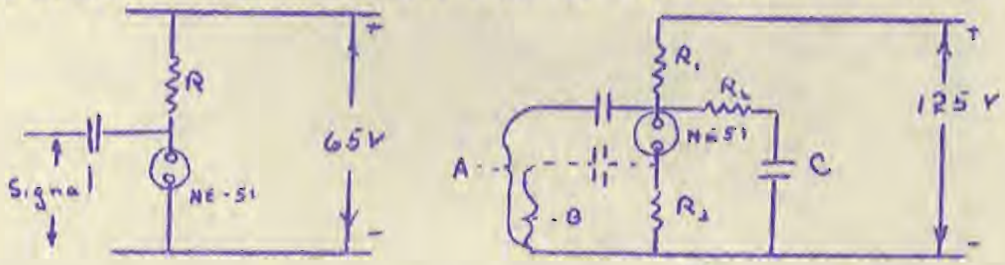
Instruments and Physical Measurements

Preliminary Experiments with Gas Tube Circuits
(J. H. Parsons)

In many applications the power consumed by an electronic mechanism is a major consideration due to the great multiplicity of electron tubes involved or due to the lack of available power. Nearly all of the power consumed by ordinary circuits is dissipated as heat. Many of the component circuits in a mechanism are binary in action, i.e., the circuits are either conductive or non-conductive. Examples of this type of circuit are scalers, multivibrators, univibrators, and some coincidence circuits. A two element gaseous tube such as the common neon glow tube can be used as binary action component in many cases with a great saving of power since these tubes require no heater power.

The binary action of the neon glow tube can be controlled by an applied voltage pulse. The controlling action can be demonstrated in the current switch shown in Figure 1A. The NE-51 (smallest of the neon glow tubes) starts conducting when a potential of about 70 volts is applied and stops conducting when the applied voltage is reduced below 55 volts. A direct voltage



1B

that is greater than the extinguishing voltage and less than the striking voltage is impressed on the tube through the series resistor. With this condition, the tube will not conduct until some positive applied pulse causes a momentary voltage on the tube that exceeds the striking voltage. The tube will remain conducting until some applied negative pulse causes the voltage on the tube to drop below the extinguishing voltage. During conduction the voltage on the tube (due to the voltage drop through the resistor) will be equal to the extinguishing voltage.

A very simple univibrator can be made using these characteristics. As shown in Figure 1B the tube will be normally conducting. A negative pulse at A or a positive pulse at B will cause the tube to be non-conductive. The tube will remain non-conductive until the condenser c changes to some voltage at which time the tube again becomes conducting. These circuits can be made quite sensitive so that a one volt pulse can cause action to start. The action occurs with a large voltage change thus there is not amplification of the input pulse. The time of action is controlled by the time constant of the $(R_1 + R_2)$ C circuit.

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Since these circuits are responsive to both positive and negative pulses and also quantitatively sensitive to pulse voltages of either sign, they may be used for either coincidence (threshold) action or anti-coincidence (inhibiting) action. These circuits have a great similarity to the electrical action of neurons and it is therefore suggested that the name "neurovibrator" be applied.

A triggered multivibrator may be made by coupling two neurovibrators as shown in Figure 2. As shown, the circuit will be stable with both tubes

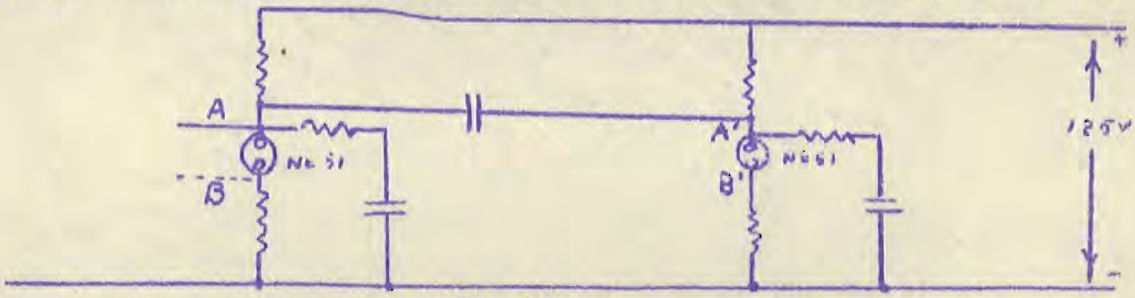

Fig 2

conducting. A negative pulse at A or A^1 or a positive pulse at B or B^1 will start the action. The action will consist of oscillation of both neurovibrators. This action will continue until some synchronized pulse is applied at A, A^1, B, or B^1. This could be supplied by connecting A^1 to B or A to B^1. This utilizes the inhibitory or coincidence action. This circuit could correspond to the so called memory neuron.

