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CLINTON NATIONAL LABORATORY

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Chemistry Division

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REPORT OF THE CHEMISTRY DIVISION

FOR THE MONTHS SEPTEMBER, OCTOBER AND NOVEMBER, 1947

* * * * *

J. R. Coe and E. H. Taylor

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ABSTRACT

1. Reactor Fuels

Basic Research

In the comparison of the hydrolytic behavior of plutonium with that of the other heavy elements, it has been found that uranium(IV) forms a polymer similar to that of plutonium(IV) in its absorption spectrum, and that it is formed under similar conditions of pH and concentration. Further studies have confirmed that neptunium(V) exists in both acid and neutral solutions as NpO_2^+ and that hydrolysis occurs only in alkaline solutions. To extend the comparison of hydrolytic behavior further, new studies of the hydrolysis of cerium(IV) are under way. The self-reduction of Pu(VI) studied previously in nitrate solution has been studied in perchlorate solution. The rate appears to be linear with concentration, and to be somewhat lower than that in nitrate solution.

Two samples of uranium 234 weighing 0.18 and 0.44 micrograms have been prepared and are ready for irradiation at Hanford to determine the neutron cross-sections.

Work has been started during this quarter on the application of ion-exchange separations to the heavy elements. It appears that it may be possible to concentrate protoactinium from $HF-H_2SO_4$ extracts of ores by adsorption on Dowex-50 resin. Experiments on the separation of protoactinium from thorium show that the separation factor is greater than 1000 in alkaline (pH = 12) solutions of citrate, oxalate, tartrate, carbonate, fluoride and pyrophosphate, and that it is less than 0.001 in 1 molar HF, with Pa being preferentially adsorbed in the first case and desorbed in the second. Using alkaline fluoride solution it appears to be possible to separate Zr from Cb, Ta, Th, U(IV) and Pu(IV), and with 0.5 M HF to separate Zr, Cb and Pa from Th.

Process Research

In the process for recovering uranium from the heterogeneous pile a beta decontamination factor greater than 10^6 has been obtained in a single cycle. The improvement seems to be due to the introduction of MnO_2 as a scavenger, to the use of higher pH (1.5 - 1.8) and reducing conditions, and to the complexing of ruthenium with s-diphenylthiourea. A scheme has been postulated to explain the anomalous distribution of Ru in the process, and the behavior of Np has been studied.

In the process for isolating U^{233} from thorium, the pilot plant has been modified to provide standby production equipment for U^{233}. Studies of column capacity and overall decontamination have been made with the

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modified apparatus. The decontamination from Pa^{233}, 6×10^6, seems entirely adequate, but the fission product decontamination, 10^5, is short of the factor of 10^6 which is required. There are indications that the necessary improvement by a factor of 10 can be attained without major changes.

2. Radioisotopes

Radioactivity Measurements and Standards

A cobalt alloy is now available for monitoring samples introduced into the pile. The monitor can be measured quite simply in the high pressure gamma ionization chamber. The program on beta ray standards is going forward, and a second comparison of different methods of measuring radioactive phosphorus has been completed. Use of a calibrated GM counter gave a deviation of +1.5%, use of the beta ray calorimeter in connection with the known average energy gave a deviation of -0.6%, and two comparisons with a Bureau of Standards radium D-E standard gave deviations of -1.8 and +0.6% from the average of the three methods, 7.78×10^8 dis/sec. A comparison of methods used at this Laboratory for I^{131} gave the following results: Beta counting by the Production Group, 3.7 mc/ml; measurement in calibrated ionization chamber, 3.45; and beta counting by calibrated GM counter, 3.43. The work to date with the thin lens beta ray spectrometer has been summarized, and results are presented for the following isotopes:

Zn^{65}	Ca^{45} (180 d)
Cs^{134} (3 h)	Ce^{144} (275 d), Pr^{144} (17.5 m)
Cs^{134} (2 y)	Cu^{64} (12.8 h)
Co^{60} (10.7 m)	Eu
Co^{60} (5 y)	Rh^{106}
Sc^{46}	Xe^{135} (10 m)
Sc^{46} (85 d)	Xe^{135} (9.2 h)
Bi^{210} (5 d RaE)	I^{135} (6.7 h)
P^{32} (14.3 d)	I^{133} (22 h)
K^{42} (12.4 h)	Er^{169} (9.4 ± 0.2 d)
Pr^{142} (19.3 h)	Er^{171} (7.5 ± 0.2 h)

Production and Processing

Work has been begun on the removal of plutonium from fission product radioisotopes. In the first experiments it appears that plutonium can be separated from cerium by eluting from resin columns with $NaHCO_3$ or $Na_2P_4O_7$ solutions. Decisions have been reached as to the best methods for preparing certain isotopes in high specific activity. For Ca^{45} it has been decided to irradiate enriched Ca^{44} at Hanford as soon as it is available and to use the Sc (n,p) process only for immediate needs or for specific activities higher than 250 mc/gm Ca. It has likewise been decided to use enriched Fe^{58} for producing Fe^{59} and discontinue the Co (n,p) reaction. The process for producing xenon for cross-section measurement seems to be approaching a final

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and suitable form. It is now possible to obtain an overall yield of 60 to 65%. A method for its assay has been worked out and equipment for the full-scale operation is nearly complete.

Apparatus

Some data are presented for the effectiveness of certain dense, transparent liquids as radiation shields. Using a 2 foot thickness of liquid to shield a source emitting gamma rays of about 1 Mev and giving about 50 to 70 mr/hr through water, it was found that 70% $ZnCl_2$ solution reduced the intensity to 1 to 7 mr/hr and that acetylene tetrabromide reduced it to less than 1 mr/hr.

Use of C^{14} in Organic Chemistry

In the synthesis of organic compounds containing carbon 14 it has been found possible to prepare methanol in 75% overall yield by the hydrogenation of CO_2 with lithium aluminum hydride in diethyl carbitol. It is expected that this method will replace the high pressure hydrogenation at present in use. A method for preparing sodium cyanate by the thermal decomposition of sodium urea in yields of 97% has been developed.

3. Supporting Research

Radiochemistry

In the field of radiochemistry a number of new observations have been made. A gamma ray of 2.7 Mev has been found in 2.6 h Mn^{56} by counting the photoneutrons produced by it in heavy water. Work with samples of selenium enriched in Se^{78} and Se^{80} confirm that the 57 m Se activity should be assigned to mass 81. Cyclotron irradiation of molybdenum enriched in Mo^{97} confirms the previous assignment of mass 97 to the 90 d technetium activity. Pile irradiation of enriched Mo samples have confirmed previous assignments of the 67 h and 15 m activities to masses 99 and 101, respectively. The half life of the long-lived technetium activity has been determined to be 9.4×10^5 y by measurement of its specific activity.

Radiation Chemistry

Work in radiation chemistry continues on the radiation decomposition of pure water and of solutions. Simultaneous experiments on purified water as a liquid and as ice indicate that the material responsible for the erratic behavior previously noted must be distributed throughout the water, since the same erratic behavior is observed with the ice, in which case the walls of the vessel could not be important. It has been shown that aluminum is inferior to glass as a container for such experiments, and other materials are to be tried. The net decomposition of water is less at 110° C. than at

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room temperature, a fact which may be of importance in the case of high temperature, high pressure homogeneous piles. In the decomposition of aqueous H_2SO_4 it has been shown that a steady state pressure actually exists by approaching this pressure from both sides.

Radiation Calorimetry

The gamma ray calorimeter previously described has been used in an attempt to find the 65 Kev gamma ray reported to be emitted in the decay of Au^{198} by using silver as a selective absorber for this radiation. An increase in energy absorption of about 8% would be expected if such a radiation were emitted in every disintegration, but no increase greater than 2% was observed.

4. Technical Services to Clinton National Laboratory Research Groups

Diffraction and Microscopy

Work in microscopy and in electron and X-ray diffraction continues to be done for a number of groups in the Laboratory. Considerable effort was devoted during this period to studies of corrosion films formed on aluminum in heat transfer experiments. Considerable attention has been given to the design of a high temperature oven for use with the X-ray spectrometer.

Instruments

In the field of instruments, studies have been made of the use of proportional counters for detecting beta and gamma radiation because of their many advantages over Geiger counters. Another type of alpha pulse analyser has been proposed and studied far enough to show its feasibility. It is intended for use with samples of lower activity than can be handled on the sweep type differential analyser previously developed.

Analytical Chemistry

Service analytical work has been performed at a somewhat greater rate than before. The control groups for the 1200 and 1300 areas seem now to be adequate for the loads expected in the near future. The groups doing general ionic analyses and analyses for the radioisotope production are at present quite understaffed for the amount of work demanded.

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1. REACTOR FUELS

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

Hydrolytic Behavior of U(IV)[1]

1. The hydrolysis of U^{+4} has been investigated as a function of concentration of U(IV). Analysis of the data has as yet not been completed.

2. Polymer of U(IV): Although as yet no systematic study of the polymerization of U(IV) has been carried out, it can now be stated that U(IV) forms a polymer under very similar conditions as Pu(IV). Polymerization occurs in general at low acidities and its rate is somewhat smaller for U(IV) than for Pu(IV). In this connection it is of interest that polymerization of U(IV) has been observed after prolonged standing at room temperature in 0.25 M $HClO_4$ at high U(IV) concentrations (e.g. 0.1 M). Also some polymer is formed, as indicated by the color of the solutions, during the reduction of UO_2^{++} with zinc with initial acid concentrations as high as 1 and 2 M and final acid concentration still ca 0.5 M.

Polymeric solutions of U(IV) are colored intensely greenish-black, in concentrated solutions they appear to be almost black. The polymer has a characteristic spectrum reminiscent of that of polymeric Pu(IV) with high absorption at short wave lengths as shown in Figure 1. The solution from which the polymer spectrum was taken was prepared by permitting a 0.12 M U(IV) solution in 0.25 M $HClO_4$ to age for 30 days at room temperature. It appears that after this time polymerization was not complete.

If polymeric solutions of U(IV) are treated with sodium hydroxide a brownish-black precipitate forms, probably the hydroxide of the polymer. If the solution also contains some unpolymerized U(IV), a light green precipitate forms at slightly higher pH. This difference in the color of the hydroxide of the polymer and of the (normal) hydroxide is much more striking than the corresponding differences in the case of Pu(IV).

Hydrolytic Behavior of Np(V)[2] (F. Nelson, K. A. Kraus) P.A. CX3-2

A few spectrophotometric measurements have been made on the hydrolysis of Np(V). It was found that the spectrum of Np(V) near pH 4 is practically indistinguishable from that in 0.1 M HCl even if the solution had previously been adjusted to pH 11.

After acidification of an alkaline (pH 11) supension of Np(V) the 985 mμ band of NpO_2^{+} grows in with measurable speed, which probably represents the rate of dissolution of the precipitate and the rate of depolymerization.

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(1) For earlier work see: Quarterly Report of the Chemistry Division, Mon N-370, September 2, 1947, p.66

(2) For previous work see: Quarterly Report of the Chemistry Division, Mon N-311, June 24, 1947, p.63

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By K. A. Kraus

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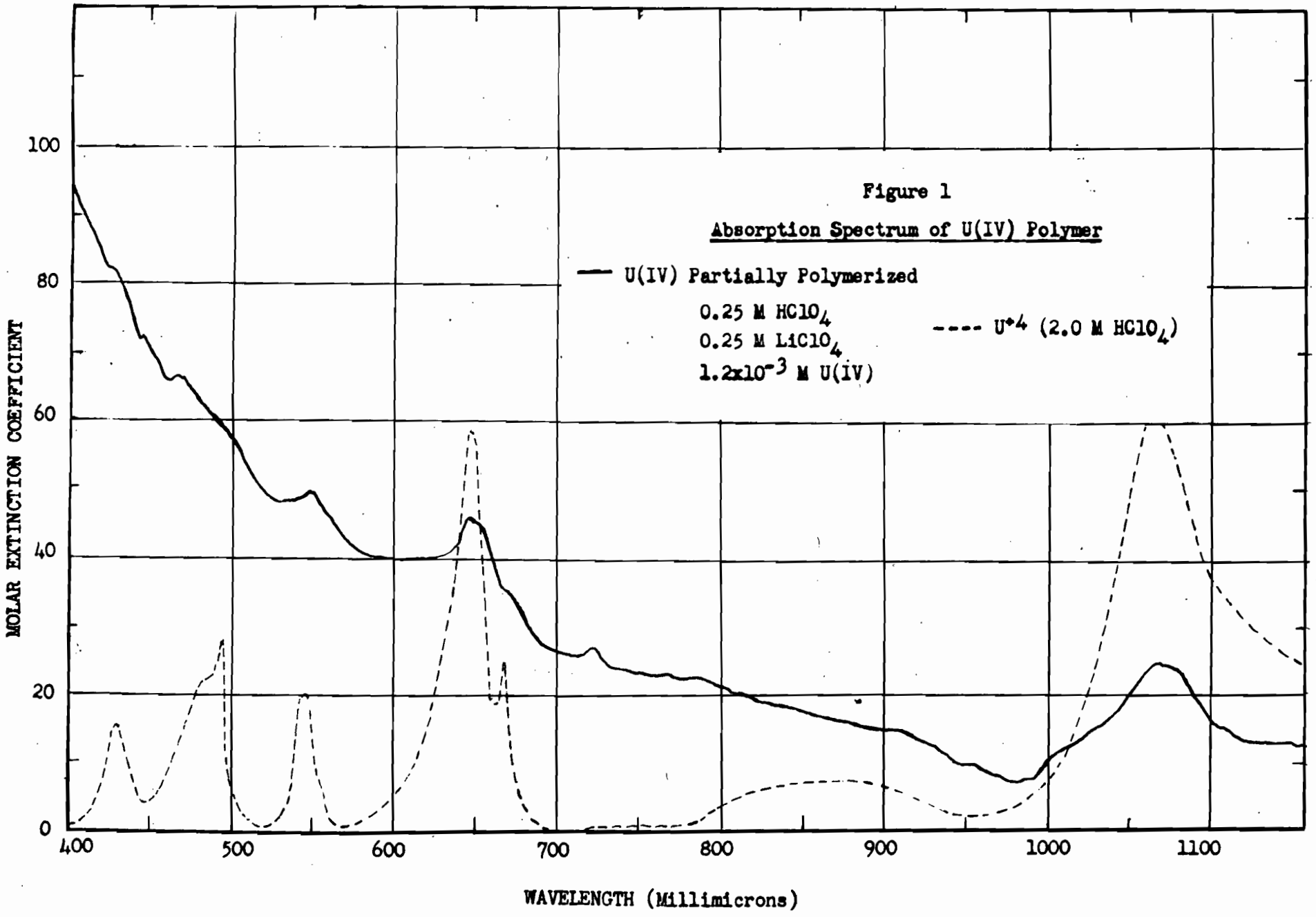

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Within five minutes of acidification to pH 3.3 the pH rises to pH 4 and the extinction coefficient of the most prominent band of Np(V) was within 95% of its value for 0.1 M HCl. On longer standing at pH 4 the spectrum is indistinguishable from that in 0.1 M HCl.

These observations are in agreement with the conculsions reached from the acid-base titrations of Np(V), that the same species (NpO_2^+) exists both in acidic and neutral solutions of Np(V), hydrolysis occuring only in weakly alkaline solutions.

The Interference of Chloride Ions in the Analysis of U(IV) with Permanganate. (F. Nelson, K. A. Kraus) P.A. CX3-2

In the previous Quarterly Report (Mon N-370, p.71) experiments were reported which showed that during the titrations of U(IV) with permanhanate in the presence of chloride ions high titres were obtained which indicated catalytic action of U(IV) on the oxidation of Cl^- by MnO_4^-. It was believed that the catalytic interference is due to the fact that an intermediate oxidation state of maganese causes oxidation of chloride ions more rapidly than oxidation of U(IV) to U(V) and U(VI). Under this assumption the catalytic effect is directly connected with the highly irreversible nature of the U(IV)-(V) couple and possibly its moderately negative (ca -0.8V)potential.

It would therefore be expected that the analagous interference which has been reported in the literatue for ferrous titrations would be less marked since the $Fe^{++} - Fe^{+++}$ potential is highly reversible and since furthermore Fe^{++} is a somewhat more powerful reducing agent than U(IV) with respect to U(V).

A number of permanganate titrations of ferrous solutions in the presence of chloride ions have been carried out, the results of which are shown in Table 1. From this table it can be seen that the interference is, as expected, considerably less for ferrous ions than for U(IV).

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

On the basis of the available data there are large differences in the hydrolytic behavior of cerium(IV) and U(IV) (see Mon N-370, p.64). Since the data on cerium(IV) had not been collected with high precision, experiments are now under way to repeat this earlier work with considerably more care.

Spectrophotometry of Pu(VI) at Low Acidity. (R. W. Holmberg, K. A. Kraus) P.A. CX3-2

As reported in the previous Quarterly Report (Mon N-370, p.76), the rather serious pH drifts during the spectral determinations caused considerable uncertainties in the calculation of the stability constant of the carbonate complex of Pu(VI). For this reason further work on this problem was temporarily abandoned and equipment to measure pH and absorption spectra simultaneously has been designed and constructed. Similarly experiments have been carried out to further improve the precision of the micro-diffusion analyses for carbonate.

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Table 1

Catalytic Action of Fe(II) and U(IV) in the Oxidation of Cl^- by MnO_4^-

ca 4.5 cc 1.7 M H_2SO_4, ca 4.0×10^{-3} M Fe^{++}		
ml 5.0 M HCl	Moles Cl^- per mole Fe(II)	Equivalents MnO_4^- per mole Fe^{++}
0	0	1.00
0	0	1.00
0.050	5.7	1.03
0.050	5.7	1.02
0.100	11.4	1.02
0.500	57.0	1.03
ca 5.5 cc 1.7 M H_2SO_4, ca 9.8×10^{-3} M U(IV)		
ml 5.0 M NaCl	Moles Cl^- per mole U(IV)	Equivalent MnO_4^- per mole U(IV)
0.050	12.3	2.96

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Self-Reduction of Pu(VI). (G. E. Moore, K. A. Kraus) P.A. CX3-2

In the previous Quarterly Report (Mon N-370, p.60) experiments were reported on the self-reduction of Pu(VI) in nitrate solutions. Similar experiments have now been carried out for perchlorate solutions and are reported here.

The Pu(VI) perchlorate solutions were prepared by oxidation of Pu(IV) nitrate solutions with fuming perchloric acid(3). The Pu(VI) perchlorate was dissolved in concentrated perchloric acid and diluted. Spectrophotometric examination showed no detectable amount of other oxidation states of Pu. The Pu(VI) solutions were kept electrolytically oxidized until used.

Self-reduction experiments were carried out near pH 2.8, 6.0 and ca 11 with ca 3.8×10^{-3} M Pu solutions, 0.9 M in ClO_4^-). As in the nitrate series all the reagents were analyzed for reducing agents by permanganate titrations. After adjustment of the pH the solutions were sealed into spectrophotometer cells with paraffin, care being taken not to establish contact between the paraffin and the solution. After 25 days the pH 2.8 solutions was divided into two parts, one resealed with paraffin and the other one placed into a clean spectrophotometer cell with ground glass stopper.

The spectra of the solutions were followed for 76 days. Direct spectral examination was used for the solution at pH 2.8 while for the other solutions acidified (pH 2-3) aliquots were used. These aliquots were discarded after the analyses.

The results of this series of experiments were very similar to those for nitrate solutions. The rate of self-reduction at pH 2.8 was linear and approximately 0.014 equivalents per day during the first ca 50 days, the rate decreasing slightly on longer standing (see Table II). There was no major difference between the solution sealed with paraffin and that closed with a glass stopper, showing that the paraffin did not cause any spurious reduction. This rate of self-reduction in perchlorate solution appears to be somewhat smaller than for nitrate solutions (ca 2% per day). Similarly the nitrate solution at this pH appears to show a more pronounced levelling off on long standing.

In view of the fact that the solutions at higher pH developed turbidity and precipitates during the interval, the analytical figures for these solutions are not very reliable. However it appears that the rate of self-reduction at pH 7 is $2.1 \pm 0.5\%$ per day during the first 25 to 30 days and $1.8 \pm 0.5\%$ at pH 11. In both cases there may be some decrease in the rate on longer standing. These results are within experimental error the same as for the nitrate solutions of corresponding pH.

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(3) See: Mon N-370, p.79

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Table II

Self-Reduction of Pu(VI) in Perchlorate Solutions at pH 2.8

3.8×10^{-3} M Pu, 0.9 M ClO_4^-

Time (days)	%Pu(IV)[a]	%Pu(V)[b]	%Pu(VI)[c]	Total
0.18	0.0	0.0	100.0	100.0
1.21	0.0	1.5	98.2	99.7
4.17	0.0	7.5	92.7	100.2
8.02	0.0	10.4	88.2	98.6
12.99	0.0	17.2	80.4	97.6
20.16	0.0	26.9	71.2	98.1
25.00	0.0	34.3	66.2	100.5
46.01	0.0	56.7	42.4	99.1
70.95	3.9	73.9	21.5	99.3

(a) From 400 mμ region
(b) Based on Pu(V) band near 569 mμ
(c) Based on Pu(VI) band near 831 mμ band

Catalytic Disproportionation of Pu(V) by Ferric Ions. (A. Garen, K. A. Kraus)

Several more experiments on the rate of disproportion of Pu(V) in the presence of ferric ions have been carried out in the range 0.25 to 1.0 M H_3O^+. The results were somewhat inconsistant, and it is believed that this was due to the poor temperature control during the spectrophotometric investigation. The experiments therefore have been temporarily abandoned until suitable temperature control equipment has been constructed.

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

In the previous Quarterly Report (Mon N-370, p.82) some details were given on the concentration of americium from Pu waste solutions using ferric hydroxide and lanthanum fluoride precipitations. During the last quarter no large scale steps have been carried out. Instead a number of procedures have been tested on a small scale, and equipment has been assembled and test runs made on the use of Dowex 50 adsorption columns in the isolation.

Attempts have been made, on a small scale, to effect a separation of Am from Pu by permanganate oxidation of the fluoride slurry. These attempts failed, only 0.1% to 0.5% of the Pu being oxidized in half an hour at elevated temperature either using the slurry directly or after evaporation to almost dryness in the presence of nitric acid. After fuming the residue with sulfuric acid and dilution with nitric acid oxidation by permanganate was successful.

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It now appears however that the oxidation with permanganate may be unnecessary and that instead after fuming of the precipitate with sulfuric acid and removal of the calcium sulfate a satisfactory separation may be achieved directly by use of adsorption columns. Experiments to test this method are under way.

Chemistry of Protactinium (A. Garen, K. A. Kraus) P.A. CX3-2

1. Isolation of Pa from Ore Residues. Attempts are being made to investigate the possibility of developing a process for the isolation of protactinium (Pa^{231}) from ore residues, which at least in the first large concentration steps would be simple and reproducible enough to be attractive for commercial production of this element. Most existing processes still suffer either from lack of reproducibility or from the need of using highly corrosive agents at elevated temperatures. However, it was felt that the process of Kraus and Van Winkle (CC-3365) could perhaps be sufficiently changed to permit large scale isolation of protactinium.

In this process the residues are first treated with nitric acid to remove a large amount of the acid soluble bulk of the material without removing protactinium.

The residue is then treated at elevated temperature with HF and sulfuric acid, to leach out the bulk of the protactinium. The fluoride solution is treated until fumes of SO_3 are evolved and thus prepare a solution from which Pa can be carried. From the point of view of large scale production the two steps involving heating fluoride solutions appeared most objectionable and efforts are being made to find suitable substitutions.

Experiments are under way to see if hot HCl, hot $H_2C_2O_4$, hot H_2SO_4, or cold HF treatments could be substituted for the leaching of the ore residue with hot HF - H_2SO_4 mixtures. Of these the cold HF treatment appears most promising at present, ca 80% of the Pa being leached out in two hours. Hot H_2SO_4 caused gel formation and hot oxalic acid gave low yields of Pa.

Similarly experiments have been carried out by S. W. Mayer (see below) to see if an adsorption method could be used to effect a volume reduction of the HF extract without fuming with H_2SO_4. These tests were also sufficiently favorable to make it appear possible to develop a commercial isolation procedure for Pa.

2. Concentration of Pa by an Adsorption Process (S. W. Mayer) Using HF- H_2SO_4 extracts of the residues a Pa isolation process has been tested which would be expected to cause large volume reductions.

Extracts containing 2 M HF and Pa^{233} tracer were passed through a Dowex 50 column to adsorb all cations which are not complexed by HF. The solution thus purified and still containing practically all the Pa was neutralized to pH 12.9. A small amount of yellow material separated. The suspension was passed through a second column of resin in the potassium form. The Pa activity remained on the column. While trying to convert the resin to the acid form with 0.5 M HCl it was found that this concentration of HCl is sufficient to elute the Pa into a small volume. A resin adsorption isolation procedure for Pa which in addition to large volume reduction also permits substitution of HCl for HF thus appears feasible.

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

Complexes of Th(IV) and IO_3^-. At an ionic strength of 0.5, under conditions of relatively high $LiIO_3$ concentration (ionic strength $\simeq$ $LiIO_3$ concentration) a crystalline precipitate has been obtained. Preliminary analyses of this substance gave an iodate to thorium ratio of around six, indicating a double salt. A series of reaction vessels designed to give the solubility of "thorium iodate" under a variety of conditions, at constant ionic strength, were seeded with the crystalline precipitate. They showed much lower and erratic solubilities under all conditions except at high Th(IV) concentration, where there was essentially no change.

The precipitates at high Th(IV) concentration had previously shown IO_3^- to Th(IV) ratios in the precipitates of one to four. More recent values which were conducted on a ten-fold larger scale, using more accurate methods for Th(IV) and NO_3^- showed the following for three precipitates which had stood in contact with the supernatants for periods of from one hour to two weeks (in the extremes).

IO_3^-/Th(IV)	NO_3^-/Th(IV)
3.23	0.07
2.98	0.17
3.04	0.05

The Th(IV) analyses were conducted gravimetrically, employing an oxalate precipitation; an iodemetric titration was used for IO_3^- determination; and a kjeldahl method was used for NO_3^-. Flame tests on a washed precipitate indicated no lithium present.

A pH change on addition of reagents of from 2.6 to 2.2 was observed. If this apparent pH change is real it is difficult to explain with the values used for the hydrolysis constant of thorium (2.5×10^{-4}) and the dissociation constant of HIO_3 (0.16).

Thermal Neutron Cross-Sections of U^{234}. Two U^{234} samples of 0.18 and 0.44 micrograms respectively have been prepared and will be sent to Hanford for irradiation as soon as approval is received.

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Ion-Exchange Separations: The Heavy Elements (S. W. Mayer, E. R. Tompkins and G. E. Boyd) P.A. CX3-5

The preliminary survey initiated last quarter (see MonN-370, page 22) of the possibilities for the employment of ion-exchange column techniques in the separation of elements 90 through 94 from each other, from the fission products, and from aluminum, has continued. Previously, the possibility for the separation of uranium from thorium and from aluminum was reported.

The Separation of Pa from Thorium

In these experiments 27 d Pa^{233} and 24 d Th^{234} (UX_1) were employed as tracers together with a sulfonated hydrocarbon exchanger, Dowex-50. It was found, after testing several eluants, that protoactinium was not eluted by alkaline (pH = 12) solutions of citrate, oxalate, tartrate, carbonate, fluoride and pyrophosphate, whereas thorium was removed readily when both elements were contained originally on a deep bed of exchanger. The ratio of the distribution coefficients (i.e., Pa:Th) for these two elements in these solutions at pH = 12 exceeded 1000. Accordingly, a breakthrough rather than a differential elution technique may be employed to accomplish their separation.

It was found also that 1 M hydrofluoric acid will elute protoactinium rapidly, whereas thorium was removed, if at all, only extremely slowly. With 1.0 M HF the ratio of the distribution coefficients for protoactinium and thorium must be less than 0.001.

The Behavior of Pa, Th, Zr and Cb in Ion-Exchange Columns

The following radioisotopes were used as tracers: 27 d Pa^{233}, 24 d Th^{234}, 65 d Zr^{95} and 35 d Cb^{95}. Buffered polycarboxylic acids at pH's less than four were found to elute all of the foregoing rapidly when the concentration of the singly charged complexing anion was greater than 0.05 M. Four normal sulfuric acid also effected a rapid desorption. A one per cent ammonium carbonate solution was found to elute Pa and Cb slowly. However, if these latter elements are present only in tracer level concentrations in such solutions they will not be adsorbed. If the pH exceeds 11.5, however, extensive adsorption was found. Correspondingly, the use of alkaline fluoride solutions appeared to furnish the basis for a possible separation of Zr from Cb, Pa, Th, U(IV), and, as will be described later, Pu(IV), and presumably Ta. (The use of an alkaline fluoride solution as an eluant could be made the basis for the recovery, concentration and separation of zirconium from other metals except titanium and presumably hafnium. There is some possibility that the fluoride solution will separate zirconium from hafnium.)

Solutions 0.5 M in hydrofluoric acid were found to elute Zr, Cb and Pa away from thorium quite rapidly. Addition of boric acid to the 0.5 M HF solution to the point of saturation served to break the Zr, Cb and Pa fluoride complex ions and to allow these elements to be re-adsorbed.

In contrast to the above, when iodate or monohydrogen phosphate was added to a solution of complexing agent (i.e., carbonate) with the intention of preventing the elution of zirconium or thorium, no such action was observed, despite the fact that zirconium and thorium iodates and phosphates are quite insoluble.

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The Cation Exchange Behavior of Plutonium

The exchange adsorption of plutonium is complicated by the possibility that the element may exist in aqueous solution in at least three oxidation states and in one polymeric hydrolytic form. When one molar hydrofluoric acid was used as eluant, Pu(IV) remained on the column while Pu(VI) was eluted, as anticipated on the basis of its probable occurrence as plutonyl ion. The experimental evidence for this consisted of the observation that no plutonium was coprecipitated with LaF_3 from the untreated eluate. Treatment of the eluate with a suitable reducing agent then gave subsequent LaF_3 precipitates containing Pu^{239} activity. Plutonium (IV) was found to be eluted rather slowly by 5% oxalic acid after washing the bed with hydrofluoric acid.

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Phase Rule Studies

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

Study of the phase relationships in the system uranyl sulfate-water through the temperature range of 200 to 400°C. is in progress. Previous reports have given quantitative data for the temperature-concentration relationships in this system below 200° and qualitative observations above 200°.

For the higher temperature range, a vessel was desired which would have sufficient strength to withstand the pressures involved, which would not show appreciable corrosion by the solution or its vapor, and which would permit visual observation of the phase changes and the critical phenomena. Pyrex glass was found unsatisfactory because noticeable etching occurred and the percentage of strength failures was rather high even in heavy-walled 2 mm. capillary. Transparent quartz tubing with a 5 mm. bore and a wall thickness of 5 mm. is now being used. No observable etching has been detected and, even though strength failures have occurred, quartz tubing of these dimensions seems satisfactory in this respect. Care must be taken to preserve adequate wall-thickness at the ends of the tube.

Some difficulty has been experienced in obtaining reliable temperature measurements. Since there is no obvious method of placing the thermocouple junction in close proximity with the solution without weakening the walls of the tube, an effort has been made to design a heating block which gives a reproducible temperature gradient from the heating coil to the solution provided the rate of temperature change of the heating coil is constant. Then, by placing the thermocouple in a well in the heating block and by applying suitable calibration corrections, the temperature of the solution could be obtained. The apparatus has undergone several changes in design and considerable time has been spent obtaining calibration curves. It is not yet entirely satisfactory and further modifications are being planned.

Although some data has been obtained for the system above 200°, doubt exists concerning the accuracy of the temperature measurements. Such data will not be reported until reliable information is obtained.

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The Recovery of Uranium from Enriched Piles. (H. R. Baxman, R. L. Belcher, G. D. Calkins, G. R. B. Elliott, J. P. McBride, F. T. Miles, J. M. Ruth, E. H. Turk) - P. A. CX5-9.

Introduction and Summary

The main problem of interest in the solvent extraction process for recovering enriched uranium continues to be the improvement of fission product decontamination. Batch tests have given β decontamination factors over 10^6 in a single cycle. This improvement is due to several factors, of which the important ones seem to be: scavenging with manganese dioxide (which removes only a small fraction of the activity but causes great improvement in later steps), use of high pH (1.5 to 1.8) and reducing conditions (ferrous iron plus a holding reductant) in the feed, and the complexing of ruthenium with s-diphenylthiourea (DPT) before the stripping step.

The anomalous distribution behavior of ruthenium tracer has been studied intensively, and a scheme has been postulated which is able to explain the results. The use of DPT to complex ruthenium has been more thoroughly tested. It has proved satisfactory in all variations of process solutions and has shown no bad effects on the distributions of uranium and neptunium. It causes no improved decontamination from zirconium or columbium.

The behavior of neptunium in the process has been investigated. While it had been assumed that neptunium would follow uranium through an oxidizing cycle and be separated from it in a reducing cycle, it now appears that the oxidizing extraction would require high acid concentration (resulting in poor decontamination), but that an extraction under reducing conditions with hydrazine present as holding reductant and complexing agent carries neptunium satisfactorily. This appears to offer the best process conditions.

The transfer of acid into hexone under the new process conditions (pH 1.5 to 1.8) has been investigated.

Techniques for analysis of hexone and for oxidation-reduction titration in strong nitrate solutions have been worked out.

Two papers were presented at the information meeting: "The Anamolous Distribution of Ruthenium" by G. R. B. Elliott, and "S-Diphenylthiourea as a Complexing Agent for Ruthenium" by G. D. Calkins. These are being prepared as reports. "Equations for Column Calculations", MonC-354, has been issued and "Determination of Reducing Substances in Hexone" by J. P. McBride will be issued soon.

Fission Product Decontamination

The effect of certain variables on mixed fission β decontamination has been studied. The variables studied were HNO_3 concentration, use of MnO_2 as a scavenger, DPT in the stripping operation, urea in the feed, oxidizing

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(0.1 M $Na_2Cr_2O_7$) or reducing (0.1 M N_2H_4 + 0.05 M Fe^{++}) conditions in the feed.

The mixed fission activity, "super-juice", was obtained by exhaustive ether extractions of $UO_2(NO_3)_2$ prepared from old irradiated U slugs.

The standard procedure for batch experiments to simulate column conditions are:

(1) Prepare feed: 1 M $Al(NO_3)_3$
"super-juice"
(0.1 M $Na_2Cr_2O_7$ and 0.2 N HNO_3 added at this point when used with 2 hr. standing at room temperature for oxidation).

(2) Add slurry of preformed MnO_2 to feed to give 1 g MnO_2/liter and let stand for 18 hours (MnO_2 prepared by the reaction of $KMnO_4$ and $Mn(NO_3)_2$ in 1 M $Al(NO_3)_3$ at the boiling point with 1 hour digestion under reflux).

(3) Separation of feed from MnO_2 by filtration through a sintered glass plate.

(For reducing cycle make feed 0.1 M N_2H_4 and 0.05 M Fe^{++} heat at 90° C for 1 hour. Cool to room temperature.)

(4) Extract feed two times with 1/2 volumes of pre-equilibrated hexone and combine extracts.

(5) Scrub hexone extract three times with 1/5 volumes of scrub solution (1 M $Al(NO_3)_3$-hexone saturated).

(6) In experiments with DPT add 10 g DPT/liter to the scrubbed hexone, heat at 60° C for 10 minutes, and cool to room temperature.

(7) Strip hexone two times with 1/10 volumes of strip solution (0.1 N HNO_3-hexone saturated).

(8) Take aqueous strip from (7) and make up for second cycle feed
1 M $Al(NO_3)_3$
0.75 M NH_4NO_3
0.05 M $Fe(NH_4)_2(SO_4)_2$
0.1 M N_2H_4
0.01 M HNO_3
Heat at 95° C for 1 hour. Cool to room temperature.

(9) Repeat step (4).

(10) Repeat step (5).

(11) Repeat step (7).

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In the experiments where DPT was being tested, the scrubbed hexone at step (5) was split into two equal fractions. One fraction was taken through steps (6) and (7), while the other fraction was taken directly from step (5) to step (7).

The β activity was measured after each step and results are plotted in Figures 1 through 7, as decontamination factor.

Conclusions

(1) The MnO_2 step gives a β decontamination factor of only 1.1-2, but the materials which have been removed by the MnO_2 appear to be the components which are difficult to decontaminate, since the steps following an MnO_2 treatment give much higher β decontamination factors. This is more marked with higher HNO_3 concentrations. (Figures 1 and 2)

(2) Increasing acidity decreases the β decontamination. (Figure 3)

(3) For the same pH in the aqueous a reducing first cycle (0.1 M N_2H_4 + 0.05 M Fe^{++}) gives a β decontamination factor eight times as large as an oxidizing first cycle (0.1 M $Na_2Cr_2O_7$). (Figure 4 and 5)

(4) DPT (10 g/l) in the hexone phase during the strip step increases the β decontamination factor in the strip step by a factor of 2.4. This is evidently caused by the complexing of Ru in the hexone. A fission product analysis on the final strip solution showed approximately equal amounts of Ru, Zr, and Ce activities (all close to background). This is contrasted with previous results (without DPT) which consistently showed a much greater proportion of Ru. (Figure 6)

(5) Using 10 g/l urea in the feed does not affect the first cycle decontamination at low acid ($\sim$0.01 N HNO_3). This same concentration of urea in the feed using 0.2 N HNO_3 does raise the first cycle β decontamination by a factor of [illegible]3; most of this increase is obtained in the extraction step (Figure 7).

Distribution of Ruthenium Tracer

Further work has been done on the behavior of ruthenium tracer during repeated extractions and scrubs using the techniques (pre-equilibration of phases, etc.) described in the previous quarterly report, MonN-370, p. 34 et seq.

Ruthenium tracer which had stood in presence of $KMnO_4$ and HNO_3 since distillation as RuO_4 was repeatedly extracted with hexone and scrubbed. The results are shown in Figure 8, which follows the same conventions used in MonN-370. On repeated scrubbing of the hexone phase the observed distribution ratio is constant at about 5. This is in agreement with previous values using less highly oxidized tracer whose original distribution ratio was low, but which reached a distribution ratio of 4 after repeated scrubs. In both cases if these scrub solutions are extracted with an organic phase, the distribution ratio equals about 0.2.