These tubes can also be used for a very simple scale of two. The scaling circuit is shown in Figure 3. The action starts with one tube conducting. A negative pulse will cause conduction to be "transferred" from one tube to the other. Thus the circuit can be used as a binary scaling pair.

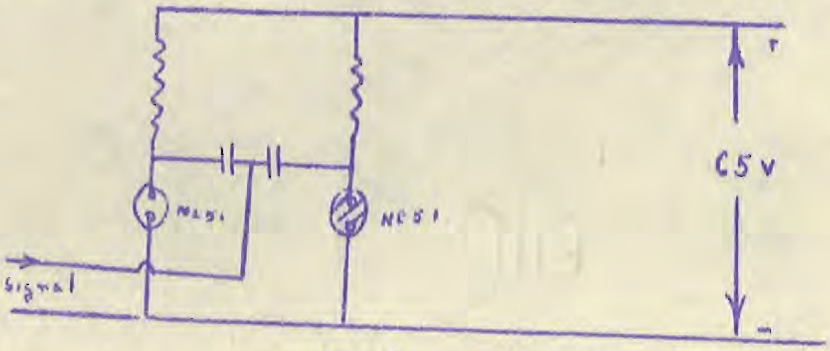

Fig. 3

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All of these circuits operate on the potential difference between striking voltage and extinguishing voltage. It is desirable that this difference be as great as possible. This difference can be increased over commercially available tubes by increasing the gas pressure to about 12 cm. Hg.

It has been found that these circuits are not only economical in power consumption but usually require fewer parts than the corresponding electronic tube circuit. They do, however, operate with longer action times than the convential equivalent.

The Use of Proportional Counters in Coincidence Measurements

(C. J. Borkowski - R. W. Dandl)

Proportional counters previously described (MonII-432) are ideally suited for beta-gamma coincidence measurements. First, the short dead time less than 1 microsecond, allows rapid counting with small coincidence corrections - 1% loss per 500,000 counts per minute and second, the rise time of pulses in a proportional counter is considerably shorter than in Geiger counters. Furthermore, since Argon-CO_2 gas fillings can be used in the proportional counters the collection time of electrons released by an ionizing event is 10 times shorter than in Geiger counters, thus there are fewer missed beta-gamma coincidences due to time lags in collection.

A beta-gamma coincidence circuit was set up for R. Brosi for the evaluation of total disintegration rates of Xe^{135} and for the determination of the fraction of the short half life isomer of Xe^{135}. In order to obtain a higher efficiency for the detection of the 0.25 Mev gamma rays from Xe^{135}, a gold plated end window counter having a 50 mg. per sq. cm. gold foil between the mica and the sensitive volume of the counter was used as a proportional gamma counter. The efficiency of this counter was nine times greater than the conventional brass mica end window counter. The Beta counting rates were 500,000 counts per minute. The Beta and Gamma channels each consisted of a fast amplifier feeding a coincidence circuit designed by W. Bradley. The resolving time of the coincidence circuit was only 0.5 microsecond and was the limiting factor in all the measurements, since the random coincidence rates determined the precision of the results.

In order to fully utilize the fast rise time and the short dead time of the beta proportional counters a coincidence circuit with a resolving time of .05 microseconds is being built.

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A Compact Beta Proportional Counter
(E. Fairstein)

An experimental model of beta proportional counter is nearing completion(which will be considerably smaller than any presently available).

The unit has a built-in rate-meter with provisions for plugging in an external recorder and/or scaler. The panel meter is a precision meter with a logarithmic movement. This feature permits reading to constant percentage accuracy anywhere on scale and decreases the number of ranges necessary for a given coverage.

The coverage is from ten to one million counts per minute in five decade ranges. The last decade has been included to give a rough idea of the rate of a hot sample, and it is not meant to give accurate readings. The dead time of the instrument is adjusted to six microseconds, which gives a coincidence loss of one percent per 100,000 c.p.m.