Figure 1

Mixed Fission Product Decontamination

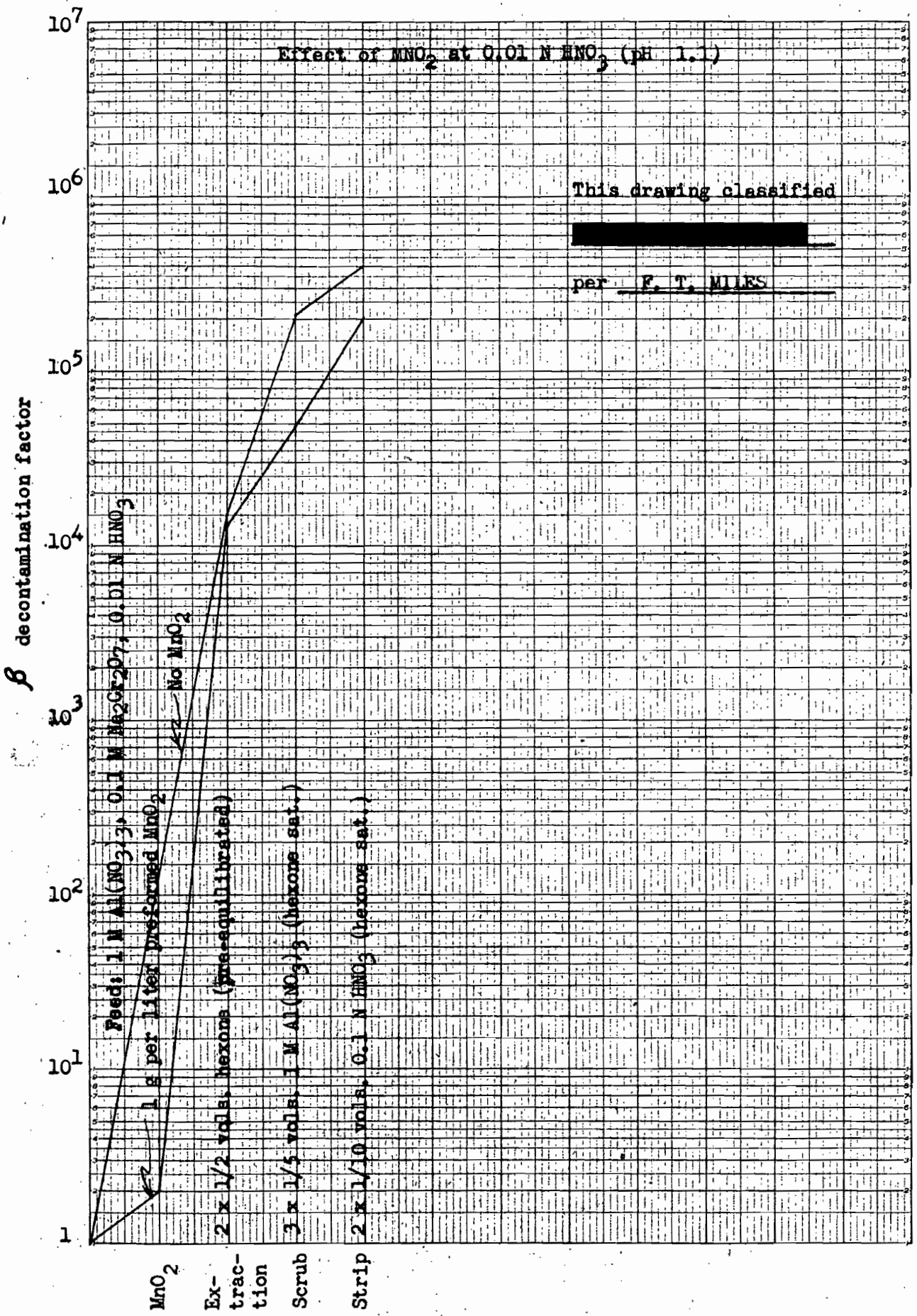

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Figure 2

Mixed Fission Product Decontamination

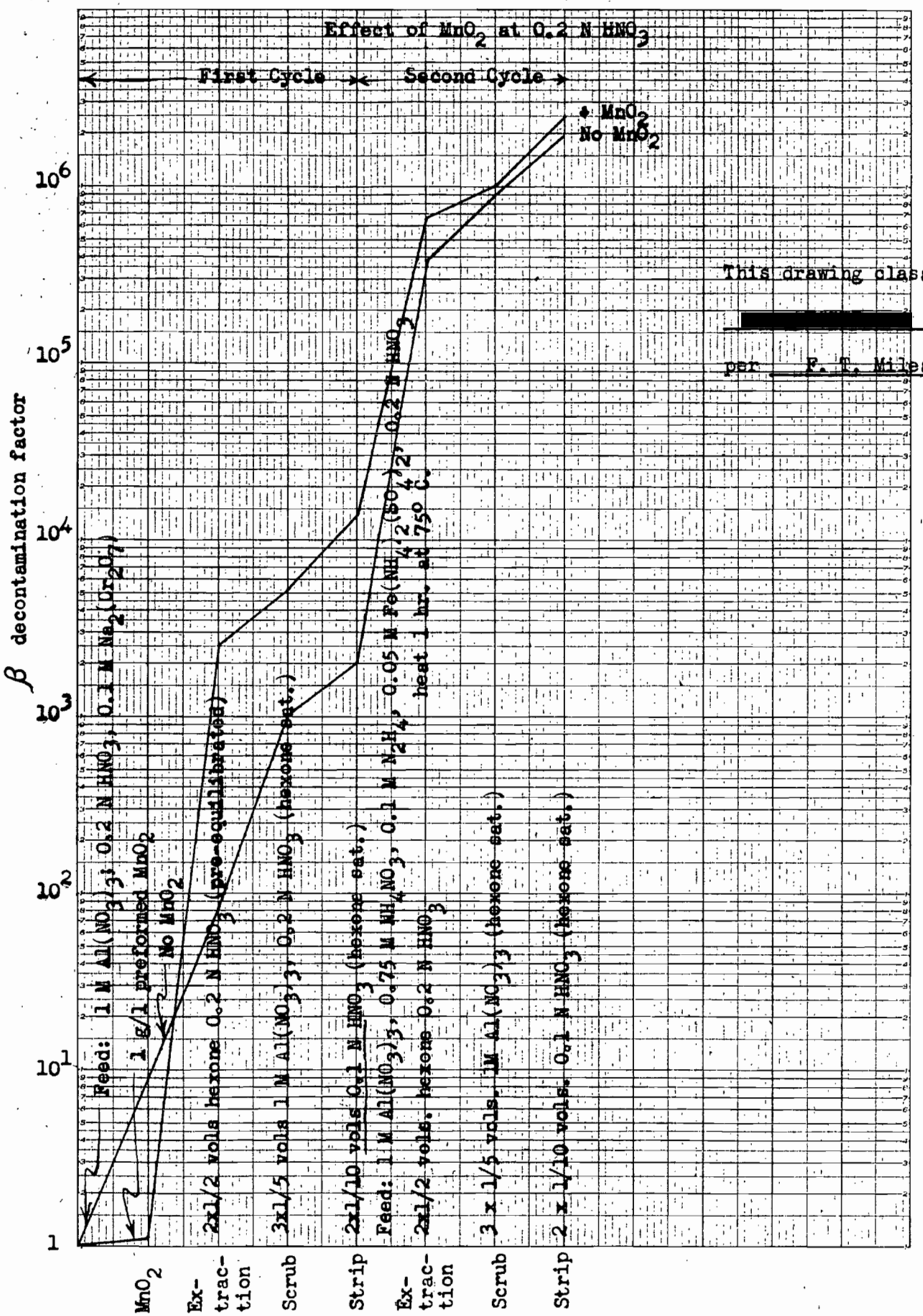

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Figure 3

Mixed Fission Product Decontamination

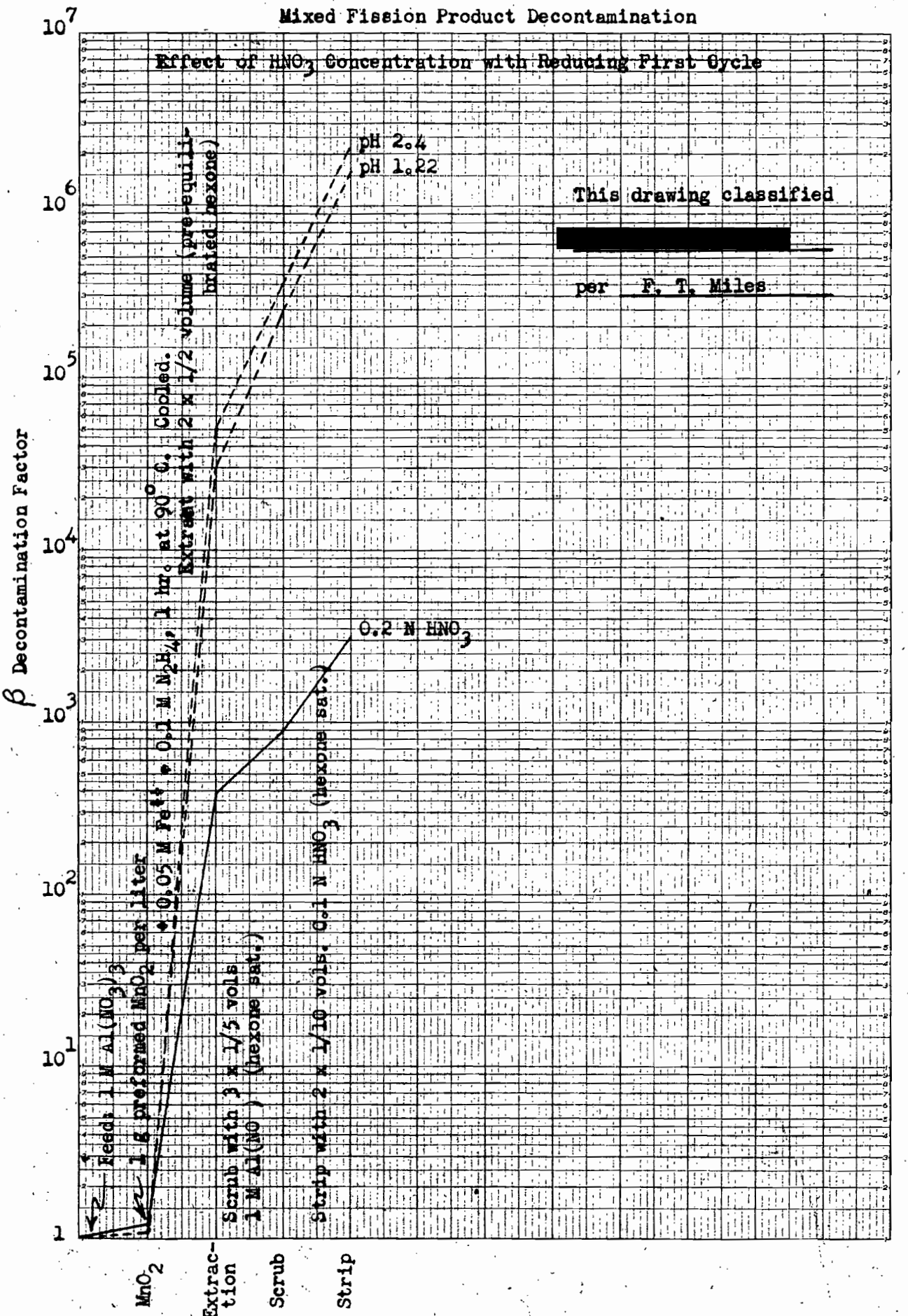

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Figure 4

Mixed Fission Product Decontamination

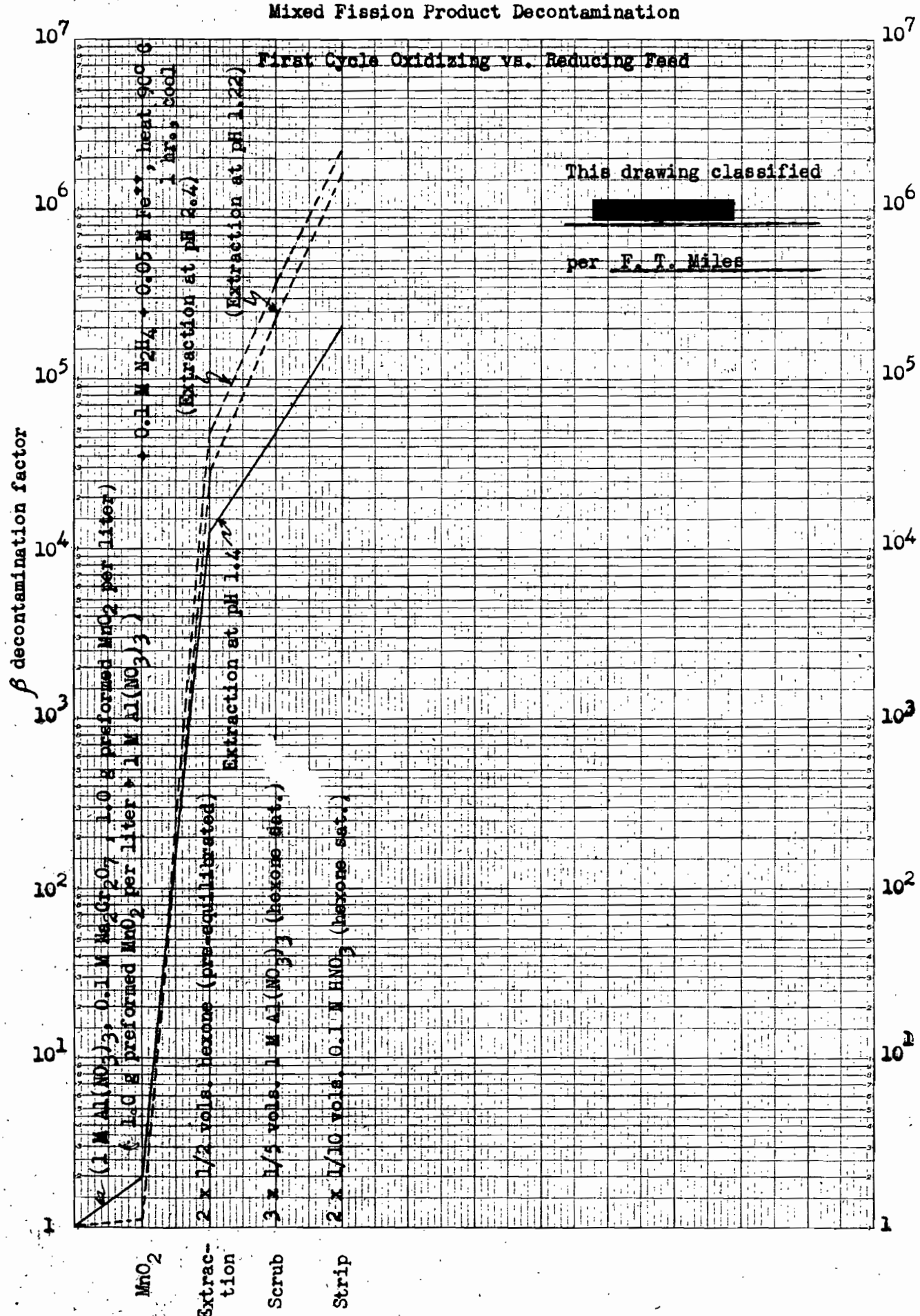

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Figure 5

Mixed Fission Product Decontamination

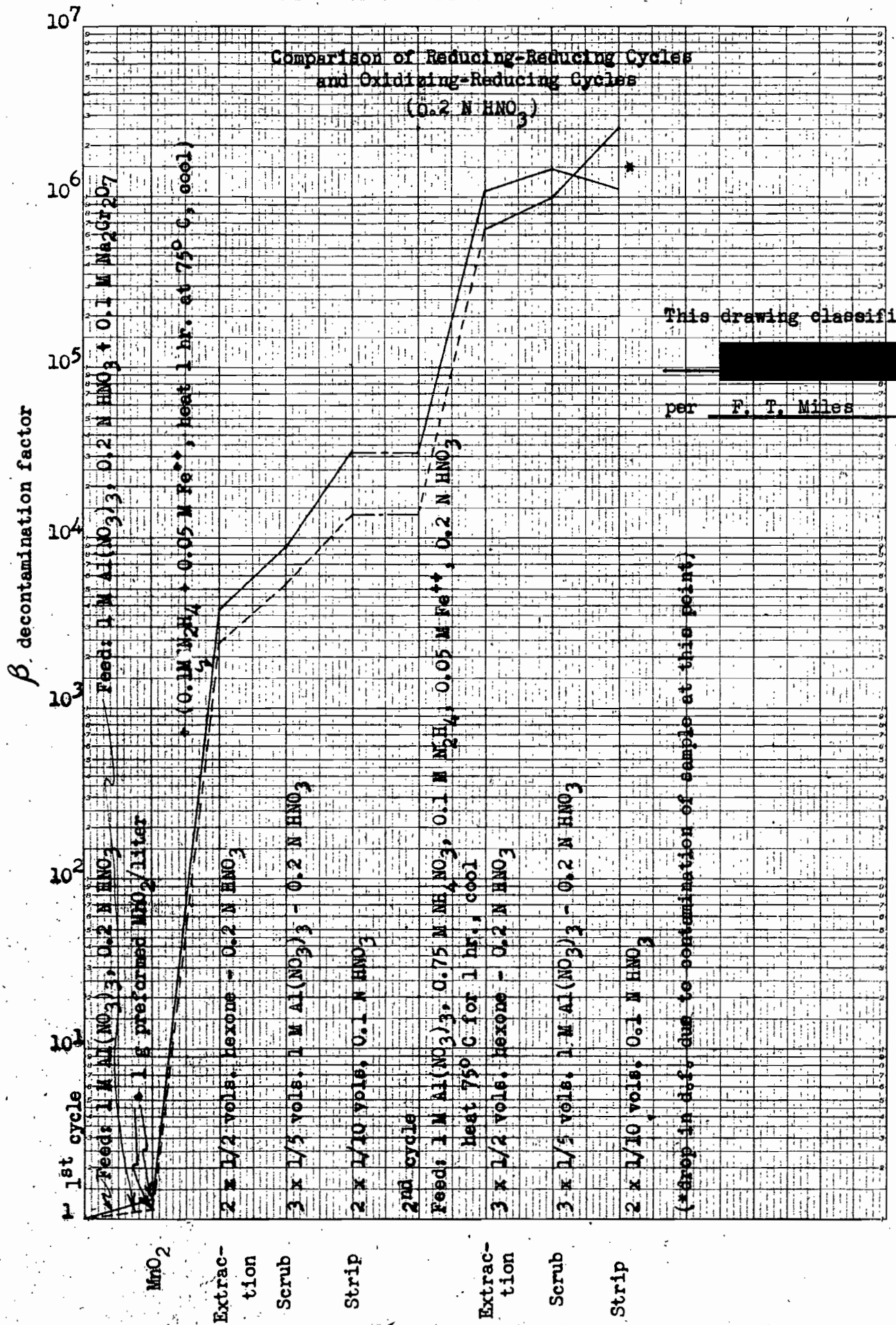

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Figure 6

Mixed Fission Product Decontamination

Effects of DPT and pH on Reducing First Cycle

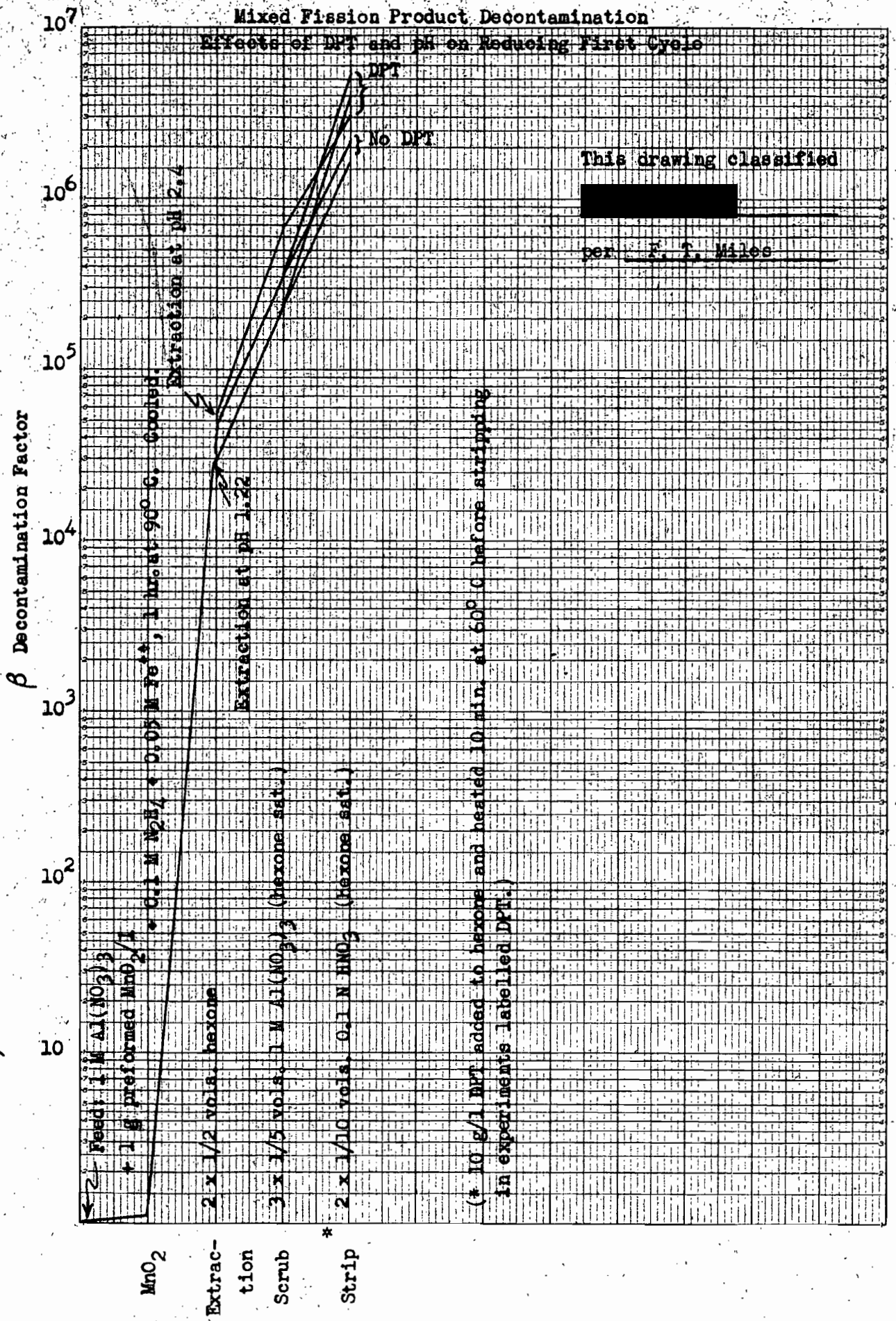

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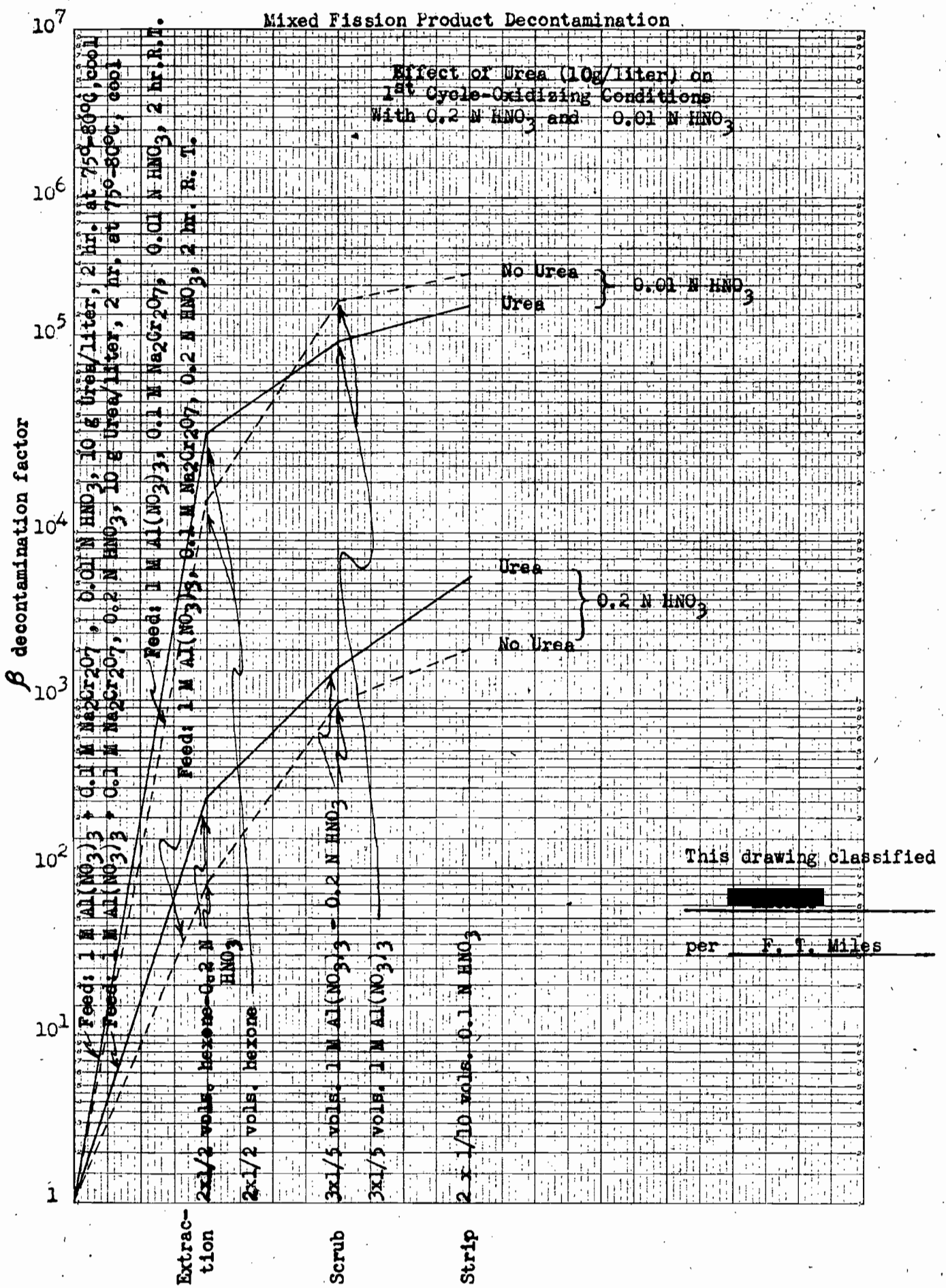
Figure 7



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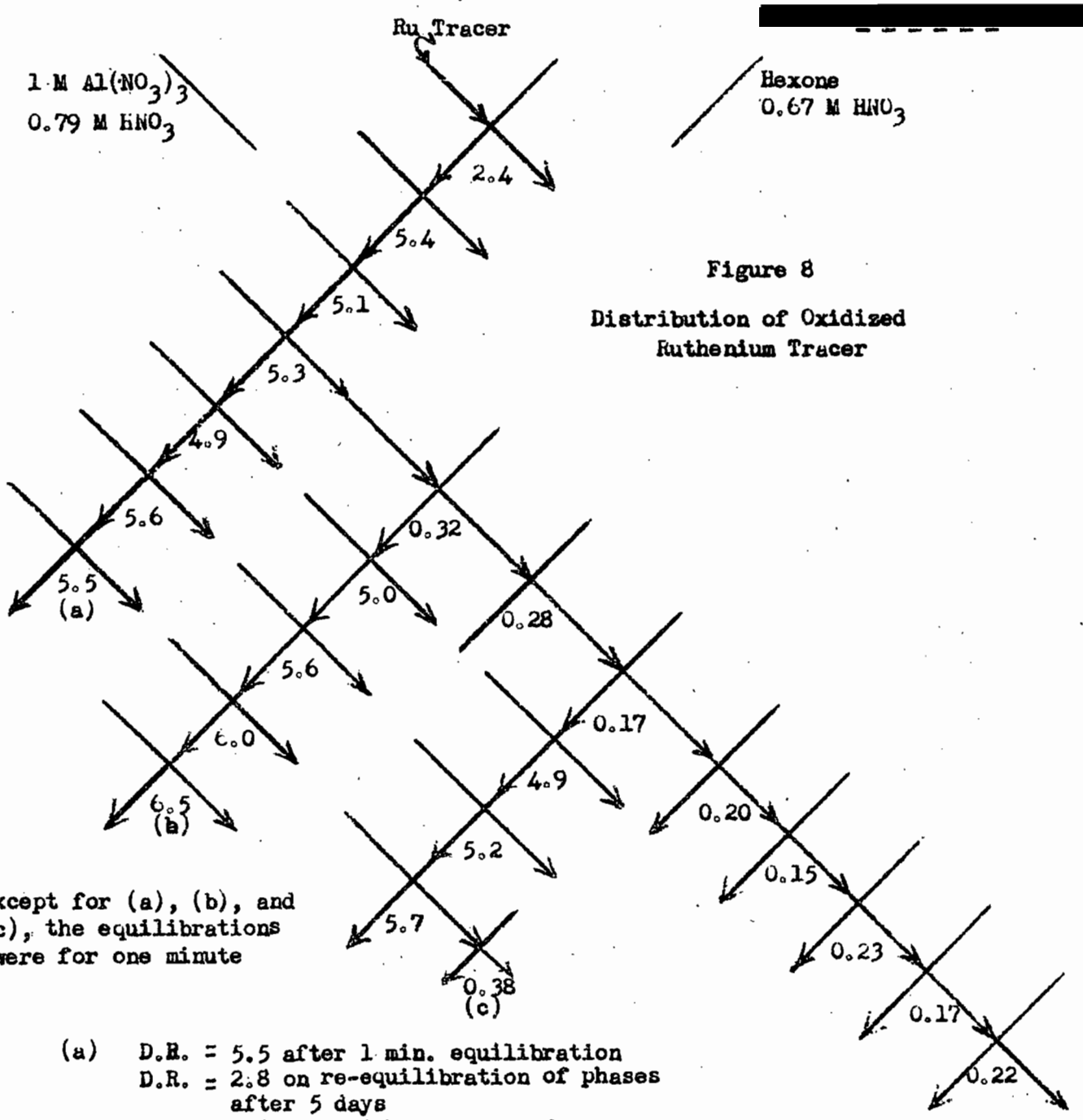

Except for (a), (b), and (c), the equilibrations were for one minute

Figure 8

Distribution of Oxidized Ruthenium Tracer

(a) D.R. = 5.5 after 1 min. equilibration
D.R. = 2.8 on re-equilibration of phases after 5 days
D.R. = 1.2 after 2 hours more of 2 phase equilibration
D.R. = 1.1 after 1 hour more of 2 phase equilibration

(b) D.R. = 6.5 extract after Ru stays in organic for 5 days.
D.R. = 4.3 after 15 min. more equilibration
D.R. = 3.6 after 15 min. more equilibration
D.R. = 2.4 after 1 hour more equilibration

(c) D.R. = 0.38 at once
D.R. = 0.80 after 1 hour equilibration
D.R. = 1.0 after 1½ hour more equilibration
D.R. = 1.0 after 1 hour more equilibration

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If a two-phase equilibration is carried out for about three hours, either scrubbing the organic phase or extracting the scrub, then a distribution ratio of about 1 is reached (Figure 8, a, b, c; Figure 2, MonN-311, G, K). Thus, if ruthenium is extracted into the organic phase and scrubbed twice or more the following state is obtained which is independent of the initial condition of the ruthenium tracer: on scrubbing any organic phase for one minute the distribution ratio is about 5; on extracting any aqueous scrub for one minute the distribution ratio is about 0.2; if two phases are stirred together for three hours the distribution is one, and is independent of the phase in which the ruthenium was introduced.

In the original extraction the system is more complicated. Depending on the amount of oxidation or reduction, HNO_2, HNO_3, N_2H_4, and time of standing, the original extraction varies from a distribution ratio of 0.001 to 2.4. If the tracer has not been oxidized the distribution ratio is about 0.001 to 0.01 (see MonN-311, MonN-370). If the tracer is oxidized very strongly with $KMnO_4$, concentrated HNO_3, and long time of standing, the extraction distribution ratio rises as high as 2.4. Heating with concentrated HNO_3 raised the distribution ratio of a reduced ruthenium tracer from 0.004 to 0.275. Boiling with HCOOH reduced the distribution ratio of the $KMnO_4$ oxidized tracer from 2.4 to 0.009. $Na_2Cr_2O_7$ appreciably raised the ruthenium distribution ratio.

HNO_2 increased the original distribution ratio of reduced ruthenium tracer linearly with increasing HNO_2 (MonN-370, page 42, figure 12). Increasing the time of standing of a hexone saturated feed markedly increased the original extractability of the ruthenium (MonN-370, page 37, figure 4).

Urea reversed this trend toward greater extractability of ruthenium with time of standing of the feed. The extractability actually decreased for a few days to later start to rise again. (MonN-370, page 42, figure 13). Urea also counteracts the effect of HNO_2 in increasing the Ru distribution ratio (MonN-370).

Successive extractions of reduced ruthenium from a feed over a short time result in a constant distribution ratio (MonN-370). No fractionation then shows on successive extractions of reduced feed. Oxidized feed shows a fractionation and decreasing distribution ratios on successive extractions.

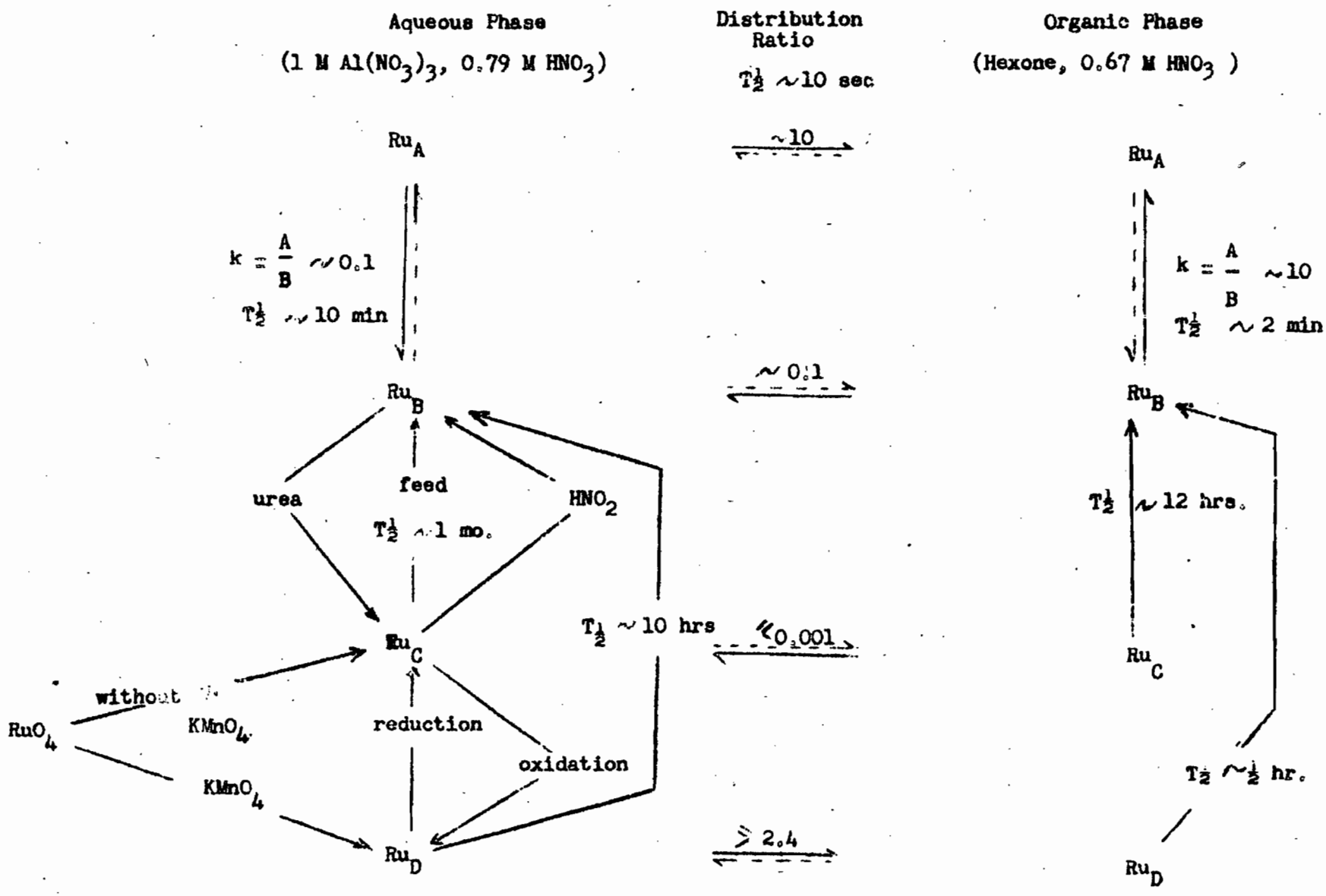
To explain all the above results it was found necessary to postulate the complicated scheme shown in Figure 9. Of the four assumed forms, Ru_A and Ru_B are considered to be the ones present in any repeatedly scrubbed hexone phase. The values shown in the figure for their distribution ratios, equilibrium constants, and approximate half lives of approach to equilibrium, explain why this fraction of tracer gives distribution ratios of 5 on scrubbing and ~0.2 on reextraction of scrub when these operations are done quickly, but gives a final distribution ratio of 1 on prolonged two-phase equilibration.

In addition to these, Ru_C, with a very low distribution ratio, is assumed to be the predominant form in old tracer which has stood in the absence of oxidizing agent, and Ru_D, with a distribution ratio of 2.4, is postulated as the form in tracer which has been in the presence of $KMnO_4$ and HNO_3 since its distillation as RuO_4.

[redacted]

Figure 9

Proposed Explanation of the Behavior of Ruthenium



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In hexone-saturated feed solution Ru_C is converted slowly (months) to an equilibrium mixture of Ru_A and Ru_B, with the resulting increase in organic solubility. Ru_D is converted more quickly (several hours) to Ru_A and Ru_B. In the hexone phase both reactions are faster, requiring about a day for Ru_C and about half an hour for Ru_D.

Different oxidation conditions convert Ru_C to Ru_D by different amounts. Varying reducing conditions give different degrees of conversion of Ru_D to Ru_C. For high conversion of forms there must be very strong oxidizing or reducing conditions.

Hydrazine increases distribution ratios for Ru_A and Ru_B. Its effect on Ru_C and Ru_D is not known.

From known chemistry of ruthenium combined with these data Ru_D appears to be Ru^{IV}; Ru_C appears to be Ru^{III}; Ru_A and Ru_B would be expected to be trivalent and appear to be (NO) complexes. The hydrazine effect may be similar to that noted by Argonne National Laboratory, where N_2H_4 increased the ionized HNO_3 in the organic phase, thereby extracting $UO_2(NO_3)_3^- \cdot ketazine \cdot H^+$ rather than $UO_2(NO_3)_2$.

Ruthenium Distribution in Dilute HNO_3

The data are less complete in the absence of $Al(NO_3)_3$ (strip conditions) since these experiments were done merely as control experiments in testing DPT complexing (see below). One of the more surprising facts under stripping conditions is that there is generally a rise in the distribution ratios on successive strips. Strip distribution ratios with 0.1 M HNO_3 in the aqueous phase and $\sim$0.002 in the hexone vary from 1 to >5. From the extraction and scrub data previously discussed (Figs. 8,9), one would expect on successive strips a constant distribution ratio representative of Ru_A and Ru_B in equilibrium. However, in 0.002 M HNO_3-hexone, approach to equilibrium appears to take much longer than in the 0.67 M HNO_3-hexone used in studying the extraction and scrubbing. Such a delay would permit a fractionation leading to increasing distribution ratios as were noted.

Adding $UO_2(NO_3)_2$ to the strips results in a slight lowering of the distribution ratio of ruthenium. Heating and cooling the solution above decreases the distribution ratio slightly more. Process amounts of uranium will not lower the ruthenium distribution ratio by more than a factor of 3. Possible explanations would involve the lowering of the HNO_2 or NO_3^- concentration in the hexone phase.

At 60° C the ruthenium distribution ratios are lower by about the same factor observed for uranium and neptunium.

The distribution ratios are lower in the presence of ferrous iron and urea, as would be expected if (NO) complexes of Ru are involved.

[redacted]

In the presence of ferrous iron and hydrazine the distribution ratios on successive strips first decreased to a minimum and later increased. Two competing reactions seem to be taking place.

s-Diphenylthiourea as a Complexing Agent for Ruthenium

Previous work (Monn-370) showed that s-diphenylthiourea (DPT) forms an organic soluble complex with ruthenium in hexone solutions and that it did not complex uranium at 26-29° C in hexone solutions.

The present work indicates the effect of DPT on uranium at 60° C, on neptunium, and on mixed columbium-zirconium tracer, and the effect of various reagents on the complexing action of DPT for ruthenium. In general the activity is obtained in the hexone phase by an extraction from 1 M $Al(NO_3)_3$ solutions containing additional reagents. The organic phase is then scrubbed once or twice with a 1 M $Al(NO_3)_3$ solution. The hexone fraction is then split into two or more parts, one of these being treated with DPT while the other is not. The reactions with DPT are carried out at 60°C and the control solution not containing DPT is heated at 60° C in a similar manner. All solutions used are pre-equilibrated to minimize the transfer of any solution component other than the activity in question unless stated otherwise. Although a reaction may be carried out at 60° C all contacts of an organic phase with an aqueous phase are at room temperature.

Further experiments with U^{233} tracer now indicate that DPT does not complex uranium at 60° C. These data are shown in Figure 10.

Results discussed above show that uranylnitrate reduces the hexone solubility of ruthenium when a hexone phase of ruthenium is washed with dilute nitric acid. The importance of this effect in the use of DPT to complex ruthenium was tested. The data are shown in Figure 11. They show that 0.1 M UNH materially reduces the effectiveness of 3 g/l of DPT in complexing ruthenium. Increasing the concentration of DPT to 10 g/l overcomes the uranium effect.

The effect of DPT on neptunium tracer under oxidizing conditions with sodium dichromate and under reducing conditions with hydrazine nitrate was studied. The data for these experiments are given in Figure 12. They indicate that oxidized neptunium may be complexed by DPT to a small extent, but this complex is not stable when the hexone phase is washed with dilute nitric acid. Under reducing conditions with hydrazine nitrate DPT does not complex neptunium.

Experiments on the effect of DPT on a mixed columbium-zirconium tracer show that DPT does not complex the columbium or zirconium which extracts into the hexone phase. (Figure 13)

An approximate determination of the solubility of DPT in hexone and dibutyl cellosolve gave the following results at 26-27° C.

	Solubility g/l
hexone	33
dibutyl cellosolve	5

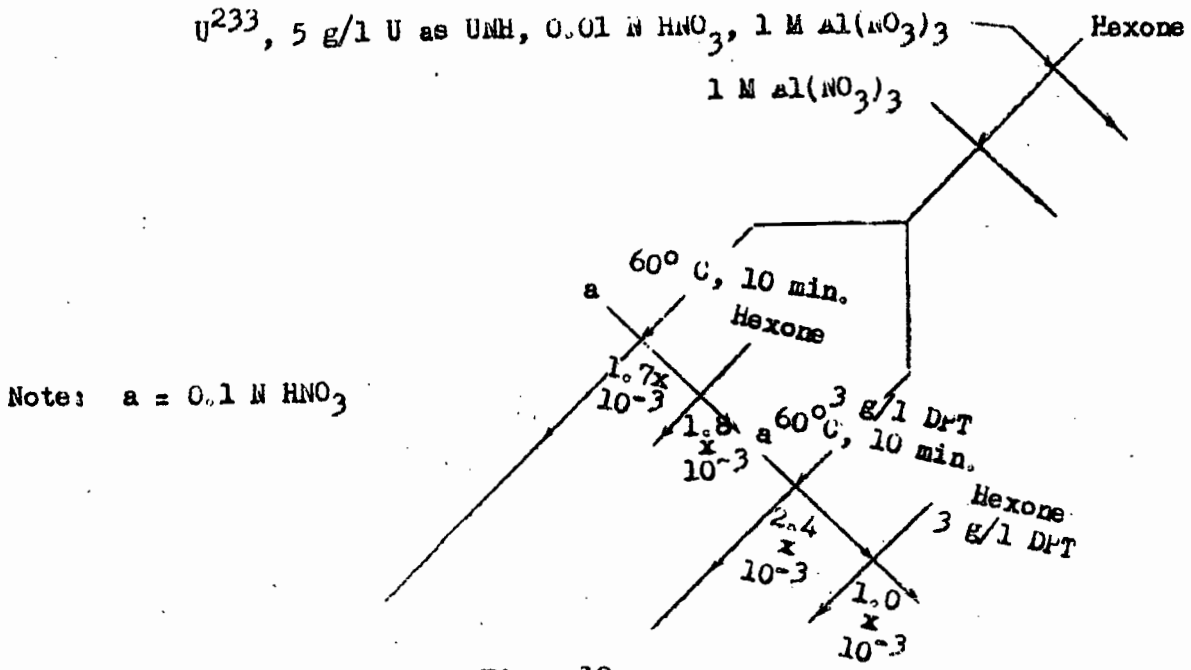

Figure 10

Effect of DPT on Uranium Distribution

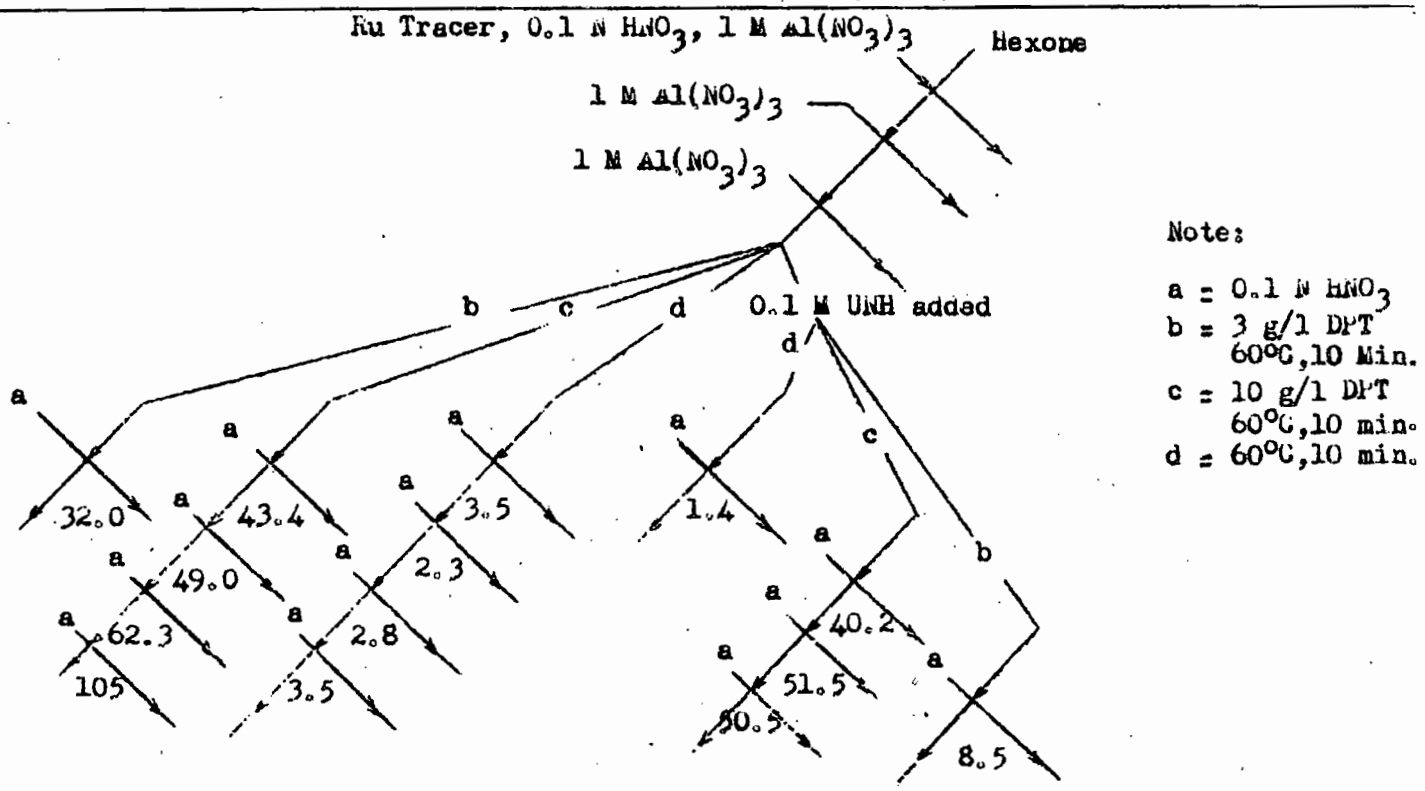

Figure 11

Effect of Uranium on Ruthenium DPT Distribution

[redacted]

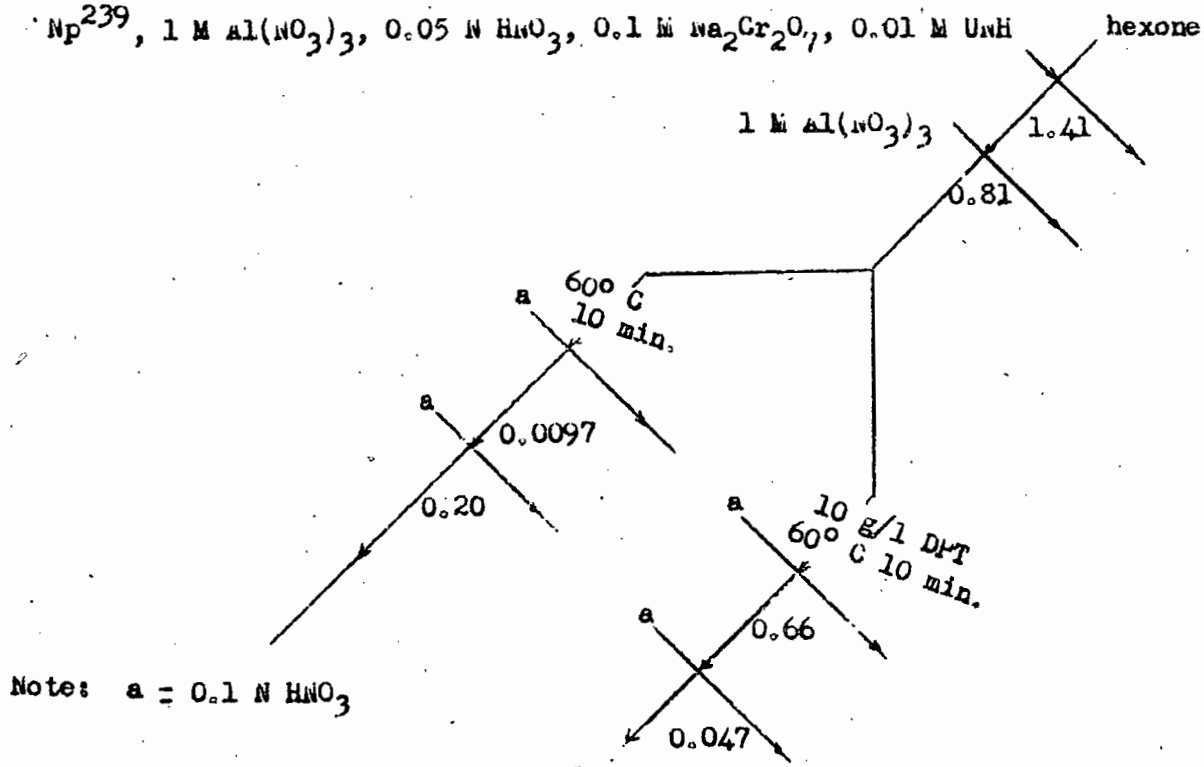

Figure 12
Effect of DPT on Neptunium Distribution

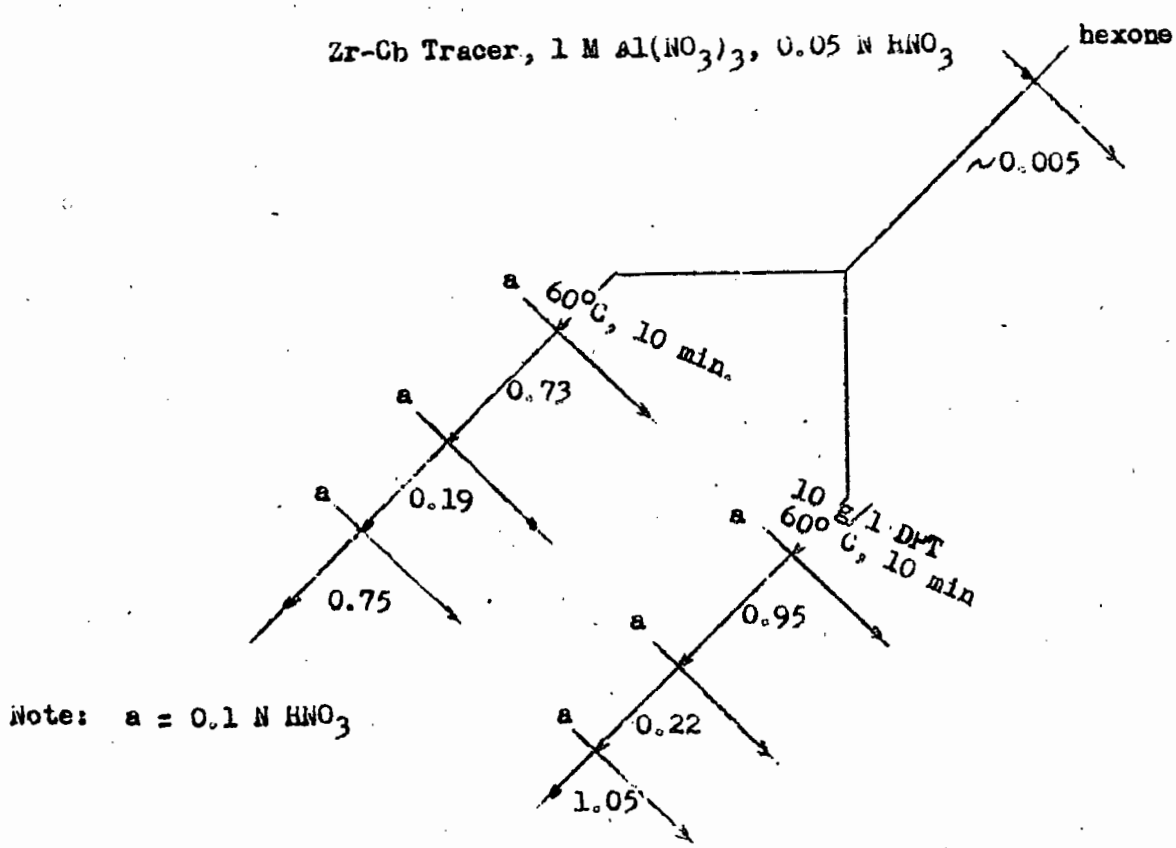

Figure 13
Effect of DPT on Zirconium-Columbium Distribution

[redacted]

[redacted]

The possibility of using DPT to complex ruthenium in dibutyl cellosolve was examined. The data for this experiment (Figure 14) show that ruthenium is complexed but not to the extent that occurs in hexone. This is probably associated with the lower solubility of DPT in dibutyl cellosolve (5 g/l) than in hexone (33 g/l). It was shown previously in hexone that with 0.1 M UNH 10 g/l of DPT is more effective than 3 g/l of DPT in complexing ruthenium.

DPT was found to be effective in complexing ruthenium in hexone in the presence of 1 N HNO_3, 0.1 M $Na_2Cr_2O_7$, 0.1 M $N_2H_4 \cdot HNO_3$ + 0.05 M $Fe(NH_4)_2(SO_4)_2$, 0.1 M $CO(NH_2)_2$ + 0.05 M $Fe(NH_4)_2(SO_4)_2$ in the aqueous phase. The data for these experiments are shown in Figures 15 through 19. Only in the case of the use of $Na_2Cr_2O_7$ did the ruthenium distribution ratios with DPT drop to lower values. In this case dichromate had transferred to the hexone phase and had begun to decompose the DPT. There was no indication of solids formation, however.

Thus, DPT has proved to be an effective complexing agent for ruthenium in hexone solutions under a variety of conditions and may be used to advantage to decontaminate uranium from ruthenium in a hexone solvent extraction process at the step where the uranium transfers from the hexone phase to an aqueous phase. DPT does not form stable complexes with uranium or neptunium. The optimum conditions for the application of DPT require a concentration of DPT in the hexone of from 5 to 10 g/l with the reaction taking place in about 10 minutes at 60° C or in the order of 10 hrs. at room temperature. The hexone phase should be cooled to room temperature before contact with the aqueous phase since ruthenium and the ruthenium-DPT complex become more aqueous soluble at elevated temperatures (MonN-370).

Distribution of Neptunium

It had been assumed on the basis of early experiments that oxidized neptunium, Np^{VI}, would be extractable into hexone and would therefore follow uranium, and that reduced neptunium, Np^{V} or Np^{IV}, would not be extracted into hexone and would be found in the raffinate. On these assumptions a two-cycle process was recommended consisting of an oxidizing first cycle and a reducing second cycle.

Since that time Chicago has reported that reduced neptunium, Np^{IV}, forms with hydrazine an organic soluble complex. It has also been found here that with $Na_2Cr_2O_7$ a high acid concentration is necessary to maintain a high distribution ratio for neptunium. Present process conditions use a pH of 1.5 to 1.8 for good decontamination. This is too high a pH to allow the oxidation of neptunium to the extractable form. Therefore, we now recommend a first cycle reduction with hydrazine and, in the cycle where neptunium is to be separated from uranium, a reduction without complex formation, probably with ferrous ironand eitherurea or hydroxylamine.

The neptunium used in the work which is described below was prepared by 8-hour pile irradiation of $U^{238}O_3$ (depleted of U^{235}). The neptunium was purified from fission products by solution of the UO_3 in concentrated HNO_3, a product precipitation with LaF_3, a by-product precipitation with LaF_3, followed

[redacted]

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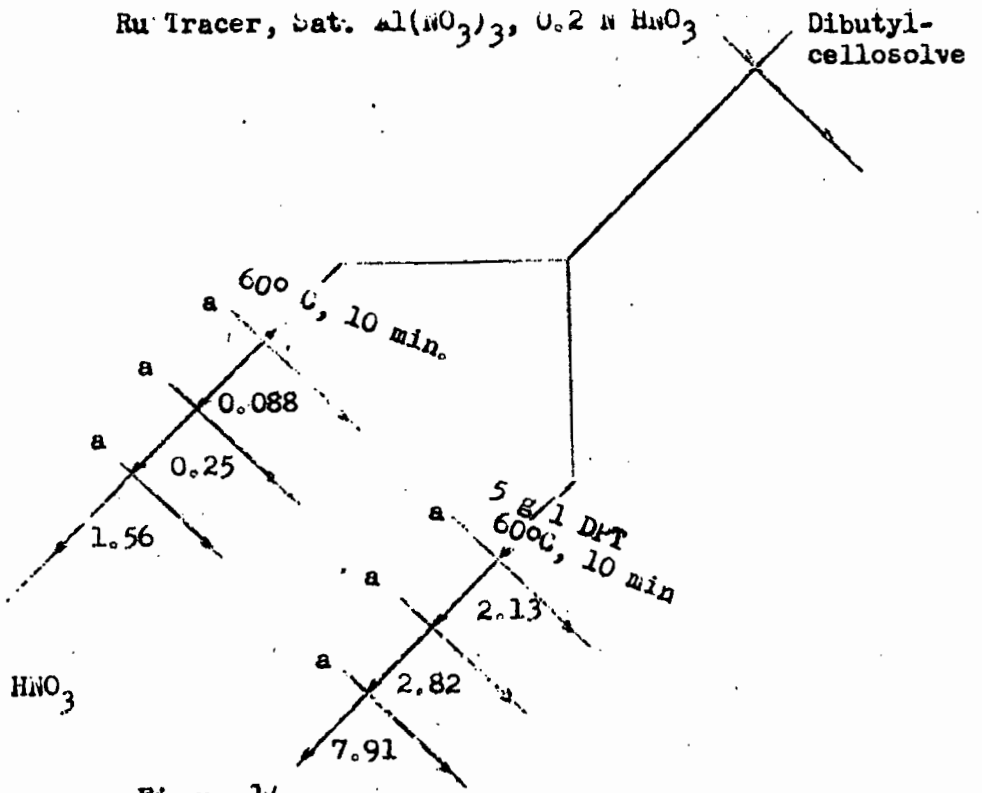
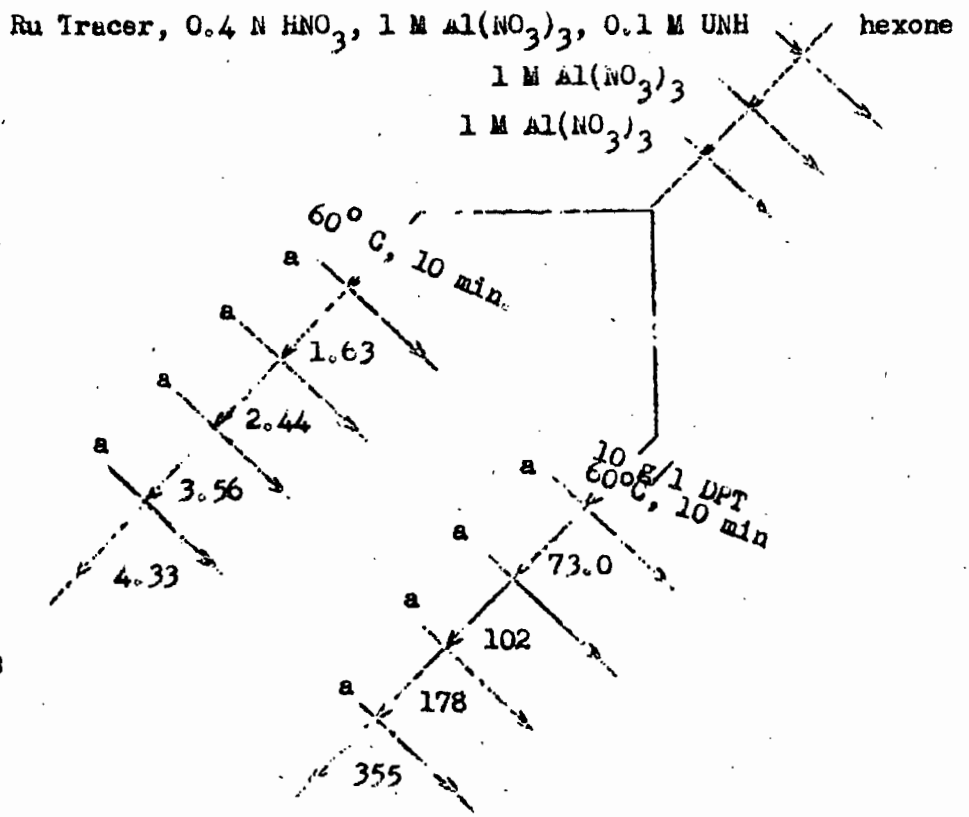


Note: a = 0.1 N HNO_3

Figure 14
Formation of Ruthenium-DPT Complex in Dibutyl-Cellosolve



Note: a = 1 N HNO_3

Figure 15
Effect of Concentrated Nitric Acid on Formation of Ruthenium-DPT Complex

[redacted]

[redacted]

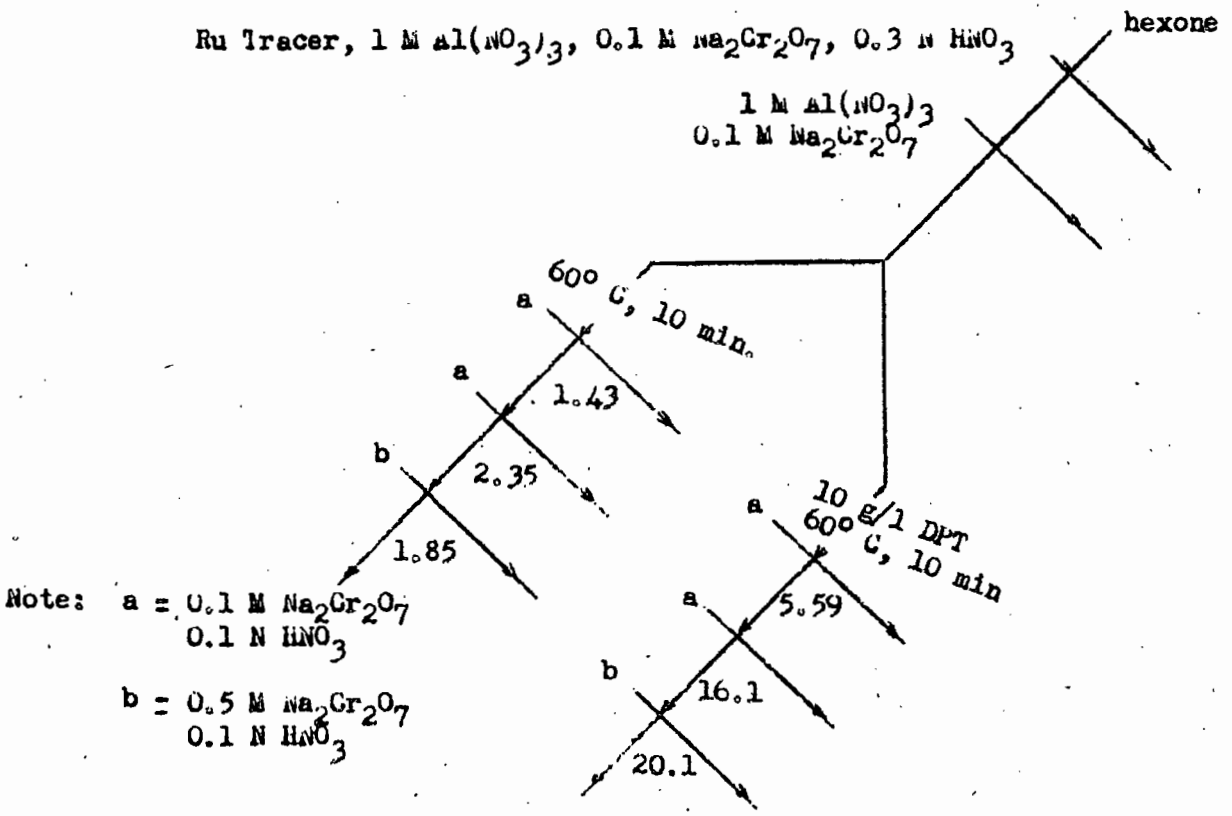


Figure 16
Effect of Sodium Dichromate on Formation of Ruthenium-DPT Complex

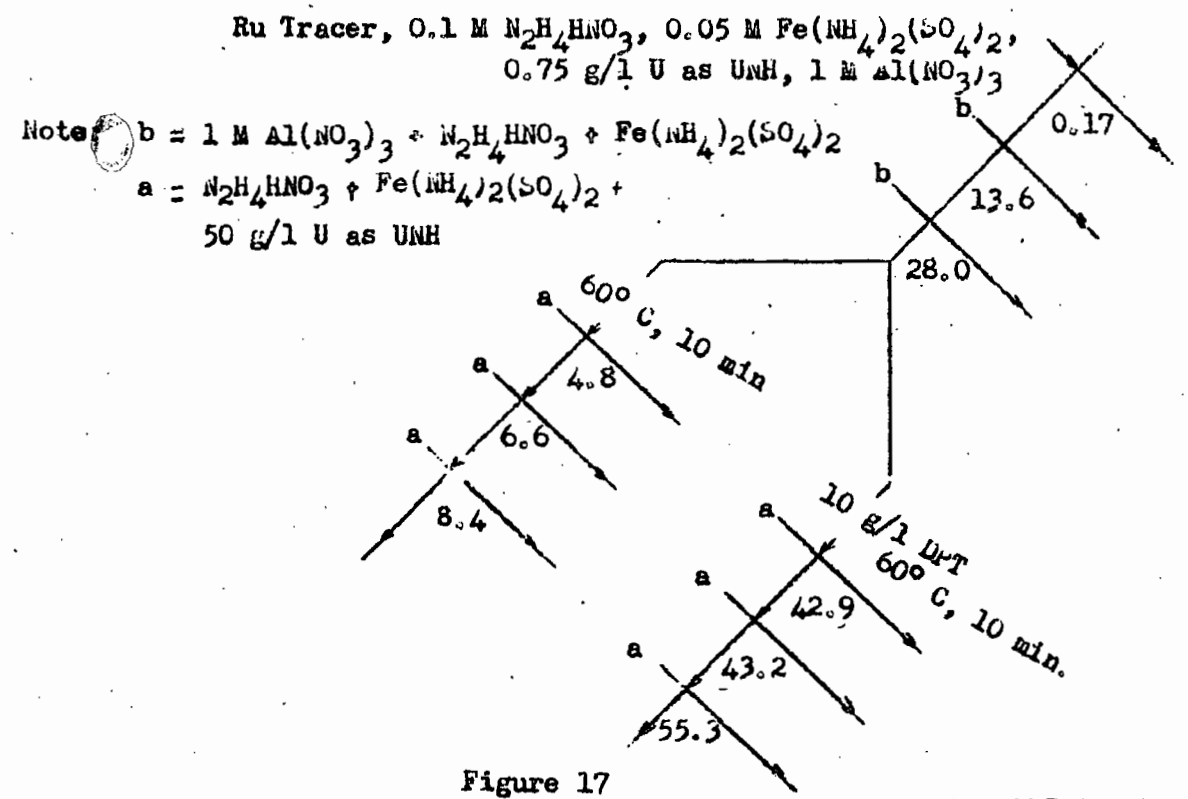


Figure 17
Effect of Hydrazine Nitrate + Ferrous Ion on Formation of Ruthenium-DPT Complex

[redacted]

[redacted]

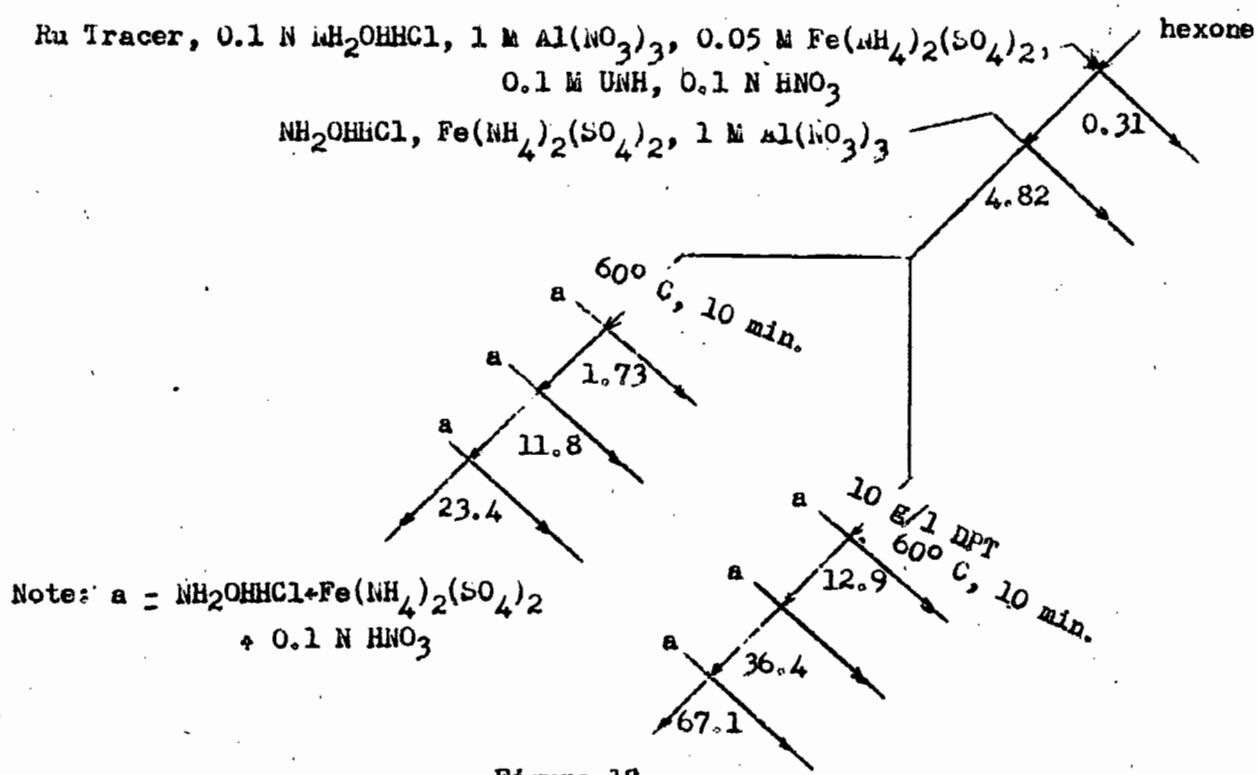


Figure 18
Effect of Hydroxylamine + Ferrous Ion on Formation of Ruthenium-DPT Complex