The overall accuracy when using the rate meter will be plus or minus two percent. This figure does not include errors due to counting statistics. These must be separately determined. The rate-meter drift is less than one-half percent per hour.

The amplifier is a three stage unit with no compensation or feed-back. The rise and fall times are each approximately one-half microsecond, which are sufficiently good for this type of instrument. The amplifier feeds a two-tube pulse shaping network, which in turn feeds an integrating vacuum-tube voltmeter for the counting-rate indication.

The unit is designed for use with a fifty percent geometry flow-type chamber mounted separately from the instrument.

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4- ANALYTICAL SERVICE

Summary of Analyses Made by Analytical Service Groups
February 15 to May 15, 1948.

	Pilot Plant Control	Lab. and Semi-Works Control	Water Analyses	Production Analyses	General Radio-Chem.	General Ionic	Spectro-graphic Analyses	Total
Present Personnel - Tech.	4	2	1	4*	8*	2	4	
Non-tech.	25	8	4	19*	11*	3	-	
Division								
Technical	9781	8566	1284	----	1203	149	73	21,056
Chemistry	----	223	----	----	97	13	200	533
Production	----	----	----	2408	----	----	43	2541
Tank Farm	---	----	60	1488	16	----	---	1564
Radio-Isotope Development	----	----	----	3304	----	----	---	3304
Metallurgy	----	----	24	----	----	----	---	24
Steam Plant	----	----	60	----	----	----	---	60
Misc.	----	----	----	----	----	12	37	49
	9781	8789	1428	7200	1316	174	354	29,041

*On April 1, five technical people and three technicians were transferred from Production Analyses to the General Radiochemical Group. However, this summary is on the same basis throughout the quarter for the sake of uniformity.

It is readily noted that as previously the major load of the analytical service groups is from the Technical Division (about 70%) with the major part of the rest coming from the Operations Division. The total number of analyses made in this quarter was about 20% greater than in the last primarily due to increased demands from the Technical Division. The demands of the Technical Division seem to have reached a fairly constant level now except that there seems to be an increasing demand for radiochemical analyses.

1200 Area Control Group (E. J. Frederick, W. T. Mullins, H. A. Parker, J. N. Weeks)

This group is doing the work for the "25" Pilot Plant only. This is sufficient load for this lab at Hanford activity levels. This group is now short one shift supervisor, which is badly needed for effective operation.

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1300 Area Control Group (L. T. Corbin, G. R. Wilson)

Since there will be little activity in the "23" process until the new Technical Division solvent extraction building is completed, this group has been doing primarily the work for the "25" laboratory and semi-works groups.

Water Analyses Group (J. H. Edgerton)

The analytical load of this group has increased by about 20%, but the present personnel seems to be adequate to handle this.

General Radiochemical Analysis (C. L. Burros, O. M. Bizzell, G. W. Leddicotte, A. Brown, D. I. Gilbert, J. S. Gill, D. J. Coombe, R. H. Sampley)

The demands on this group have increased considerably during this quarter. The part of the radio-isotope analysis group doing analyses for development groups has been consolidated with this group, but due to lack of space will remain in the 706-D building until other facilities are available.

General Ionic Analysis (D. E. LaValle, W. Wolkowitz)

This group is at present inadequate for the number of samples submitted. If there is any indication that this load will continue at the present level, further personnel must be obtained.

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

The work of this group is now confined to radio-isotope production activities, all development work having been transferred to other groups.

Spectrographic Laboratory (C. Feldman, M. Murray, A. J. Estepp, J. Gillespie)

In addition to routine spectrographic analyses the following development work was done:

It was found that the addition of an internal standard is unnecessary if the OH line 3084 A is used as a comparison line for determining Al in 8% $Ca(NO_3)_2$ solutions (as Ca).

The circuit of the intermittent A.C. arc was altered to permit more spark-like operation.

Work was begun on the following:

(a) Determination of traces of Ag in Pd. A briquetting method is being investigated.
(b) Surveying available sparking and A.C. arcing conditions preliminary to setting up low-background standard plates for the R.E.
(c) Preparation of an absolutely calibrated working curve for Hf in Zr.

Sensitivity limits were determined for 23 additional elements by the porous cup method.

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