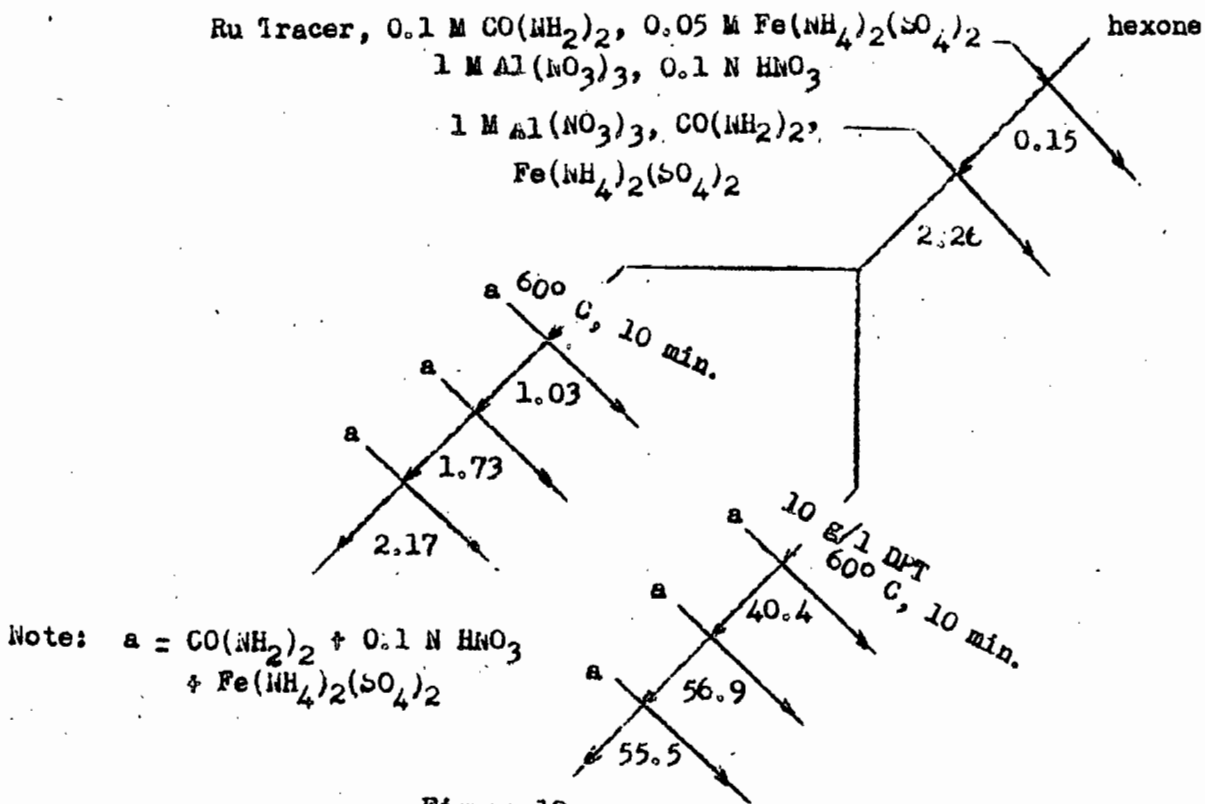


Figure 19

[redacted]

[redacted]

by a product precipitation with LaF_3, metathesis to the hydroxide and solution in concentrated HNO_3. Beta and gamma half-life determination gave a value of 56 hours for all samples. One sample was followed over a period of 16 half-lives and showed less than 0.03% of a longer lived impurity.

In all the experiments described below, unless otherwise noted, the hexone and aqueous phases were equilibrated before the addition of tracer, and the neptunium tracer was then added to the aqueous phase. The scrubbing of both aqueous and organic phases was done with pre-equilibrated solutions, except where noted. The pH's of the aqueous solutions were measured with a glass electrode immediately after extraction.

Preliminary results showed that in the case of oxidized neptunium, lower distribution ratios were obtained when the solutions were allowed to stand some time before counting than when they were counted immediately after extraction. This was probably due to the reduction of Np by the hexone. Also, if the oxidation was carried out with heating, the distribution ratios of Np were lower than when the oxidation was performed at room temperature.

The variance of the distribution ratio of Np^{VI} with $Al(NO_3)_3$ concentration at high acid strength is shown in Figure 20. The oxidation and distribution were carried out with 0.1 M $Na_2Cr_2O_7$ and 0.23 M HNO_3. The curve for uranium is given for comparison. Repeated extractions and scrubbing indicated little if any fractionation of the neptunium.

In Figure 21 is shown the distribution ratio of Np^{VI} under these conditions as a function of temperature. The curve is similar to those obtained with uranium and other metals and is in line with the fact that the extraction is highly exothermic. The heat of the reaction here was calculated to be 6.01 Kg. Cal. Repeated extraction showed that at constant temperature the distribution ratio was independent of which phase contained the neptunium originally.

On measuring the Np distribution ratio under present process conditions (pH 1.5-1.8) much lower values were found. An attempt was made to explain this by assuming incomplete oxidation of neptunium. The equation for the oxidation of neptunium with dichromate

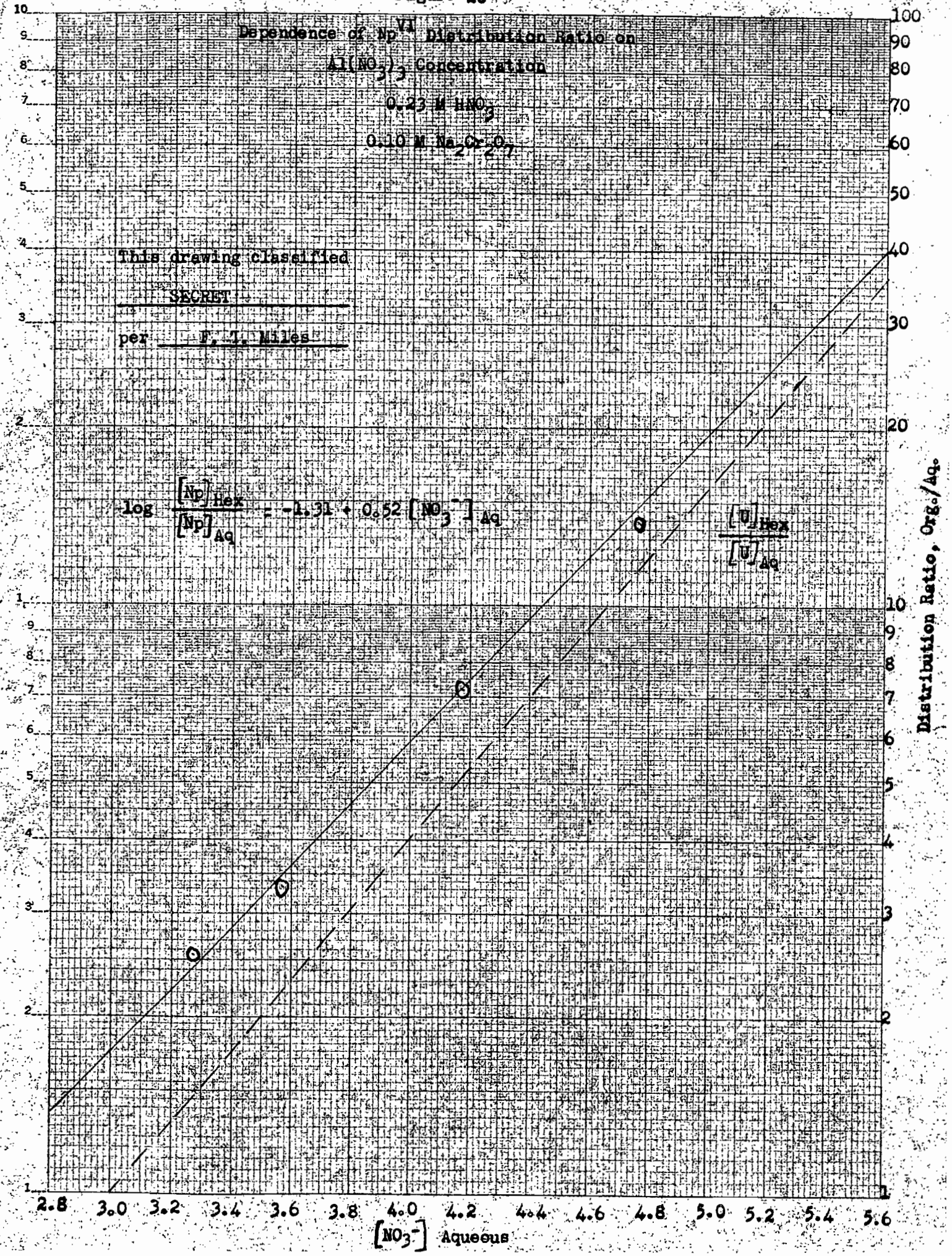
$$Cr_2O_7^{=} + 6NpO_2^{+} + 14H^{+} \rightleftharpoons 6NpO_2^{++} + 2Cr^{+++} + 7H_2O$$

shows that a negative pH dependence of the fraction oxidized is to be expected. This effect is not large enough alone, however, to explain the observed pH dependence, if the distribution ratios of the oxidized and reduced forms are independent of pH. Therefore it was necessary to measure d_1, the distribution ratio of the oxidized form of neptunium, and d_2, the distribution ratio of the reduced form, both as functions of pH.

The dependence of d_1 on pH was determined from distribution ratios obtained using 0.1 M $Na_2Cr_2O_7$ + 0.1 M Cr^{+++} at low pH's and excess $KMnO_4$ at higher pH's as the oxidizing agents. The amount of $KMnO_4$ present was sufficient to maintain a purple color after extraction with hexone. The pH dependence of the distribution ratio of reduced neptunium, d_2, was determined from points obtained

[redacted]

Figure 20


Dependence of Np^{VI} Distribution Ratio on
$Al(NO_3)_3$ Concentration
0.23 M HNO_3
0.10 M $Na_2Cr_2O_7$
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per F. T. Miles
$\log \frac{[Np]_{Hex}}{[Np]_{Aq}} = -1.31 + 0.52 [NO_3^-]_{Aq}$
$\frac{[U]_{Hex}}{[U]_{Aq}}$
Distribution Ratio, Org./Aq.
$[NO_3^-]$ Aqueous
2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6
1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10
KEUFFEL & ESSER CO., N. Y. NO. 359-93
Semi-Logarithmic 2 cycles X 10 to the ½ inch, 65th lines accepted
MADE IN U.S.A.

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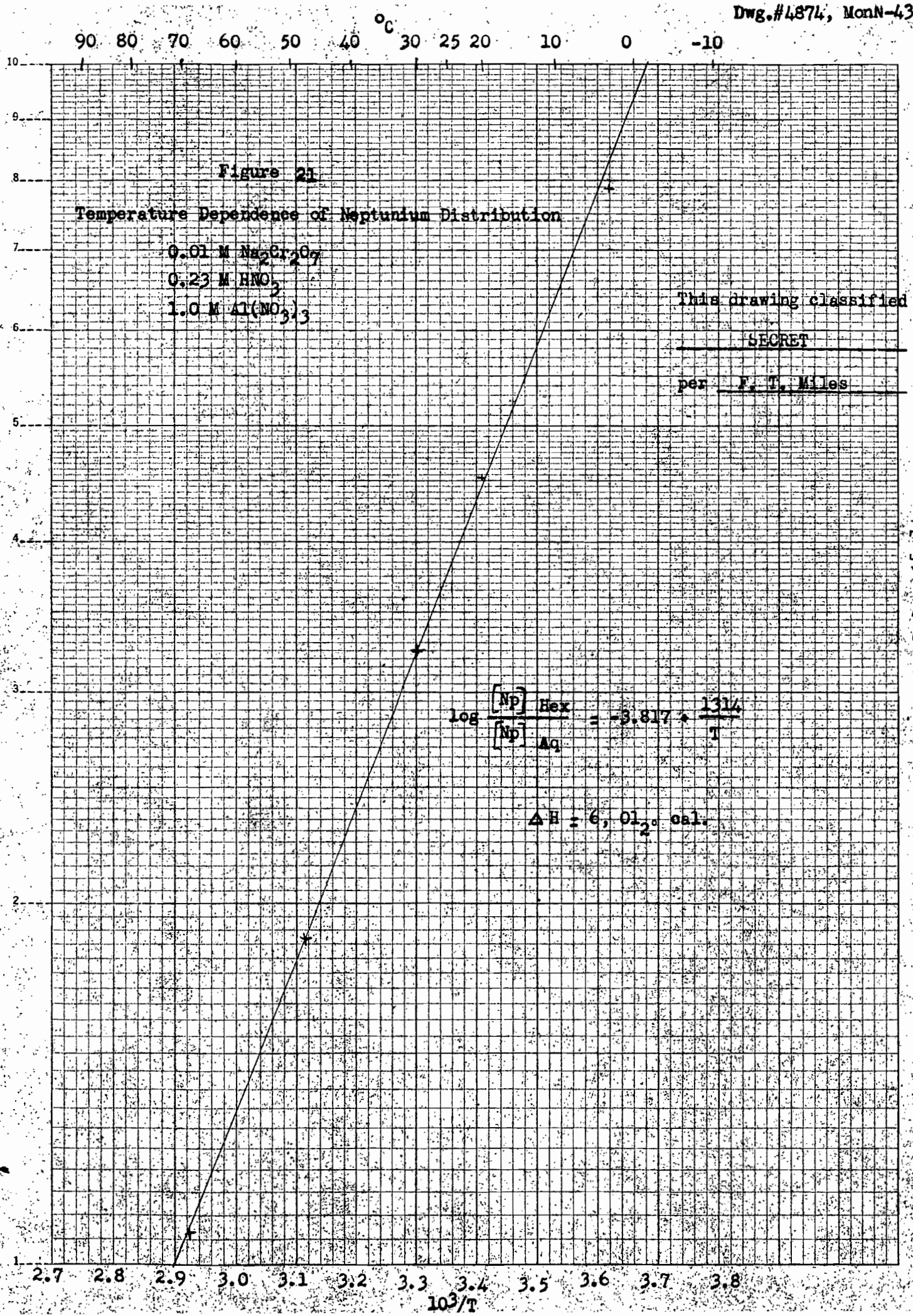

Figure 21

Temperature Dependence of Neptunium Distribution

0.01 M $Na_2Cr_2O_7$
0.23 M HNO_3
1.0 M $Al(NO_3)_3$

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KEUFFEL & ESSER CO., N. Y. NO. 359-61
Semi-Logarithmic, 1 Cycle X 10 to the Inch, 5th lines accented.
MADE IN U.S.A.

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using either ferrous iron plus urea or ferrous iron plus hydroxylamine as the reducing agent. In these latter cases, the distribution ratios obtained from both a first and second extraction were used.

d_1 and d_2 were then combined with the fraction of neptunium oxidized, x, to give the following expression

$$\frac{D}{1 + D} = \frac{d_1}{1 + d_1} x + \frac{d_2}{1 + d_2} (1 - x) \quad .$$

where D is the observed distribution ratio. For high x, d_2 can be neglected and the equation simplified to

$$\frac{D}{1 + D} = \frac{d_1}{1 + d_1} x \quad .$$

An attempt has been made to fit the observed distribution data to the curves calculated from the above two expressions by finding four (or three, if d_2 is assumed to be 0) arbitrary constants, A, B, C and k, in the expressions:

$$\log d_1 = A - B\ pH$$

$$\log d_2 = C - B\ pH$$

$$\log k = \log \frac{[NpO_2^{++}]}{[NpO_2^{+}]} + \log \frac{[Cr^{+++}]^{1/3}}{[Cr_2O_7^{=}]^{1/6}} - \frac{14}{6} \log[H^+]$$

$$= \log \frac{x}{1 - x} + \log \frac{[Cr^{+++}]^{1/3}}{[Cr_2O_7^{=}]^{1/6}} + 2.33\ pH$$

$$= \frac{F}{RT} \left(E_{o(Cr^{+++}-Cr_2O_7^{=})} - E_{o(NpO_2^{++}-NpO_2^{+})} \right)$$

The reported values of $E_{o(Cr^{+++}-Cr_2O_7^{=})}$* and $E_{o(NpO_2^{++}-NpO_2^{+})}$** give a value of log k = 3.81. However, neither of these values was determined in nitrate solutions. The fact that our arbitrarily determined value of log k = 3.94 using 0.1 M $Cr_2O_7^{=}$ and 0.1 M Cr^{+++} does not agree too well is, therefore, not surprising.

Figure 22 shows (1) the final calculated curves using the chosen constants and (2) the experimentally determined points using excess $KMnO_4$, 0.1 M $Na_2Cr_2O_7$ plus 0.1 M $Cr(NO_3)_3$, and 0.1 M $CO(NH_2)_2$ plus 0.05 M $Fe(NH_4)_2(SO_4)$.

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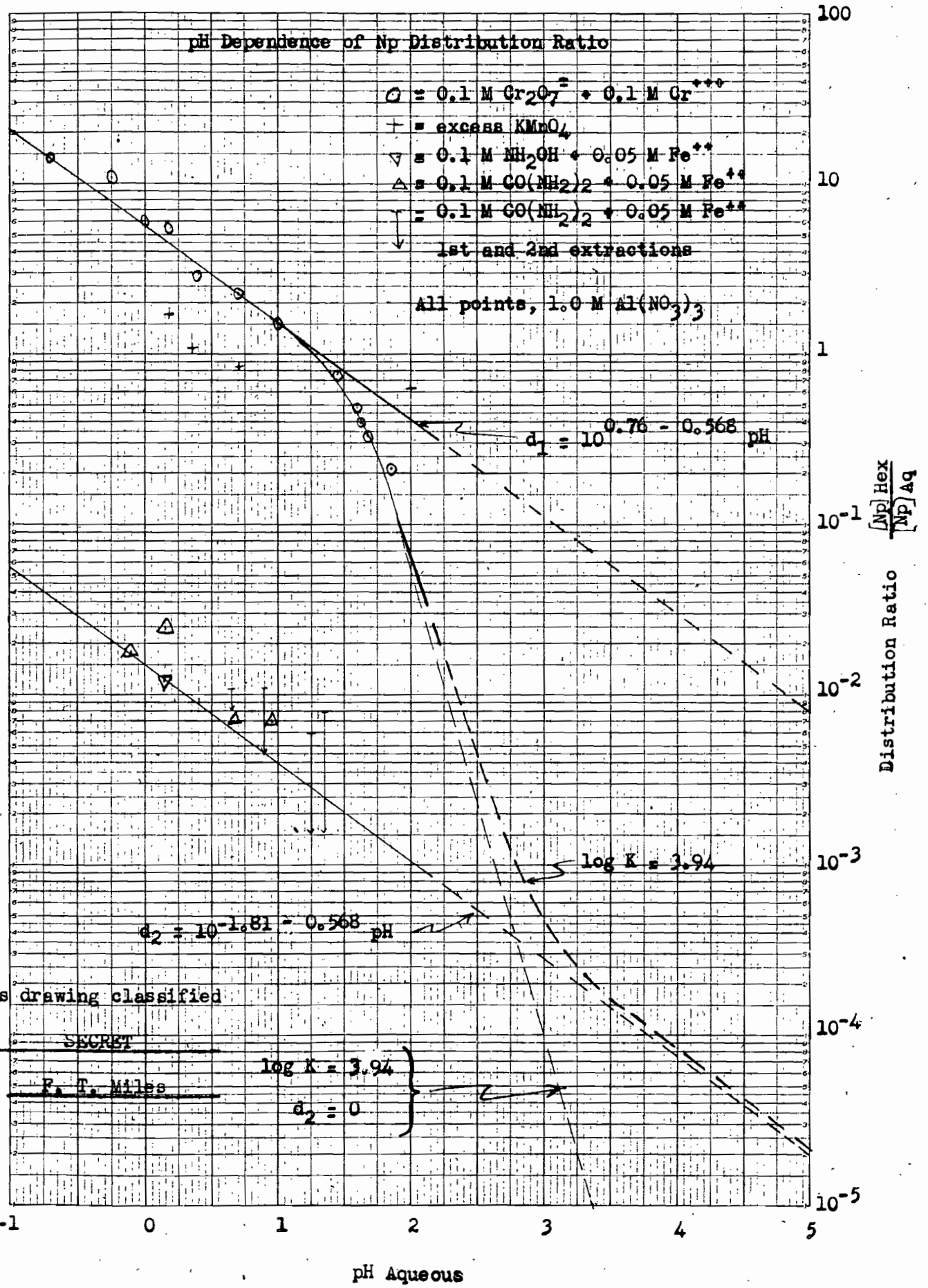
*Latimer, W. M., "Oxidation Potentials", (Prentice-Hall, Inc., New York, 1938), page 231.

**CC-3655, Vol. 14A, PrR, Chap. 15.

[redacted]

Figure 22



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d_1 was chosen to fit the upper limit of the dichromate points obtained at low pH and the $KMnO_4$ points obtained at high pH. Then log k was chosen to make the dichromate points fit at high pH. d_2 was chosen to have the same slope as d_1 and to fit the lower limit of the points obtained using ferrous iron and urea.

From the graph it is obvious that high acid concentrations are necessary to oxidize the neptunium to the extractable form. The disadvantage of this is that at high acid concentrations the fission product decontamination factor is low.

Experiments have been begun to determine the variation with pH of the distribution ratio of Np between 1 M $Al(NO_3)_3$ and hexone in the presence of 0.05 M Fe^{++} and 0.1 M N_2H_4.

The results obtained are listed in the table below:

pH	Distribution Ratio		
	Original Extraction	Scrub of Organic Extraction	Reextraction of Aqueous Fraction
-0.05	27.0	26.5	1.83
0.30	27.5	26.5	3.0
1.10	2.29	16.8	1.04

The hexone used was pre-equilibrated with $Al(NO_3)_3$ containing N_2H_4.

As yet insufficient data have been collected to draw any conclusion regarding the variat ion of D.R. with change in pH.

<u>The Determination of Reducing Substances in Hexone</u>

Samples of commercial hexone (La Pine), doubly pretreated hexone, and treated hexone which had been aged for five months were analyzed for reducing power by the Ce^{+4} and $Cr_2O_7^{=}$ procedures. The cerate oxidation involved a direct potentiometric titration with 0.02 N $(NH_4)_2Ce(NO_3)_6$ of a solution prepared by mixing 50 ml glacial acetic acid, 20 ml H_2O, and 5 ml of the hexone sample. Reducing normality by the dichromate method was determined by adding 10 ml of a 0.01 N $K_2Cr_2O_7$ solution to 5 ml of the hexone sample, swirling the mixture for one minute, diluting with 15 ml 6 N H_2SO_4, and, after the mixture was allowed to stand for 15 minutes (with intermittent shaking), back titrating with Fe^{+2} solution. One drop of 0.025 N feroin was used as the indicator. The results are tabulated in the following Table.

[redacted]

[redacted]

The Determination of the Reducing Normality of Hexone Solutions

Sample	Reducing Normality as Determined by	
	Ce^{+4} Titration	$Cr_2O_7^{=}$ Procedure
Commercial Hexone	0.002*	0.008**
Fresh Pretreated Hexone	0.000*	0.002*
Aged Treated hexone	0.003*	0.007**

*mean of two determinations
**mean of four determinations

The dichromate procedure shows a considerably larger reducing power which, as shown by the low value for the reducing normality of the freshly treated hexone, cannot be attributed to decomposition of the dichromate by the hexone itself.

<u>The Effect of the Addition of Probable Hexone Impurities on the Reducing Power Determinations</u>

On the assumption that mesityl oxide, methyl isobutyl carbinol, and butyl alcohol were the more probable impurities in hexone, it was decided to determine the effect of the addition of these substances upon the reducing power procedures.*

A 50 λ aliquot of each substance was used in the determinations. For the cerate method the aliquot was added to a mixture of 50 ml acetic acid-20 ml H_2O-1 ml HCl, and the solution titrated with 0.02 N $(NH_4)_2Ce(NO_3)_6$. No reduction of the cerate was noted.

The dichromate procedure was carried out as in the previous section, using a 5 ml sample of the freshly treated hexone to which was added the 50 λ aliquot. The greatest reduction occurred in the case of the isobutyl alcohol but even in this case a maximum of 2.5% of the impurity was oxidized assuming an equivalency of one.

Hence, the reducing normality of hexone as shown by either method for determining reducing power carried out as above does not indicate the amount of any of the above impurities in the hexone.**

*Isobutyl alcohol was used instead of the butyl alcohol and should be only slightly more readily oxidized.
**Recent information from J. Marsden of Knoll's Laboratory indicates that they have developed a method for the determination of methyl isobutyl carbinol based on the oxidation of the alcohol with dichromate and a colorimetric estimation of the chromic ion produced. The procedure involves a 5 minute, two-phase treatment with 0.1 M $K_2Cr_2O_7$-1 M HNO_3 of the hexone containing the alcohol. The fact that but little reduction occurred in the above experiment may be due to a difference in rate of reaction.

[redacted]

Iodometric Titrations in Nitrate Systems

As an aid to the interpretation of data on extraction from nitrate systems and in particular to determine Ru valences in nitrate extraction solutions investigation of methods of determining oxidation-reduction potentials in nitrate systems has been undertaken. Efforts have been initially directed toward a study of iodometric reactions in these systems.

Iodometric Titrations in Pure HNO_3 Solutions

The oxidizing properties of NO_3^-, NO_2^- and NO_2 and the fact that even a trace of NO catalyzed the liberation of I_2 by oxygen from acid iodide solutions gave reason to expect some difficulty in iodometric titration in nitric acid solutions. however, it was felt that nitrate ion itself was sufficiently stable for such determinations and that the other substances could either be removed by physical or chemical means or, at the least, their interference could be accurately determined and limited by running the titration in a solution protected from air by a CO_2 atmosphere.

A stock nitric acid solution was prepared by bubbling dry CO_2 through the 70% C.P. reagent for 24 hours to remove the dissolved nitrogen oxides. Some difficulty was experienced in the first few titrations from the ordinary distilled water available in the plant which contained considerable copper and which was $\sim$0.0001 N in I^- oxidant. Also it was found that in titrating dilute I_2 solutions with 0.024 N thiosulfate, dilute KI concentrations (ca 0.02 M) in 1 to 2 N acid gave a blue end point with starch, and that at concentrations of the order of 0.1 M the color change was violet-blue to violet to colorless. A potentiometric titration of the I_2 showed this color change to indicate correctly the end point (Figure 23).*

A solution prepared by adding 10 ml of the stock HNO_3 solution and 1 g KI to 100 ml of the good distilled water and protected from air by a CO_2 atmosphere gave no color upon the addition of starch (20 drops of a 0.2% solution). At the end of 15 minutes a slight color had developed but was removed by the addition of 0.07 ml of a 0.0244 N thiosulfate solution. Figure 23 illustrates potentiometric titrations with the thiosulfate of solutions prepared by adding 5 ml

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*Since a violet end point is commonly associated with a bad starch solution, several experiments were performed to establish this color change as being a normal property of iodometric titrations, not due to bad starch or an impurity in the titrating solutions, and not a peculiar property of nitrate systems. Titrations were performed in both HCl and H_2SO_4, liberating I_2 using $(NH_4)_2Ce(NO_3)_6$, KIO_3 and $K_2Cr_2O_7$. Four starch preparations were used, two from Arrowroot (Coleman and Bell Co.) and two from Merck soluble starch, according to Lintner, using HgI_2 in 3 cases and $CHCl_3$ in the later case as preservatives. Two distilled waters were used, one an especially pure water obtained from the analytical group. Three separate bottles of C.P. KI were used as well as some KI especially purified by recrystallization from absolute alcohol. The color changes in all cases were the same, with a definite violet tint prior to obtaining a colorless solution. It is probable that the color change noted here differed from those commonly encountered in starch iodine end points because of a lengthening of the color scale by the use of 0.024 N thiosulfate instead of 0.1 N solution ordinarily used in iodine determinations.

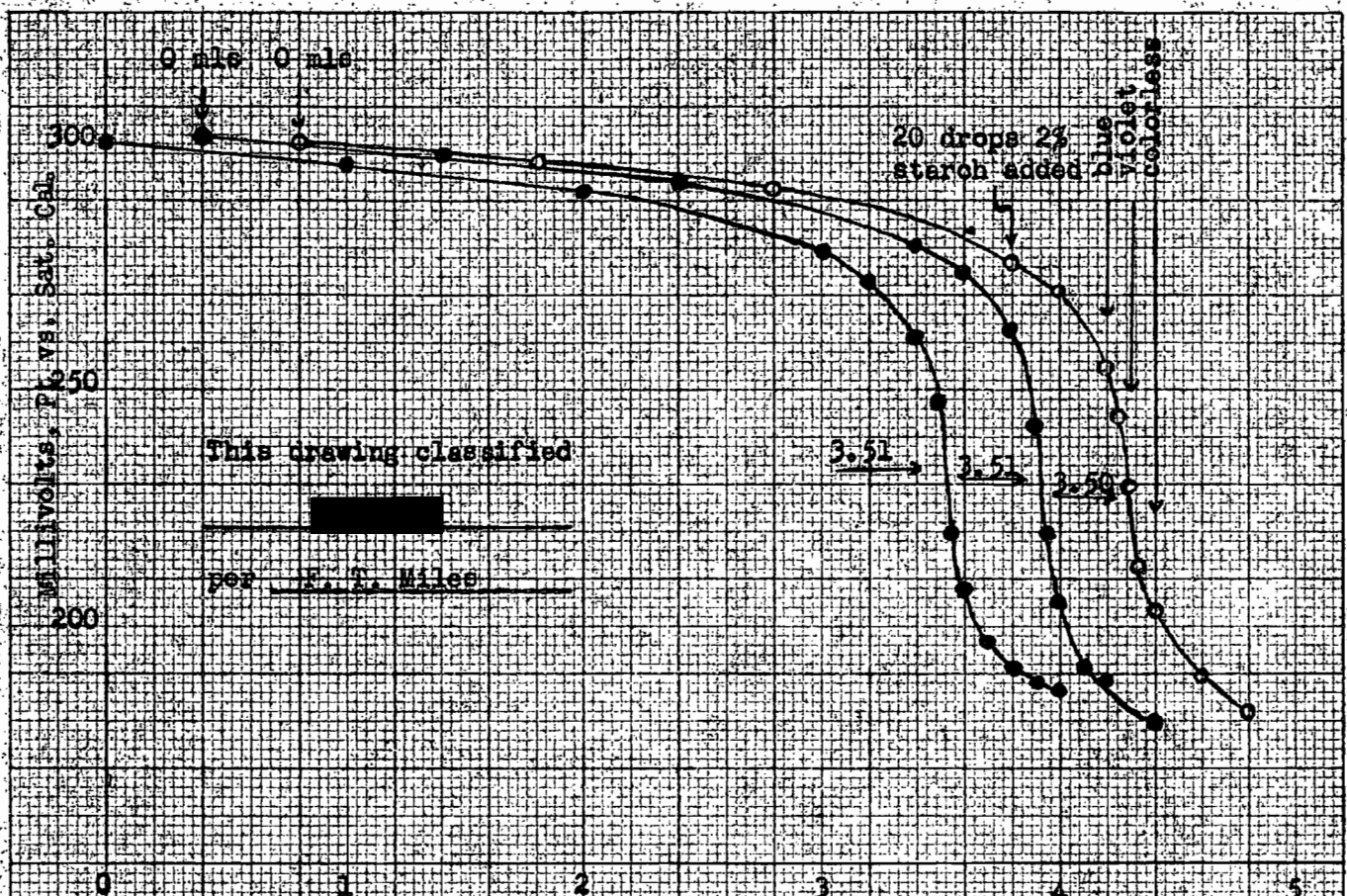

Figure 23. Potentiometric Titration of 0.0865 meq I_2 in 1.4 N HNO_3-KI Solution

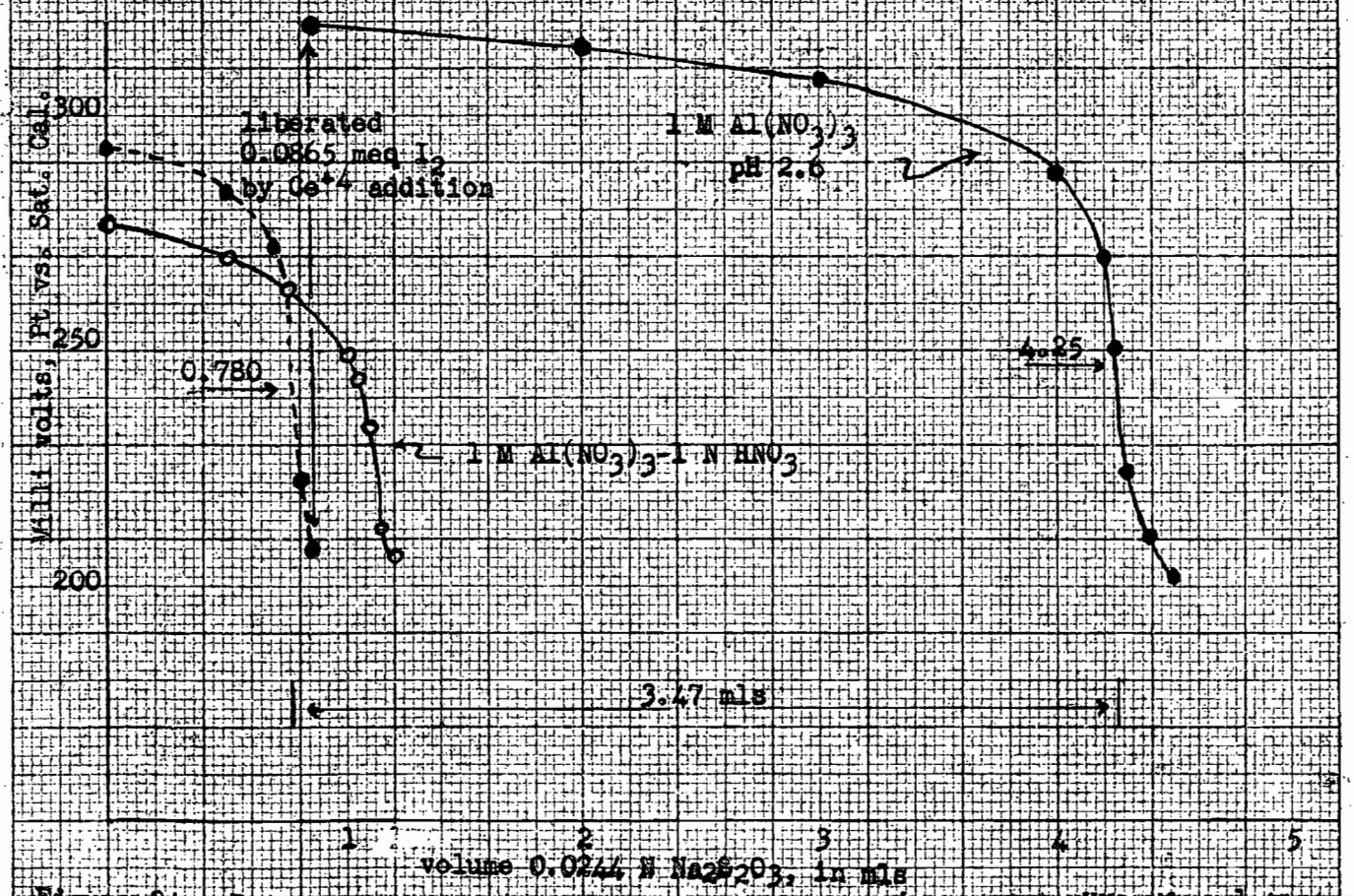

Figure 24. Potentiometric Titration of 0.0865 meq I_2 in $Al(NO_3)_3$-HNO_3-KI Solution

KEUFFEL & ESSER CO., N. Y. NO. 359-11
10 X 10 to the ½ inch, 5th lines accented
Engraving, 7 X 10 in.
MADE IN U.S.A.

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of a 0.0173 N $(NH_4)_2Ce(NO_3)_6$ solution to 110 ml of a 1.4 N HNO_3 solution containing 1 g KI. The titration was performed using a platinum wire and a calomel half-cell. No drift was noted, and the end point was sharp and reproducible. The color changes produced at the end point in one of the solutions to which 20 drops of starch solution had been added are indicated on the graph.

Iodometric Titrations in $Al(NO_3)_3$-HNO_3 Solutions

Figure 24 illustrates the potentiometric titration of several $Al(NO_3)_3$ solutions, one, prepared by mixing ca 50 ml of an old 2 M $Al(NO_3)_3$ with 60 ml of a 2.5 N HNO_3 solution containing 1 g KI, and the other by diluting 1:1 the $Al(NO_3)_3$ with good distilled water and adding 1 g of KI to 100 ml. The pH of the latter solution was 2.6. In the latter case, also, 5 ml of 0.0173 N $(NH_4)_2$-$Ce(NO_3)_6$ was added at the blank end point and the titration continued to a new end point. The additional thiosulfate required is seen to be equivalent to the cerate added.

A new $Al(NO_3)_3$ stock solution was prepared and neutralized somewhat with NaOH. The final solution was 2.6 M in $Al(NO_3)_3$ and ca 0.2 N in $NaNO_3$. Upon 1:1 dilution with H_2O this solution had a pH of 1.9. The following illustrates the results of 3 titrations with 0.024 N thiosulfate of the I_2 liberated in 50 ml aliquots of the diluted solution on the addition of 1 g KI, and the effect of time of standing in a CO_2 atmosphere before titration.

Time of Standing (in min.)	Meq I_2 Liberated
5	0.0154
10	0.0151
15	0.0156

The titration blank is seen to be reproducible, and 5 minutes is sufficient time for the liberation of I_2.

The titration blank is probably due to the presence of dissolved NO_2. An effort will be made to free the stock solution from nitrogen oxides as in the case of HNO_3 by bubbling CO_2 through the solution.

Distribution of HNO_3 into Hexone

The concentrations of nitric acid in hexone in equilibrium with 1.00, 1.25, and 1.50 M $Al(NO_3)_3$ covering the new process conditions (high pH) have been measured. The results are plotted in Figure 25. The data have been fitted by the equation

$$\log \left[HNO_3\right]_{Hex} = -0.74 + 0.4 \log \left[Al(NO_3)_3\right]_{Aq} - 0.02\ pH$$

for the range $0.6 < pH < 2.0$. The equation is shown by the lines in Figure 25 for the three $Al(NO_3)_3$ concentrations. Below pH 0.6 the lines show a definite

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Dwg.#4874, MonN-432

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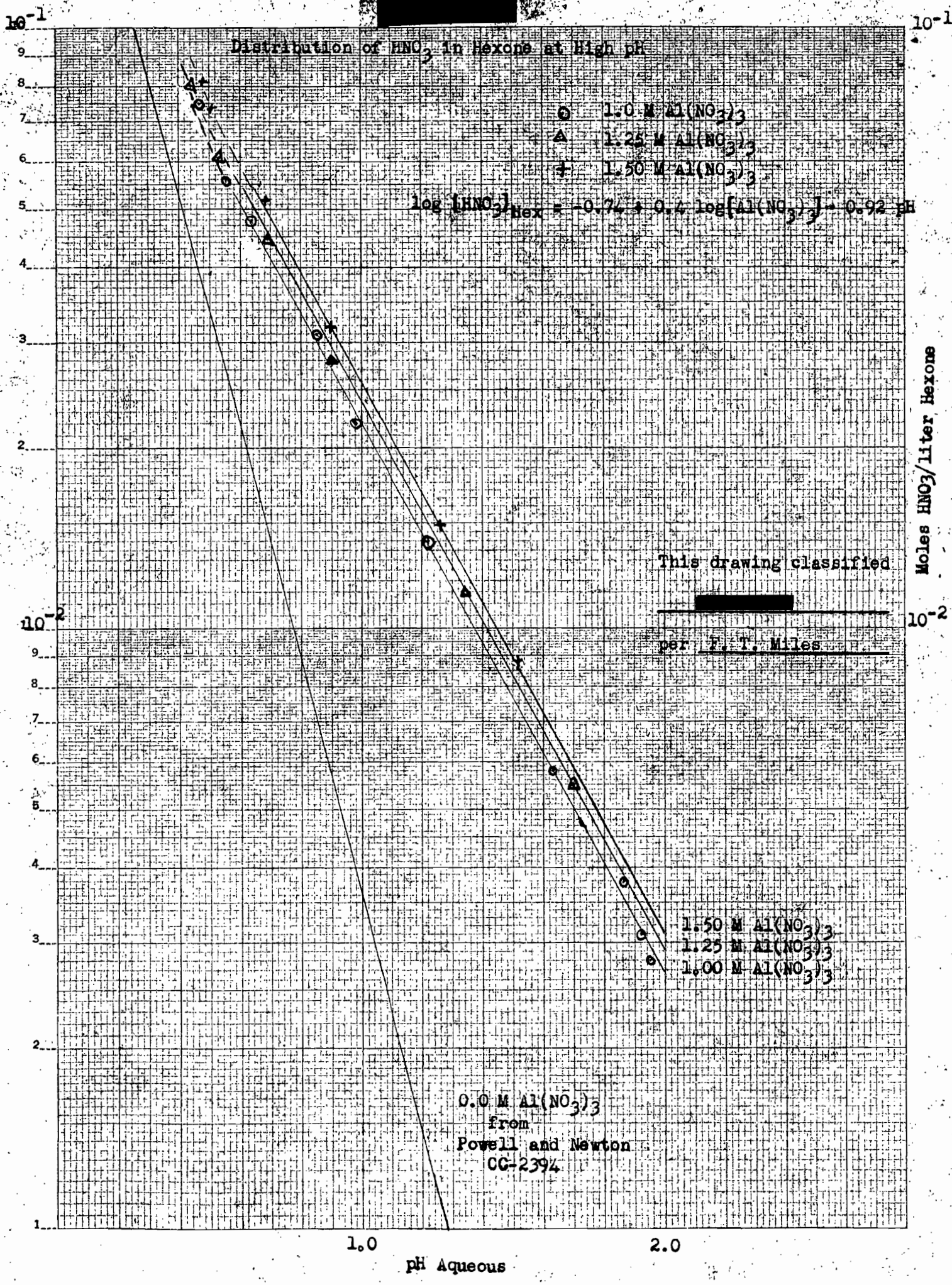

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per F. T. Miles

KEUFFEL & ESSER CO., N. Y. NO. 359-63
Semi-Logarithmic, 2 cycles X 19 to the ½ inch, 5th lines accented
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upward curvature. The fourth line for no $Al(NO_3)_3$ was calculated from the data of Powell and Newton, CC-2394, and published activity values.

The above equation can be put in the form:

$$\frac{C_{HNO_3\,Hex}}{C_{NO_3^-\,Aq}^{0.4} \times A_{H^+\,Aq}^{0.92}} = 0.11$$

Note that this contains <u>concentrations</u> of HNO_3 in hexone and NO_3^- in the aqueous, but <u>activity</u> of H^+ as determined by glass electrode measurement.

[redacted]

[redacted]

Isolation of U^{233} from Thorium by Solvent Extraction. (E. G. Bohlmann, G. E. Creek, C. V. Ellison, J. V. Gost, D. N. Hess, C. E. Higgins, R. E. Wacker)- P. A. CX9-1.

Introduction

Work in the Chemistry Division on the problem of separating U^{233} from the thorium blanket of the heterogeneous pile has resulted in the development of a solvent extraction process utilizing dibutyl cellosolve as the organic solvent. Briefly, the process consists of:

(1) Dissolution of the thorium metal slugs with 70% nitric acid containing 0.05 M HF.

(2) Precipitation of ca. two grams MnO_2/liter from the resulting solution adjusted to 5 N thorium nitrate 1 N in nitric acid. This step serves to clarify the solution by removing dissolver "crud" and also carries Pa^{233} and fission products with resultant decontamination.

(3) Continuous counter-current solvent extraction separation of the U^{233} from Th^{232}, Pa^{233}, and fission products.

Feed: 1 vol. 5 N $Th(NO_3)_4$, 1 N HNO_3.

Scrub: 1 vol. 6 N $Al(NO_3)_3$, 2 N $Ca(NO_3)_2$, ca. 2 N $Ca(OH)_2$ to adjust the pH to 1.6.

Solvent: 2 vols. untreated dibutyl cellosolve.

(4) Counter current stripping of the U^{233} from the organic phase.

Solvent: 5 vols. extract from the extraction column.

Aqueous: 1 vol. distilled water.

The aqueous solution from the strip column is concentrated by evaporation and the U^{233} product worked up in the laboratory.

During the past quarter the 706-C pilot plant has been modified to provide standby production equipment for separating U^{233} in the eventuality of a sudden demand for relatively large quantities of this material. Studies of column capacity, solvent recirculation, and overall process decontamination factors have been made with the modified set-up.

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Run C-22 - Decontamination Data

The most interesting data has been obtained in a run made with Hanford bombarded thorium metal. The metal was made up in the form of ten 1100 gram slugs which had received an exposure of 92.6 effective days. This corresponds to an average of 176.3 MWD/MT of heavy metal or to an nvt of 5.26×10^{19} n/cm^2 in the adjacent heavy metal. The slugs had cooled for eighty days before processing was begun. Table 1 compares these slugs with "a typical delivery of irradiated thorium to the 1300 area".(1)

Table 1

Comparison of Irradiated Hanford Thorium Metal with Estimated Typical Delivery to the 1300 Area

Source	Irradiation (days)	Cooling (days)	Th^{232} (kg.)	U^{233} (g)	Pa^{233} (g)	F. P's. (g)
Hanford	92.6	80	50	18	0.8* 0.35**	0.17
Het.Pile(1)	30% 100 70% 15(2)	245(2)	50	75	0.1	2.25

*Calculated from irradiation and cooling data.
**As measured by β counting assuming 100% counting efficiency.

The metal used in the test run contained about 1/5 the U^{233}, 1/13 the fission products, and four to eight times the Pa^{233} anticipated in the thorium metal feed to the 1300 area. Thus the results obtained are indicative of the performance which might be expected in processing thorium metal from the heterogeneous pile. Tables 2 and 3 give the activity concentration in the dissolver feed, and the aqueous strip solutions and the decontamination factors measured in the run.

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1. G. H. Hanson to 12-1300 Area Design File, October 30, 1947.

2. G. H. Hanson to 12-1300 Area Design File, July 22, 1947.

[redacted]

[redacted]

Table 2

Distribution of Beta Activity in Dissolver, Feed, and Aqueous Strip Solutions

Solution	Gross β	Pa β	Ru β	Ce β	Zr β	Cb β
Dissolver	1.24×10^{10}	1.27×10^{10}	--	--	--	--
Feed	2.0×10^{9}	1.7×10^{9}	6.6×10^{5}	2.1×10^{7}	4.3×10^{7}	5.1×10^{5}
Aq. Strip	9.0×10^{3}	2.5×10^{3}	1.3×10^{3}	74	2.4×10^{2}	30

The estimated[1] decontamination requirements of 2×10^5 for Pa^{233} are more than met by the measured factor of 6×10^6 obtained without adequate scrubbing, but the factor of 10^5 obtained for the fission products is rather short of the 10^6 required. There are, however, several factors that suggest that another factor of ten is obtainable:

(a) The fission product decontamination factor obtained in the MnO_2 precipitation could not be measured because of the great preponderance of Pa^{233} activity in the dissolver solution; however, the low columbium to zirconium ratio suggests that a substantial proportion of the columbium is carried on the MnO_2 and that, although small, some small fission product decontamination could be expected.

(b) The beta and gamma decontamination factors of 7 and 3 obtained on further scrubbing the extract from the column indicate further fission product decontamination since the majority of the activity present was due to fission products. The decontamination figures given do not take into consideration the beta activity from conversion electrons from the disintegration of U^{233} present in the beta samples. On the basis of data obtained by Studier, this would amount to about 4000 of the 9000 gross counts per minute in the aqueous strip solution with a resultant increase of a factor of 2 or 3 in the decontamination figures obtained.[3]

(c) The tables indicate that ruthenium decontamination is poorest. This is probably due to the fact that nitrite is added to the feed solution after centrifugation to make certain any small particles of MnO_2 which may not have been removed will be destroyed before they can plug the column. Miles and co-workers[4] have shown that the presence of nitrogen oxides increases the organic/aqueous distribution coefficient of ruthenium. Batch data has indicated

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3. Studier, The Radiation Spectrum of the Transition $U^{233} \longrightarrow Th^{229}$ - CB-3793.
4. Miles and co-workers, MonN-311.

Table 3.

Specific and Gross Decontamination Obtained in Run C-22

Process Step	Gross γ		Gross β		Pa β		Ru β	Ce β	Zr β	Cb β	Mixed F.P.
	Step	Overall	Step	Overall	Step	Overall	Step	Step	Step	Step	Step
MnO_2 Ppt'n	3.5	3.5	4.0	4.0	5.0	5.0					
Column(1)	3.2×10^5	1.1×10^6	4.8×10^5	1.9×10^6	1.2×10^6	6.0×10^6	1.1×10^3	6.3×10^5	3.9×10^5	3.6×10^4	1.1×10^5
Scrub 1(2)	3.0	3.3×10^6	7.1	1.3×10^7							
Scrub 2(2)	1.1	3.6×10^6	1.0	1.3×10^7							

1. The column was packed with 3/16" Fenske helices and gave approximately two extraction plates and one-half of a scrub plate.

2. The scrub tests were made on a sample of extract from the column taken over a three hour period.

[redacted]

that the process should separate ruthenium by a factor of several times 10^4 and it is believed that this can be achieved in the column operation by adding a small amount of urea after the nitrite.

Table 4 summarizes the results of a batch decontamination test made with the solutions from run C-22.

Table 4

Decontamination Obtained in Batch Test Using Solutions from Run C-22

Step	Volumes			Gross β		Gross γ	
	Feed	Scrub	Organic	Step	Overall	Step	Overall
Extraction	1	1	2	6.8×10^3	6.8×10^3	7.3×10^3	7.3×10^3
Scrub 1	0	1	2	6.8	4.6×10^4	19*	10^5
Scrub 2	0	1	2	1.3	6.0×10^4	--	--

*No counts were measured so 4 c/m were assumed for the calculation.

Comparison of the results after the first scrub with those obtained in the column alone in the run shows correspondence for the gamma decontamination obtained with definitely better beta decontamination in the column. It might be of interest to point out that, contrary to the results often obtained with hexone in the past, studies with cellosolve have usually given as good decontamination results in column operation as in batch tests.

The general conditions and yield figures for the run are summarized below:

<u>Solution compositions.</u>

Feed: 5.0 N thorium nitrate, 0.83 N nitric acid, 0.091 mg U^{233}/ml. (10^6 c/m/ml).

Scrub: 6 N aluminum nitrate, 2 N calcium nitrate, 80 g calcium hydroxide per liter to adjust the pH to about 1.6.

Organic: Untreated commercial dibutyl cellosolve.

<u>Stream volumes to the column.</u>

Feed:Scrub:Organic = 1:1.22:2.8.

[redacted]

[redacted]

Distribution coefficients.

Extraction section
U(org/aq) 6.6
Th(org/aq)0.0054

Scrub section
U(org/aq) 4.5
Th(org/aq) 0.009

HETS

Extraction section 4.6 feet
Scrub section 4.1 feet

Thorium separation factor.

1.4×10^3

Pa^{233} carrying on MnO_2 = 80%.

The results of the MnO_2 precipitation were disappointing from the standpoint of Pa^{233} carrying. Only 80% of the Pa^{233} was carried by the MnO_2 compared with greater than 95% carrying obtained in laboratory studies. The problem in this case did not appear to be a matter of scale up since a laboratory test on some of the same solution also gave only about 85% carrying.

Table 5

Yield and Material Balance for Run C-22

	Mg U^{233}	%
Feed	3770	100
Strip Aqueous	3467	92.0
Raffinate	60	1.6
Stripped Extract	77	2.0
Material Balance		95.6

[redacted]

The recovery based on the feed is rather low but is not a true measure of the process performance. The low material balance which results in the low recovery figure is due to the holdup of the feed pumping system. The previous run made in the system was on low concentration feed. Thus the pumping system was full of low concentration material at the start of the run and this was replaced with the high concentration feed of this run with resultant low material balance. Taking into account this two or three liter holdup containing 90 milligrams of U^{233} per liter the material balance will be within analytical error of 100%. If, as a consequence of the feed holdup, we base the yield on the amount of U^{233} left in the raffinate and the total recovered we find that the recovery was 98.3%. This loss is the result of the high HETS obtained in this run since batch tests on the raffinate showed the distribution coefficient was unchanged and the residual U^{233} was extractable. Previous runs made since the column packing was changed from 1/8" to 3/16" Fenske helices have given HETS values of 1.7 to 2.2 feet. The value of 4.6 feet obtained for this run suggests that the channeling which made the 1/8" packing unsatisfactory in the limited head room available for column operations in the 706-C cells may have reappeared with the larger packing. This higher HETS first appeared during a run in which the effect of recycling cellosolve after a hot water wash treatment was studied. It was not possible to determine whether the increased HETS was due to the accumulation of crud in the column or to the formation of channels as a result of packing settling.

The column was washed successively with acetone, water, 20% sodium hydroxide, water, 8 N nitric acid, and water after the run on the recycled cellosolve and appeared to give satisfactory results on a re-run of raffinate from that run, but the data from C-22 indicates that the unsatisfactory performance persists. A further attempt to clean the column has been made by letting it soak filled with concentrated nitric acid containing 0.05 N HF. Determination of the results of this treatment await the next run.

Run C-20 - Cellosolve Recycle

Laboratory batch studies indicated that decontamination factors obtained with dibutyl cellosolve are improved by a factor of five to ten if the cellosolve used is washed with water before being used in the batch test. R. Blanco of Technical Division, Section I, also investigated the effect of water washing on reducing substances in dibutyl cellosolve and found that essentially complete removal was obtained by washing the cellosolve with several volumes of water at 60-80° C. These results suggested that it might be possible to operate columns using dibutyl cellosolve in a cyclic manner by taking the solvent from the water strip column, passing it through a hot water scrub column and returning to the solvent feed. In order to test this a 1½" column containing about eight feet of 1/4" Fenske helice packing was set up and the cellosolve from the strip column washed by passing it through this column counter current to approximately five volumes of water at ca. 50° C.

After the fifteen liters of cellosolve in the system had been recycled five times, analysis of the raffinate indicated that the losses were mounting steadily so the run was completed with fresh solvent. Preliminary results obtained in the run are summarized in Table 6.

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Table 6

Use of Continuous Solvent Recycle in Dibutyl Cellosolve Process for Recovery of U^{233} from Th^{232}

Time (hrs.)	Solvent Pass	% U^{233} in Raffinate	HETS (ft.)
6	1.08	1.9	1.8
12	2.42	2.8	2.8
18	3.75	4.5	3.2
23-3/4	5.05	7.7	4.0
*			
26-3/4	1	6.9	3.6
29-3/4	1	6.8	3.5
32-3/4	1	5.5	3.0
33-1/2	1	5.3	3.0

*Changed to new solvent

The rise in HETS with re-use of the cellosolve followed by a slow decrease on switching to new solvent is interesting. Thus far no explanation of this effect can be made, nor is it possible to say beyond doubt, from this data alone, that it was the result of re-use of the cellosolve. Batch studies with the re-cycled cellosolve indicate no difference from the new solvent in the distribution coefficients obtained so the problem seems to be one of column packing efficiency.

Run C-19 - Effect of Flow Rate on HETS

Run C-19 was made to study the effect of flow rate on HETS; the data is summarized in Table 7.

Table 7

Effect of Flow Rate on HETS in 706-C Pilot Plant Column

Rates L/hr			Extraction Factor	% U^{233} Recovery	HETS ft.	
Feed	Scrub	Solvent			Extraction	Scrub
1.7	1.6	2.8	2.5	99.4	1.8	3.7
3.5	3.2	6.1	2.7	97.5	2.7	4.4
4.5	5.2	9.0	2.8	95.8	3.3	---

[redacted]

[redacted]

It is evident that the column cannot be operated at rates very much greater than the 1500 cc/hr. designed feed rate without increasing the HETS substantially. It is probable that the loss could be reduced by operating at a higher solvent to aqueous ratio, but this has not been demonstrated.

Summary

The pilot plant has been modified to provide standby U^{233} production equipment.

A run has been carried out on 80 day cooled Hanford bombarded thorium metal slugs. Decontamination factors demonstrated were:

gross beta - 1.9×10^6
gross gamma - 1.1×10^6
protactinium beta - 6.0×10^6
mixed fission product beta - 1.1×10^5

with probable increases in all these factors indicated with adequate scrubbing. The recovery in the run, 98.3%, was a bit low due to unusually high HETS.

Studies of the effect of recirculation of the cellosolve after a hot water wash and increasing flow rates showed increased HETS in both cases.

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2. RADIOISOTOPES

Radiochemical Measurements and Standardization (R. T. Overman, W. C. Peacock, L. R. Zumwalt, L. M. Fry, J. W. Jones, (E. Lamb, on loan from Operations))

Flux-Yield Experiments (R. T. Overman, L. M. Fry, E. Lamb, J. W. Jones)

The activity of this group has centered around two problems. The first is that of determining yields for the (n, γ) produced activities in the pile. Approximately thirty-five activities are being studied in this program with about twelve of them having been done. The calculations on these are not complete so no results are being reported yet. The program consists of performing the following operations on each of the samples:

1. Two samples are irradiated both with cobalt monitor clips on them.

2. One sample is kept at the pile building and a decay curve is run on the sample in the can using the Beckman ion chamber that is used for determination of the activity level for shipping samples.

3. The other sample is brought to the Chemistry Division and a gross decay curve is started on the sample. This will make a record of short-lived impurities that may be present.

4. The sample is purified chemically and a decay curve is started on the purified sample to determine its characteristics.

5. Absorption curves are run on the purified samples and yields are calculated.

6. The cobalt monitor clip is measured in the pressure gamma chamber and the total integrated flux which the sample was in is calculated.

7. From these data an effective pile cross section is calculated. These numbers will be reported as n which is the neutron density in the pile at the position of the sample and $\overline{\sigma v}$ which is analogous to the pile reaction constant. These concepts are developed in a memo (Jones to Overman, November 1947).

The Operations Division is cooperating with us in this program and has loaned us the services of Mr. Lamb to assist in the preparation of the data. Mr. Lamb will then be in a position to take the data back to the Operations Division and will know its value and its limitations.

The second activity which has engaged the attention of this group has been the flux monitoring program. As has been indicated in previous quarterly reports, we have had clips made up which fasten on to the outside of the can. The same clip may be used inside of a rabbit for a determination of the flux of the rabbit although many determinations have given extremely consistent results of the flux at the rabbit position. As is given in the report of the measurement of the pile flux, (Mon C-398), the rabbit neutron

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density is 0.71 n/cm^3/watt and the flux (nv) is 1.56 x 10^5 n/cm^2/watt. We have corroborated this with a number of gold measurements made during this quarter. From these measurements we have calculated the weight of cobalt in the monitor alloy.

The flux may be determined from the monitors now by irradiating one of them along with the other material being studied. After a suitable length of time the monitor is placed in the pressure ionization chamber and the ionization current is measured. This time is of the order of five days. This is made necessary by the fact that the alloy has in it a certain percentage of Mn which gives a 2.56 hour half-life and is useful for short bombardments. The alloy also contains some sodium activity which was introduced inadvertently in the melt. These activities decay away to negligible proportions in about five days. The flux is then calculated by using an equation of the form

$$f = \frac{R_v \times v \times K}{s}$$

where f is the flux in neutrons/cm^2/sec

R_v is the number of rutherfords per volt of cobalt. This is a function of the scale on which the measurements are read.

v is the number of volts per gram of monitor alloy and is read on the ion chamber potentiometer

K is a constant containing in it the number of atoms of cobalt per gram of monitor and the cross section of cobalt

s is the saturation factor $(1 - e^{-\lambda t})$

All of these terms are known for the particular instrument which is now in operation and for the alloy now being used with v being the variable. We will be glad to make samples of this alloy available to anyone desiring to make such a measurement. Such a measurement and calculation takes a matter of minutes and it is hoped that all those making irradiations will make use of these clips. It is hoped that all samples going into sample stringers in the pile will be routinely measured in the near future.

Some of the results of studies made with these monitors are given in the following table. The table includes the stringer position, the flux, as reported in Mon C-398, and the ratio of the flux at the stringer position compared to the center flux, calculated from the curves of H. Jones in CP-2602 using the average power level of the month's bombardment and the flux as measured with the monitors.

It is seen from the table that while the curves of H. Jones predict smoothly varying vflux from one position to the other, such is not the case. In section 13 H positions there is a plus and minus variation of the order of 15-20%. The variation of flux with time at these positions is under investigation.

[redacted]

[redacted]

Stringer Position	Flux Calculated (All values x 10^{11})	Flux Measured (All values x 10^{11})	$f_{calc.}$ / $f_{meas.}$
13 H 21	4.74	4.43	1.07
13 H 22	4.74	4.49	1.06
23	4.83	4.05	1.19
24	4.83		
25	4.83	4.48	1.08
26	4.83	4.57	1.06
27	4.76	4.31	1.10
28	4.85	4.42	1.10
29	4.85	3.91	1.24
30	4.85	4.32	1.12
31	5.03	4.85	1.04
32	5.03	5.04	1.00
13 G 17	2.92	3.13	0.93
18	3.01	3.26	0.92
19	(3.10) Est.	2.87	1.08
20	(3.20) Est.	2.46	1.30
13 K 3	4.84	4.30	1.13
4	4.75	4.25	1.12
14 A 17	3.98	4.12	0.97
18	4.07	4.20	0.97
21	4.25	4.40	0.97
23	4.34	4.76	0.91
24	4.43	4.90	0.90
26	4.61	4.94	0.93
14 C 5	7.03	7.98	0.88
8	7.03	7.75	0.91
		Avg.	1.04

[redacted]

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Other work that has been done has been the determination of the cross section of Fe^{54} from various samples that have been irradiated in the Clinton pile and at Hanford. The X-ray measurements have been made by R. G. Fluharty of M. I. T. Some irregularity is noted in the various measurements. In the first set the Hanford flux was determined by the ratio of the Fe^{59} and the Fe^{55} in two samples that had been irradiated in the two piles. From this ratio the cross section was calculated for the long-lived isotope with the calculation giving a result of about 0.8 barns. On the second sample the actual number of megawatt days at Hanford was used in the calculation. This gave a cross section of about 1.6 barns. It is obvious that more work will have to be done on this problem. On the irradiation mentioned last, the ratio of Hanford to Clinton flux was found to be only about 10. Some work seems necessary in the determination of the flux used in such irradiations before such calculations will be highly significant. The corresponding value as determined by Pomerance in the pile oscillator was 2.4 barns.

Beta Ray Standards and Measurements (L. R. Zumwalt)

A second comparison of the determination of the disintegration rate of radiophosphorous by absolute beta counting and by calorimetric measurement was made. This comparison was marked by a greater certainty in the accuracy of the calorimetric measurement and by an independent absolute beta count determination through the use of a recently acquired National Bureau of Standards radium D-E standard where the procedure recommended by the Bureau was followed. The results obtained were:

Method	Disintegration Rate (d/s) at a given reference time (with estimated probable error)	Per cent Deviation from Average
1. Use of Calibrated G-M Tube with our usual technique	$7.90 \pm 0.17 \times 10^8$	+1.5
2. Calorimetric Measurement and average energy of 0.700 Mev (by Cannon & Jenks)	$7.73 \pm 0.10 \times 10^8$	-0.6
3. Use of NBS RaD-E Std.	$7.64 \pm 0.17 \times 10^8$	-1.8
	$7.83 \pm 0.17 \times 10^8$	+0.6
Average	7.78×10^8	

Three radium D-E secondary standard sources were calibrated and sent to the National Bureau of Standards for intercomparison. The sources were prepared by evaporating a few lambda of carrier free RaD-E-F solution on a small square of 2.5 mg/cm^2 polystyrene film centrally disposed on and cemented to an aluminum card, the dimensions of which were $2\frac{1}{2}$" x $3\frac{1}{2}$" and 220 mg/cm^2 thick. The backing of this source was found to increase the

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extrapolated counting rate by 26% while the covering increased the counting rate by another 3%.

The results of the intercomparison are given below:

RaE Std.	d/m Determined by Calibration	d/m Determined by NBS	% Difference
#1	10,530	10,360	1.6
#2	9,940	9,620	3.3
#3	10,780	10,620	1.5

A study was made of the absolute beta counting of 10 mg/cm^2 gold foil in an effort to aid in the determination of the neutron flux in the experiment of Snell and Miller on the half-life of the neutron. It was found that the net effect of self-scattering and self-absorption by the gold foil was that of increasing the extrapolated counting rate (source 2 cm from a 30 mm diameter end-window G-M tube) by 41% over the counting rate which the same gold activity would give if the source were "weightless".

In connection with studies of the effect of beta particle scattering on the counting rate of radioactive sources, a series of forescattering and backscattering curves have been obtained with various beta particle sources (Co^{60}, I^{131}, RaE and P^{32}) for foils of various thickness and of materials of atomic numbers ranging from Z = 4 to 82. Recently, a series of absorption curves were taken of Co^{60}, RaE and P^{32} sources mounted on 50 μg/cm^2 Formvar-polystyrene laminated films with no backing and also with a backing of thick plates of material (which give saturation backscattering) of atomic numbers ranging from Z = 4 to 82. These data are to be used to determine the effect of backscattering by thick materials of various Z in increasing the extrapolated counting rate and also to determine the absorption curves of backscattered radiation. It is found in connection with the latter that backscattered radiation is less degraded in energy, i.e., the absorption curve of the backscattered radiation--which in general, has a greater slope than that of the unscattered radiation--becomes more nearly similar to the curve of the unscattered radiation, the higher the Z of the backscattering material. Thus, in the case of RaE with a lead backscatter the absorption curve for the backscattered radiation has almost the same slope as that for unscattered radiation, while with an aluminum backscatter the slope of the absorption curve is about twice that for the unscattered radiation.

A formula for the solid angle subtended by a circular disk at any given point, P, has been derived as an expansion in even powers of ρ/R where ρ is the perpendicular distance of the point from the axis of the disk, and R is the distance from P to the center of the disk. This has been derived so that the geometry of elements of the area of a source which are not on the axis of an end-window G-M tube may be calculated. This will be included in report Mon C-397 which will give a detailed discussion of much of our previous work on beta counting and the effects of beta particle scattering.

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Recently an intra-laboratory check has been made on an I^{131} sample. The results obtained are given in the following table:

Method of Determination	Activity mc/ml
Beta counting by production laboratory	3.7
Use of calibrated ionization chamber (RTO)	3.45
Use of calibrated G-M counter (LRZ)	3.43

The fraction of positrons emitted per disintegration of Zn^{65} was determined. A Co^{60} source was used for comparison together with data on the relative counting efficiencies of gamma rays as a function of gamma ray energy in the case of a copper cathode G-M counter. The determination gives a result of 0.028 ± 0.005 positrons per disintegration of Zn^{65}.

A report has been prepared by L. G. Fry on the preparation of ultra-thin films for low scattering-mounting for sources.

Decay Schemes: Summary of All Spectrometer Data to Date (W. C. Peacock, J. W. Jones and R. T. Overman)

Zn^{65}. A new value was obtained for the positron endpoint. The value of 0.32 ± 0.01 Mev replaces the former value of about 0.4 Mev which was given in a private communication from DuBridge and his group as a result of cloud chamber measurements.

Cs^{134} (3 h). Highly converted gamma ray of 0.150 ± 0.03 Mev going to lower state (Cs^{134} 2 y). The alternate transition from Cs (3 h) to ground state is now being studied.

Cs^{134} (2 y). Gamma energies of 0.610 ± 0.02 and 0.799 ± 0.02 Mev compared with values by Siegbahn and Deutsch of 0.584 ± 0.012 and 0.776 ± 0.015 Mev. The beta ray maximum was found to be 0.635 ± 0.02 Mev as compared with the value of Siegbahn and M. Deutsch of 0.645 ± 0.02 Mev.

Co^{60} (10.7 m). A gamma ray energy of 0.056 ± 0.003 Mev to the ground state of Co^{60} (5 y) reported by Deutsch, Elliott and Roberts has been checked. The decay of Co^{60} (10.7 m) to Ni directly has been found to be by a beta ray of 1.56 ± 0.07 Mev followed by a gamma ray of 1.32 ± 0.03 Mev. The values previously reported for the beta are 1.25 ± 0.06 by Deutsch, Elliott and Roberts and 1.35 ± 0.01 Mev by Nelson, Pool and Kurbatov. Both used spectrometers for the beta ray determination. The gamma ray energy was determined by Nelson, Pool and Kurbatov as 1.5 ± 0.2 Mev by absorption in lead.

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Co^{60} (5 y). The gamma ray energies were found to be 1.16 ± 0.02 and 1.30 ± 0.02 Mev. They had previously been determined by Deutsch, Elliott and Roberts to be 1.10 ± 0.02 and 1.30 ± 0.02. They were also given by L. C. Miller and L. F. Curtiss as 1.16 and 1.32 Mev.

Sc^{46}. This was found to have an isomeric state of about 24 m half-life. Its radiations are being studied.

Sc^{46} (85 d). The gamma ray energies were found to be 0.89 ± 0.02 and 1.11 ± 0.02 Mev. They had previously been measured by A. Miller and M. Deutsch at 0.90 ± 0.02 and 1.12 ± 0.02.

Bi^{210} (5 d RaE). The spectrum was compared in shape with that of Tl^{206} (3.5 y). The Tl isotope has a Kurie plot that is straight from the endpoint at 0.770 ± 0.015 Mev down to below 150 Kev energy (corrections due to window absorption have not been made), while, on the other hand, Bi^{210} does not have a straight Kurie plot as has been pointed out by many previous observers. We confirm the energy maximum at 1.17 Mev for Bi^{210}.

P^{32} (14.3 d). We agree with K. Siegbahn that the Kurie plot of P^{32} is straight from below 150 Kev to the endpoint at a maximum energy of 1.715 ± 0.005. (Our value) We have found the average energy to be 0.701 ± 0.007 Mev.

K^{42} (12.4 h). We find the beta spectrum complex, having endpoints at 3.60 ± 0.05 and 1.9 ± 0.1 Mev and a gamma ray of 1.50 ± 0.05 Mev in agreement with Siegbahn's more accurate value of 3.58 ± 0.07 and 2.04 ± 0.07 Mev for the beta rays and 1.51 Mev for the gammas. Our source thickness for the beta counting was too thick to make an accurate estimate of the relative abundance of the two beta groups but Siegbahn's value does not seem to be unreasonable.

Pr^{142} (19.3 h). This isotope was studied because the beta ray shape was reported to deviate appreciably from a straight line Kurie plot. The spectrum was found to be complex explaining the deviations. There appear to be three beta rays with the maximum being 2.23 ± 0.05 Mev in reasonable agreement with the value of 2.14 ± 0.02 found by DeWire, Pool and Kurbatov. They also report a 1.9 Mev gamma ray associated with this isotope having an abundance of about 4%. Our preliminary results indicate that there are gamma rays associated with about 18% of the disintegrations--one of about 1.3 Mev, the other of about 1.65 Mev. They are not in coincidence.

Ca^{45} (180 d). Found to have a beta ray endpoint at 0.248 ± 0.010 Mev. No gamma rays were found.

Ce^{144} (275 d), Pr^{144} (17.5 m). Pr^{144} is the daughter of Ce^{144} and the two were in equilibrium throughout the measurements. Pr^{144} has a beta ray maximum of 2.99 ± 0.05 Mev with a straight Kurie plot and Ce^{144} has a beta ray maximum of 0.302 ± 0.010. Conversion electrons are observed at 0.075 ± 0.005 Mev and at 0.117 ± 0.05 Mev. Work on these isotopes is continuing.

Cu^{64} (12.8 h). The ratio of negatrons to positrons was found to be 2.08 ± 0.04 in good agreement with the value of 2.1 by H. Bradt, et al.

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We are in reasonably good agreement with the endpoint energies of Tyler for the negatrons and positrons. Our values are β^- 0.570 ± 0.010 Mev and β^+0.644 ± 0.010 as compared with Tyler's values of 0.578 ± 0.003 Mev for the negatron and 0.659 ± 0.003 Mev for the positron.

Eu (Long-lived isotopes). Unreported work is also in progress on the long-lived isotopes of this element.

Rh^{106}. A paper is in print in Physical Reviews which gives the decay scheme of the 30 s daughter of Ru^{106} (1 y).

The following disintegration schemes are being worked on by W. C. Peacock in collaboration with A. R. Brosi and A. D. Bogard:

Xe^{135} (10 m). This isotope decays by isomeric transition with the emission of a 0.524 ± 0.010 Mev gamma ray. Previous values by lead absorption range from 0.5 to 0.6 Mev.

Xe^{135} (9.2 h). Decays by a 0.93 ± 0.03 Mev beta ray followed by a 0.247 ± 0.003 Mev gamma ray. These values all agree well with previously determined values in the fission product table which has been published in the open literature.

I^{135} (6.7 h). This isotope has a complex beta spectrum with endpoints which seem to be at 1.40 (25%), 1.00 (40%) and 0.47 (35%) and at least two gamma rays at 1.27 and 2.00 Mev. The average energy per disintegration of this chain including the isomeric state in Xe^{135} is about 2.11 Mev. These I^{135} values are all tentative and work is still in progress.

I^{133} (22 h). The gamma ray previously published in the fission table as having a gamma ray of 0.55 Mev by absorption in lead was found to have an energy of 0.528 ± 0.010 Mev.

Two activities in erbium have been studied by B. H. Ketelle and W. C. Peacock:

Er^{169} (9.4 ± 0.2 d). This is found to emit no gamma rays and has a beta ray endpoint of 0.33 ± 0.01 Mev.

Er^{171} (7.5 ± 0.2 h). This is a beta emitter which has been assigned to Er^{171} since it decays to Tm^{171} which has a half-life of 500 ± 100 d. Er^{171} has three alternate modes of beta decay. 71 ± 5% of the betas have an energy of 1.05 ± 0.03 Mev and are followed by two gammas of 0.305 ± 0.010 and 0.113 ± 0.005 Mev in cascade. The 0.113 Mev gamma ray is highly converted and has a half-life of 2.5 μseconds according to DeBenedetti and McGowan. 6 ± 1% of the betas have an energy of 1.49 ± 0.05 Mev and decay directly to the ground state of Tm. 22% of the betas have an energy of 0.67 ± 0.03 Mev and are followed by a 0.805 ± 0.025 Mev gamma.

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Analysis of Rare Earths from Canadian Pitchblende: (H. W. Kohn, J. A. Swartout)

I. Introduction:

A rare earth fraction from the process for recovering radium from Canadian pitchblende has been examined to determine its usefulness as a source of europium. The sample analyzed was obtained from the Radium Refinery of Eldorado Gold Mines, Ltd., at Port Hope, Ontario.

II. Analytical Procedure and Results:

The analysis of the rare earth fraction was made using a high temperature (100° C) Dowex 50 cation-exchange column to achieve separation of the rare earths. The cations from an HCl solution of 30.6 mg. of the rare earth oxides, including 10 mg. activated in the pile, were adsorbed on the column and eluted with ammonium citrate-citric acid at pH= 3.0. Fractions of the eluant were collected, the rare earths recovered, weighed and analyzed spectrographically to identify the individual species. The results are shown in the following table.

Analysis of Rare Earth Fraction from Canadian Pitchblende

Eluant Fraction	Weight Milligrams	% Total	Lu	Yb	Tm	Er	HoY	Dy	Tb	Gd	Eu	Sm	Nd	Pr
1*				W										
2*	0.8	2.8	VW	M										
3*				M										
4*	0.9	3.0		W		M	T	T						
5*	0.9	3.0					M	W						
6*	11.2	36.6					VS	M						
7*	5.1	16.7					VS	M	FT					
8	0.5	1.6					T		FT					
9	< 0.3	< 1.0							T					
10	1.4	4.6							MT	M	M			
11	1.3	4.2								W	M			
12	0.9	3.0								M	W			
13	1.2	3.9								M	VW	T		
14*	< 0.1	< 0.3									FT			
15	0.4	1.3										VS		
16*	1.0	3.2								T	VW	T		
17	4.9	16.0										W	VS	M
	31.1 mg.	101.3%												

* Fraction shows activity

III. Conclusion:

Because of the experimental error involved and the relative insensitivity of the europium lines, more than an approximation of the europium content is probably unjustified. Europium appeared in the eluant from the column chiefly in Fractions 10 and 11, constituting about one-third of Fraction 16 and most of 11, or a total of about 1.7 mg. of the 31 mg. of oxides recovered. This corresponds to about 5% europium in the rare earth fraction from Canadian pitchblende. The major rare earth constituents are yttrium, neodymium and dysprosium with yttrium comprising greater than 50% of the mixture.

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

I. Introduction:

The present ion-exchange processes for the separation and isolation of fission products do not reduce the plutonium contamination to the maximum level permissible for shipment outside of the Atomic Energy Commission. This maximum level is now considered to be 0.01 ug of Pu per ml. of solution. Since the production procedures involve the readsorption of the separated species (i.e. rare earths, zirconium and columbium) on cation-exchangers for metathesis to some readily usable form and for volume reduction, it would be convenient to remove the Pu contamination in conjunction with these steps. Furthermore, there are now on-hand large amounts of fission elements rendered unavailable to non-project users by their Pu contamination. Therefore, it appeared desirable to seek a simple ion-exchange separation which could be included in the present production process and could also be applied to the removal of Pu from existing fission element preparations.

II. Experimental:

The general procedure used for the exploratory studies was the adsorption of the fission elements concerned and the plutonium on a cation-exchange column followed by a determination of the separation effected by various eluting agents. Since the plutonium is contained in citrate or oxalic acid solutions prior to readsorption, with the result that the form of the plutonium is uncertain because of possible complexing, polymer formation or equilibria between valence states, this type of experiment seemed more applicable than equilibrium experiments.

A. Separation of Pu from Ce: Plutonium and Ce^{144} were adsorbed from a citrate solution at pH 1.3 on eight 50 cm x 0.6 cm diameter columns, 4 of 70 mesh Dowex 50 and 4 of 40 mesh Amberlite 1R-I. The effluent fractions were at first evaporated and transferred to platinum plates, but the loss of Pu due to adsorption on glass and/or spattering subjected these results to considerable doubt. Therefore the LaF_3 precipitation method was used, which, since it carried the Ce activity also, could be used to determine both Pu and Ce.

Two of the eluting agents used (3% $H_2C_2O_4$ - NH_4OH at pH= 3.0, and 2.5% $H_2C_2O_4$ - 2.5% NH_4Cl) showed little or no separation of Pu and Ce. Five percent citrate at pH=3 and 1% NH_4HCO_3 gave inconclusive results due to the analytical method then in use. Apparently no movement of the activities was obtained with these. Oxalic acid (5%) moved most of the plutonium without moving the cerium, but the rate of movement was slow, so an intermediate pH (1.25) was tried on a 13 cm Amberlite 1R-I column. Although this showed a poor separation, a column 50 cm long would be expected to give a decontamination factor of 10. $Na_4P_2O_7$ and 5% $NaHCO_3$ eluted most of the cerium with very little Pu.

An examination of the elution curve for 5% $H_2C_2O_4$ on an Amberlite 1R-I column indicated that the Pu might be present in more than one form,

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the larger part (92.5%) being eluted by the $H_2C_2O_4$, the rest being eluted with 4NHCl.

III. Program:

The possibility of the presence of more than one state of Pu complicates the problem. A procedure using $NaHCO_3$ or $Na_2P_4O_7$ to elute cerium followed by a second readsorption cycle to effect further decontamination and concentration appears promising. The study of complexing agents and variation in conditions will be continued.

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Preparation of Radioisotopes of High Specific Activity: (H. M. Rice, J. A. Swartout)

I. Ca^{45}

A. Introduction:

The problem of producing Ca^{45} of sufficiently high specific activity to satisfy biological research requirements has received, and is now receiving, considerable attention. The Operations Department of Clinton National Laboratory is now developing the TTA solvent-extraction process of A. Broido and P. C. Tompkins for extracting Ca^{45}, produced by an (n,p) reaction on Sc^{45}, from the scandium. As will be pointed out, this process has the disadvantages of (1) low yield, (2) necessity of handling very high levels of Sc^{46} activity, and (3) requires the use of a major portion of the supply of scandium. To clarify the relative merit of various possible modes of production of satisfactory Ca^{45}, a comparison was made with emphasis on the Sc (n,p) process and the use of enriched Ca^{44}.

B. Comparison of Modes of Production:

Three general neutron irradiation methods are available for the production of Ca^{45} of higher specific activity than that obtained by bombarding calcium in the Clinton graphite pile; (1) irradiation of natural calcium in the Hanford pile, (2) the Sc^{45} (n,p) reaction in the Clinton or Hanford piles and (3) irradiation of enriched Ca^{44} in the Clinton or Hanford piles. A detailed comparison of the specific activities obtainable by these procedures, the amounts of target material required and advantages or disadvantages of each process is given in CL-JAS-12 (CNL Central File No. 47-11-265). Because of the obvious difficulty of transporting and handling a sample of Sc_2O_3 bombarded at Hanford (containing ~ 90C Sc^{46} per gram), comparison was made between production of Ca by the Sc (n,p) reaction in the Clinton pile and by irradiation of 50% Ca^{44} at Hanford. According to available data, the present supply of Sc_2O_3 of 30 gms, which constitutes a major portion of the world supply, would produce 5 mc of Ca^{45} in 180 days. Associated with this would be 180 C of Sc^{46}. For the production of an equal amount of Ca^{45}, 5 mg. of 50% Ca^{44} would suffice with no subsequent chemical processing required yielding a product with a specific activity of about 950 mc per gm. Ca.

C. Conclusion:

After consideration of these comparisons, the recently organized Steering Committee for Radioisotope Research and Development decided to initiate efforts to obtain enriched Ca^{44} for bombardment at Hanford. The Sc (n,p) process will be continued to supply immediate needs or requirements for very high specific activity. It is expected that the specific activity of about 250 mc/gm Ca obtainable by irradiation of natural Ca in the proposed high-flux pile will be satisfactory for most users.

II. Fe^{59}

A. Introduction:

For many uses, particularly in biological research, the Fe^{59} produced by irradiation of iron in the Clinton pile is of too low

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specific activity (0.3 - 0.6 mc/gm Fe) and, in addition, is undesirable because of its 4y Fe^{55} content. The former defect is alleviated somewhat by irradiation of the iron in the Hanford pile which increases the specific activity about 15 fold: the 4y Fe^{55} is, of course, still present. The Operations Department is also investigating the $Co^{59}(n,p)$ reaction utilizing the TTA solvent-extraction process of A. Broido and F. C. Tompkins to separate the Fe^{59} from the cobalt. This process possesses the disadvantages of the Sc (n,p) process discussed above. As in the case of Ca^{45}, a comparison was made of the various modes of production of Fe^{59}, especially with respect to the biological requirements of high specific activity and freedom from Fe^{55}.

B. Comparison of Modes of Production:

Four general neutron irradiation methods are potentially capable of producing Fe^{59} of higher specific activity than that resulting from bombardment of iron in the Clinton pile; (1) irradiation of natural iron at Hanford, (2) the $Co^{59}(n,p)$ Fe^{59} reaction, (3) irradiation of enriched Fe^{58} and (4) utilization of the Szilard-Chalmers reaction on ferrocyanides. Comparisons of these are given in CL-JAS-13 (CNL Central File No. 47-11-265). On the basis of the data presented, it appeared that only the Co (n,p) reaction and the irradiation of enriched Fe^{58} at Hanford would produce satisfactory Fe^{59}. If 15% Fe^{58} containing 3% Fe^{54} is bombarded at Hanford for 46 days, the product contains 255 mc Fe^{59} per gram of iron and less than 1% Fe^{55}. Whereas 182 gms. of Co would be required for the production of 1 mc of Fe^{59} in the Clinton pile, 4 mg. of 15% Fe^{58} would produce an equal amount in the Hanford pile and without the necessity of handling high levels of Co^{60} activity.

C. Conclusion:

In view of the availability of enriched Fe^{58} and the advantages of its use as a source of Fe^{59} in comparison with the Co (n,p) process, the Radioisotope Research Steering Committee agreed to utilize enriched Fe^{58} for the preparation of high specific activity Fe^{59} and discontinue work on the Co (n,p) process.

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Ion-Exchange Separations: The Separation of the Fission Products in the Presence of Uranium (S. W. Mayer, E. R. Tompkins and G. E. Boyd)

In the radioisotope production program for the preparation of the fission product activities, one kg uranium slugs are dissolved in a slight excess of boiling nitric acid (2.5 liters). After a ten-fold dilution of the dissolver solution, the extraction and separation of the cationic fission products is conducted by use of a series of ion-exchange columns. In view of the recent improvements in the understanding of these matters, it was decided to examine the possibility for the bettering of these operations.

It is planned to test several procedures. One of these upon which some results are available is the following: One gram of uranium nitrate was dissolved in 2.5 ml of dilute nitric acid and then a mixture of fission products which had decayed for one week was added. The solution was passed into a six gram bed of exchanger initially in the sodium form. The uranium was adsorbed completely. A small volume of water was then used to wash out the anionic fission products, consisting chiefly of ruthenium. Then, a 2% sodium fluoride solution adjusted to a pH of 12 was used to differentially elute the zirconium activity. The degree of alkalinity was sufficient apparently to hold back U(VI), whereas the fluoride ion served to retard the desorption of those elements which form insoluble fluorides and do not give complex ions. Next, a 1% ammonium bicarbonate solution, 0.02 M in fluoride, was used to elute the uranyl ion. Subsequently, twenty per cent citric acid solution of pH = 2.5 containing 0.02 M fluoride was used to elute the Cb, and then 10% citric acid at a pH of three was employed to elute the Y, Cl, Pr, Nd, Ce. Finally, a 20% citrate solution at a pH = 6.0 was used to remove Sr and Ba and generally to clean up the column.

One interesting observation was made incidental to the carrying out of the foregoing sequence. In the step in which the occluded anions were washed from the bed with distilled water, it was found that the continued passage of the water (pH = 6.4 to 6.8) caused a yellow, uranium-containing compound to be washed out of the column. Possibly the precipitate may have been uranic acid formed by the hydrolysis of the adsorbed uranium.

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Betadiketone Extractions: (A. Broido, P. C. Tompkins) P. A. CX1-24.

Introduction:

During the past quarter work has progressed on practical procedures for the preparation and purification of various isotopes. A sample of Be^7 has been separated from a lithium cyclotron target. The extractability of strontium with TTA has been determined to check the possible use of this extraction to separate calcium and strontium. A few microcuries of carrier free Fe^{59} have been extracted from a pile-bombarded cobalt sample. Work has continued on the separation of the 65 day fission product zirconium and its 35 day columbium daughter from each other and from other fission product impurities present.

Zirconium - Columbium Separation:

Further work on the determination of the zirconium species in aqueous solutions has been discontinued, since this problem is being undertaken on a full time basis at Berkeley.(1)

Since the fission product Zr-Cb solutions available at Clinton Laboratories were 0.5% in oxalic acid, an attempt was made to separate these elements from oxalic acid solutions. It was found that when the 0.5% oxalic acid solution of a 6 mo. old Zr-Cb fraction(2) was diluted with an equal volume of conc. HCl, three extractions of the aqueous phase with equal volumes of 0.5M TTA in benzene reduced the zirconium in the aqueous phase to less than 0.1% of its original value. The aqueous phase contained several activities in addition to the 35-day columbium isotope.

The aqueous phase was fumed repeatedly to near dryness with HNO_3 to destroy the oxalate, and the columbium together with the rest of the zirconium were extracted with cupferron-chloroform from 6N HCl.(3) Remaining in the aqueous phase were the following radiations:(4)

Conversion electrons - 90 Kev and 120 Kev
β-rays - 0.14 Mev, 0.5 Mev, 1.2 Mev and >2 Mev
γ-rays - 0.6 Mev and 0.32 Mev.

None of these radiations followed rare earths, alkaline earths, or ruthenium in the radiochemical analysis scheme.(5)

Further work is being done on the separation and identification of these activities, and a report will be issued upon completion of this work.

Preparation of Fe^{59}:

An attempt was made to separate some carrier-free Fe^{59} from pile

(1) Connick, R.E. - personal communication.
(2) CC-2827
(3) CC-2009
(4) Spectrometric determination by W. C. Peacock.
(5) Reynolds, S. A. - personal communication.

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bombarded cobalt. A cobalt sample (2.7 gm Co_3O_4) was dissolved in HCl, the excess HCl evaporated, and the $CoCl_2$ dissolved in 25 ml 0.05M HCl. This solution was then shaken for ~24 hours with an equal volume of 0.2M TTA-benzene solution. The benzene phase was washed several times with 0.1N HCl and the Fe^{59} reextracted into 5 ml of 6N HCl. The yield (~2.5 uc) compared favorably with that calculated from the determinations of Irvine[6] and a $\beta - \gamma$ coincidence determination by Peacock indicated that the sample contained less than 10% Co^{60} impurity. When analyses are complete a report will be issued on this work.

Extractability of Strontium with TTA:

Since a procedure was desired to remove calcium impurity from strontium samples, the extractability of strontium with TTA was determined. As was expected, strontium is even less extractable than calcium. The accuracy of the value for K_{Sr} is not too high since strontium does not extract until the pH (and, therefore, ionic strength) is quite high. Further, fission product Sr^{89} - Sr^{90} was used for the determination and it was necessary at all times to correct for the Y^{90} present. The experimental results are tabulated below.

Table I

Extraction of Strontium with TTA

Conc. TTA in C_6H_6	pH	$\frac{(Sr)_B}{(Sr)_A}$	K_{eq}
0.4 M	7.5	0.68	11×10^{-15}
0.4 M	7.55	0.44	9×10^{-15}
0.4 M	7.7	0.85	7×10^{-15}
0.2 M	8.3	2.1	$\sim 5 \times 10^{-15}$*
		$K_{ave} \cong$	9×10^{-15}

* Ionic strength here is high, i.e. u ≅ 0.3.

Preparation of Be^7

A sample of Be^7 has been separated from lithium and impurities for use by Dr. Bolomey of the Biology Division. A report on the separation is being written in co-operation with Dr. Bolomey and it would be useless repetition to give all information here. Several points of interest may, however, be mentioned.

It has been found possible to separate pure Be^7 from cyclotron bombarded lithium with TTA. Unfortunately, the beryllium reextracts from the benzene phase at an extremely slow rate - one week's shaking with concentrated HCl extracting about 80% of the Be^7 activity.

(6) NenC-142.

The purification was finally accomplished using acetylacetone instead of TTA and reextracting into oxalic acid. The rate of re-extraction from acetylacetone-benzene is much more rapid than from TTA - benzene. In checking the distribution of Be^7 in this process, an interesting observation was noted. When an aliquot of the benzene phase was pipetted into a capsule and allowed to evaporate at room temperature, the Be^7 activity disappeared as the solution evaporated. This result was not predicted by us from the characteristics of macro quantities of beryllium acetylacetonate given by Arch and Young.(7)

(7) Fernelius, W. C., Inorganic Synthesis, Vol. II (1946).

[redacted]

Dependence of Cross Section of Xenon^{135} on Energy of Neutrons (A. D. Bogard A. R. Brosi, S. Freed, G. M. Hebert, G. W. Parker, J. W. Ruch with S. Bernstein, J. Dial, M. M. Shapiro and G. P. Stanford of the Physics Division)

Spectrometry

The performance of the spectrometer and counting equipment is satisfactory. Also, satisfactory is the reproducibility in the positioning of the xenon holder in the neutron beam. The spectrometer has been calibrated for higher order reflections and their contributions to the intensity in the region between 0.01 and 0.03 electron volts will be taken into account.

Computations have been completed for determining the optimum transmission, that is the optimum thickness of the xenon sample in the path of the neutron beam.

Chemical Processes

Introduction

In the work of Borst and co-workers on the cross section of Xe^{135} as a function of neutron energy, fission product iodine was recovered and precipitated with carrier iodine as PdI_2. After growth of the Xe^{135} daughter, the PdI_2 precipitate was used as the absorbing sample in the crystal spectrometer.

Their process for recovery of fission product iodine consisted of dissolving the uranium metal in HCl, oxidizing U^{+4} to UO_2^{+2} with concentrated $Na_2Cr_2O_7$ and distilling off the iodine into a $PdCl_2$ solution saturated with SO_2. PdI_2 precipitated when the SO_2 was removed by boiling.

Very erratic results have been obtained in attempts to repeat this process. The work done in order to get consistently high yields is reported here. Essentially the same process has been used, the most important modification being more precise control of the oxidation step.

Experimental

The reaction vessel was a three liter flask with nine standard taper necks. Into these necks were fitted (1) a reflux condenser, (2) a Pt electrode, (3) a saturated KCl salt bridge, (4) a thermocouple well, (5) a tungsten electrode, (6) a stirrer, (7) (8) and (9) capillary tubes for the addition of various oxidizing and reducing solutions. The flask was mounted in a glycerine bath on a hot plate so that iodine could be distilled out.

In order to follow the oxidation reaction the potential of the Pt (U^{+4}, UO_2^{+2}) electrode with a saturated calomel reference electrode was measured using a continuous reading vacuum tube voltmeter which drew 10^{-9} to 10^{-10} amps. In some of the later work, tungsten was used as a reference electrode in order to eliminate use of a salt bridge.

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In order to determine iodine yields and study distillation rates, 1 to 2 mc of I^{131} tracer was used. The γ radiation was detected and recorded using a counting rate meter. In different experiments the G-M tube was located in order to determine the change in the amount of iodine (1) in the reaction vessel, (2) in the vapor over the solution, (3) in the reflux condenser, and (4) in the receiving flask.

Solution of Uranium Metal

It is proposed to isolate the iodine from six uranium slugs in the active runs. The process development work was done with one quarter slug (1/24 scale). In the first experiments about three hours were required to dissolve a quarter slug in 550 ccs of concentrated HCl. Later, the metal was suspended in a Pt gauze basket so it could be removed from the solution after one hour. It was found that contact with the Pt gauze increased the rate of solution to such an extent that practically all of the metal was dissolved after one hour. In many of the succeeding experiments all of the metal was dissolved and never did more than 5% remain undissolved after one hour.

Since it was thought that this increase in rate of solution was due to a reduction in overvoltage the Pt basket was platinized. Any increase in the rate of solution caused by this was too small to be readily apparent.

In two experiments the gases from the dissolving reaction were scrubbed with an alkaline sulfite solution. In these cases iodine carrier and tracer were added to the concentrated HCl before the metal was dissolved. Analysis of the scrubbing solution showed that about 10% of the HCl escaped from the condenser but not more than a few tenths of a per cent of iodine was lost.

Oxidation of Uranium and Iodine

In preliminary experiments on the oxidation of iodide ion in boiling UCl_4 solutions with concentrated $Na_2Cr_2O_7$ solutions, iodine yields were found to vary from 10 to 50%. It was found that on reducing with $NH_2OH \cdot HCl$ more iodine was liberated giving a total yield which was seldom more than 60% and in most cases much less.

When potentiometric measurements were made it was found that iodine was evolved only at the U^{+4} end point. Even with dilute dichromate solutions the end point was so sharp that it was impossible to stop addition at the optimum point. When iron was added to catalyze the U^{+4} oxidation it was found that iodine was liberated in the region buffered by the Fe^{+2}, Fe^{+3} couple.

Attempts were then made to measure the relative iodine vapor pressure as a function of oxidation-reduction potential. One milligram of iodine and 2 mc of I^{131} were added to a solution of one-fourth uranium slug in 550 ccs of concentrated HCl. The solution was boiled and counting rates were determined using a shielded tube located between the flask

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[redacted]

and a reflux condenser. In these crude measurement it appeared that the iodine vapor pressure was a maximum in the region where Fe^{+3}/Fe^{+2} was from 1 to 6. Since iodine was collecting in the reflux condenser during the measurements they were not very reliable. Distillation of iodine was possible in this region but the rates were too slow.

When $Na_2Cr_2O_7$ was used as oxidant the solubility of NaCl was exceeded. Since the presence of this solid phase might complicate the process it was eliminated by using $Li_2Cr_2O_7$. With $Li_2Cr_2O_7$ as oxidant and a Fe^{+3}/Fe^{+2} ratio of two, yields of 65 to 70% were obtained after one hour of distillation.

Since sulfate ion decreases the solubility of iodine the iron was added as a concentrated $Fe_2(SO_4)_3$ solution in the next experiments. One-third of the iron (25 ccs of a saturated $Fe_2(SO_4)_3$ solution) was added before the $Li_2Cr_2O_7$ and two-thirds (50 ccs) was added after oxidation to the U^{+4} end point.

In the presence of sulfate ion the iodine could be distilled out at a rate proportional to the amount of iodine present until the total iodine was reduced to about 0.25 mg when the rate decreased more rapidly. The time required to distill 50% of the iodine was 4 to 8 minutes. By adding one-half the carrier (0.5 mg) and distilling for 10 minutes, then adding the remaining 0.5 mg and distilling, it was possible to collect 90% of the tracer in thirty minutes.

An attempt was made to oxidize with H_2O_2 rather than $Li_2Cr_2O_7$ in order that the U^{+4} end point could be determined by the color change. At the end point $FeSO_4$ and $Fe_2(SO_4)_3$ were added to give a Fe^{+3}/Fe^{+2} ratio of two. The time required to distill out 50% of the iodine (0.5 mg) was twenty-five minutes. This was considered too slow for a process involving the 6.7 h I^{135}.

In another experiment no carrier iodine was added. The U^{+4} was oxidized with $Li_2Cr_2O_7$ and a Fe^{+3}/Fe^{+2} ratio of two was established using $Fe_2(SO_4)_3$ as above. In this case the iodine tracer was distilled out at the rate of forty-seven minutes for a 50% yield. When 1 mg of carrier was added the time required for recovery of 50% of the iodine was four minutes.

Data obtained in the distillation experiments discussed above are plotted in Figure I. Approximately the same amount of I^{131} tracer was added in every case. The counting rate of a shielded GM tube located near the still is plotted versus time of distillation. These curves show the marked increase in the rate of distillation when part of the chloride ion was replaced by sulfate ion. The difference between the upper and lower curves shows the effect of iodine concentration on rate of distillation.

Recommendations

Dissolution: Wrap uranium metal in platinum gauze. Dissolve in 2.2 liters of concentrated HCl per slug at the boiling point for one hour.

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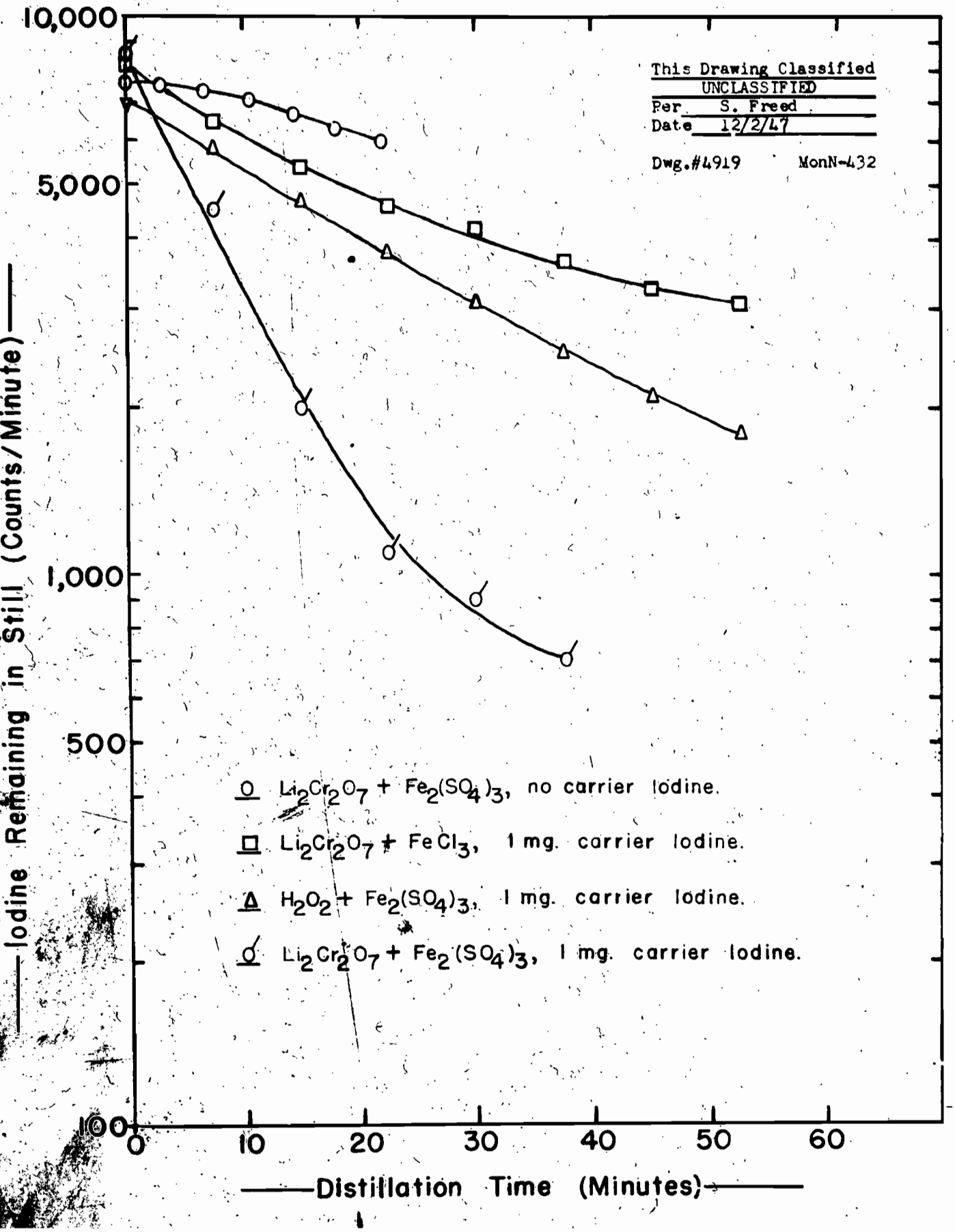
Figure I.

RATE OF DISTILLATION OF IODINE FROM VARIOUS SOLUTIONS.



At this time 90% of the metal should be dissolved. Since the I^{135} will have decayed to 90% of the initial activity the over all yield should be about 80%.

Oxidation: Add 100 ccs of saturated $Fe_2(SO_4)_3$ solution and 2 mgs of carrier iodine as iodide per slug to the dissolver solution. Then add a saturated $Li_2Cr_2O_7$ solution as rapidly as the violence of the reaction permits until the end point is approached. In the experimental work, 100 ccs of solution was required for a quarter slug of metal and this was added in twenty to thirty minutes. The $Li_2Cr_2O_7$ solution was added through a coarse sintered glass filter below the surface of the UCl_4 solution. Add the $Li_2Cr_2O_7$ solution until the U^{+4} end point is reached as indicated by platinum and tungsten electrodes. With the tungsten electrode no EMF is shown until within a few per cent of the end point where the EMF reaches a maximum. When the end point is reached, add 200 ccs of saturated $Fe_2(SO_4)_3$ solution per slug.

Distillation: Because of the low iodine concentration and the high chloride ion concentration, the vapor pressure of iodine over the solution is very low relative to that of water. It is therefore necessary to use a fractionating column in order to reduce the amount of water distilled over. It is estimated that two theoretical plates, one in the still and one in the condenser, are sufficient. In the experimental work an unpacked twelve inch egg condenser was used. Cooling water was run in at the top at such a rate that about 95% of the water was condensed.

Use a $PdCl_2$ solution into which SO_2 is bubbled as a receiving solution for the iodine. Pass a slow current of air into the still to prevent back diffusion of SO_2. Reflux the solution as rapidly as possible without flooding the column. Control the temperature of the condenser so that not more than 15 to 20 ccs of water are distilled over in thirty minutes. Reflux for ten minutes, then add 2 mgs of iodine carrier per slug and continue refluxing until the rate of distillation is approximately equal to the rate of decay of I^{135}. At this point, shut off the SO_2 and remove the cooling water from the condenser. Aeration of the hot receiving solution will remove the SO_2 and allow precipitation of PdI_2.

Assuming that the oxidation and distillation are completed in one hour, a yield of 80% including decay should be expected for these steps. The over all yield of I^{135} including decay from the time solution of the metal is started should be between 60 to 65%.

We would like to thank L. B. Rogers for numerous helpful discussions.

Large Scale Processing of Slugs

See report by G. Parker under heading "Preparation of I^{135}-Xe^{135m}".

[redacted]

Assay of Xe^{135}

Equipment has been built for the assay of curie amounts of Xe^{135} in PdI_2 precipitates. It consists of a sample holder surrounded by four inches of lead and mounted in a fixed position with respect to a high pressure ionization chamber. Ion currents are measured with a vibrating reed electrometer. Ionization is produced by the hard gamma radiation of the iodine parent of Xe^{135}. Beta ray spectrometer measurements, reported elsewhere, have shown that gamma radiation from other iodine and xenon activities will not interfere.

In order to calibrate the ionization chamber with respect to the disintegration rate of I^{135} the deviation from linearity of response at any given ion current has been determined using radium sources. The ion current from I^{135} samples with known disintegration rates is then observed and corrections made for non-linearity in response of the instrument. Previous work has shown that the disintegration rate of aliquots can be obtained by beta counting with an instrument of known geometry. It is estimated that calibration errors will not exceed 5%.

Additional errors are introduced because the amount of xenon at any given time is calculated from the amount of I^{135} at the time of measurement, the time elapsed between precipitation of PdI_2 and measurement and the decay constants of I^{135} and Xe^{135}. The largest of these errors, which amounts to 8% at the maximum of the Xe^{135} growth curve, results from an uncertainty of about 2% in the half life of 6.7 h I^{135}. Work is in progress to measure this decay constant with greater precision.

We would like to thank C. J. Borkowski for help in the design and construction of the assay equipment.

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[redacted]

Preparation of I^{135}-Xe^{135}: (G. W. Parker, G. M. Hebert, J. W. Ruch, J. Reed, P. M. Lantz), PA CXI-9.

Introduction:

Much effort in preparation has been expended toward continuing the work initiated by L. B. Borst and others for the direct measurement of the cross section of Xe^{135} by crystal spectrometer. With renewed interest in the problem, a much larger number of people has been co-ordinated toward its completion on a considerably larger scale than that attempted by Borst. The division of labor has naturally allotted the radio-chemical separation of the required amount of Xe^{135} from fission to this group in the 706-C (Hot-Laboratory) Building. (For a general introduction see MonN-311, p. 182). See also "Cross-Section of Xe^{135}", S. Freed et al., this report.

Scale of Operations:

In the original work, the group working with Borst attempted chemical processing of only one unenriched slug; however, it is unlikely that reproducable results could ever have been obtained with this limited amount of material. In a detailed treatment, (Memo, March 15, 1947) Shapiro has recently outlined the limiting factors which may determine the required minimum of mounted Xenon with a predetermined area and scattering background. Some earlier decisions had set the general optimum number of slugs (limited by the amount of cell wall shielding) at six, presuming no enrichment and immediate (1/2 hr. cooling) processing. Freed has shown (MonN-311) that if it were possible to process a larger number of slugs in the available space, several factors in quantity of Xe might be obtained with the same level of biological radiation hazard by allowing a 6.7 hr. cooling period (one half-life of the Iodine Parent) of unenriched slugs during which time the total gamma radiation decays to one-tenth that observed after only one-half hour out of the pile. By this reasoning it would be possible to undertake separation from ten times as many slugs and obtain a five-fold yield in Xenon product. However, in order to handle any increased quantity of metal, above six slugs, it would require a much more elaborate design of equipment involving extended procurement delays and search for additional cell space.

By reducing the area of mounting of the six-slug sample to a minimum ($\sim 0.03 cm^2$) accomplished by use of the centrifuge technique, replacing filtering, the maximum concentration of sample in the neutron beam is obtained.

Design of Cell and Equipment (See Drawing)

1. Cell Lined With Lead for Radiation Protection and Aid to Decontamination.

The interior wall protecting the operating face of the cell is lined with 2" of lead affording a factor of 10 in reduction of radiation. All other surfaces except the ceiling are covered with 1" lead. No interior paint is used on the lead since it is readily decontaminated by acid washing.

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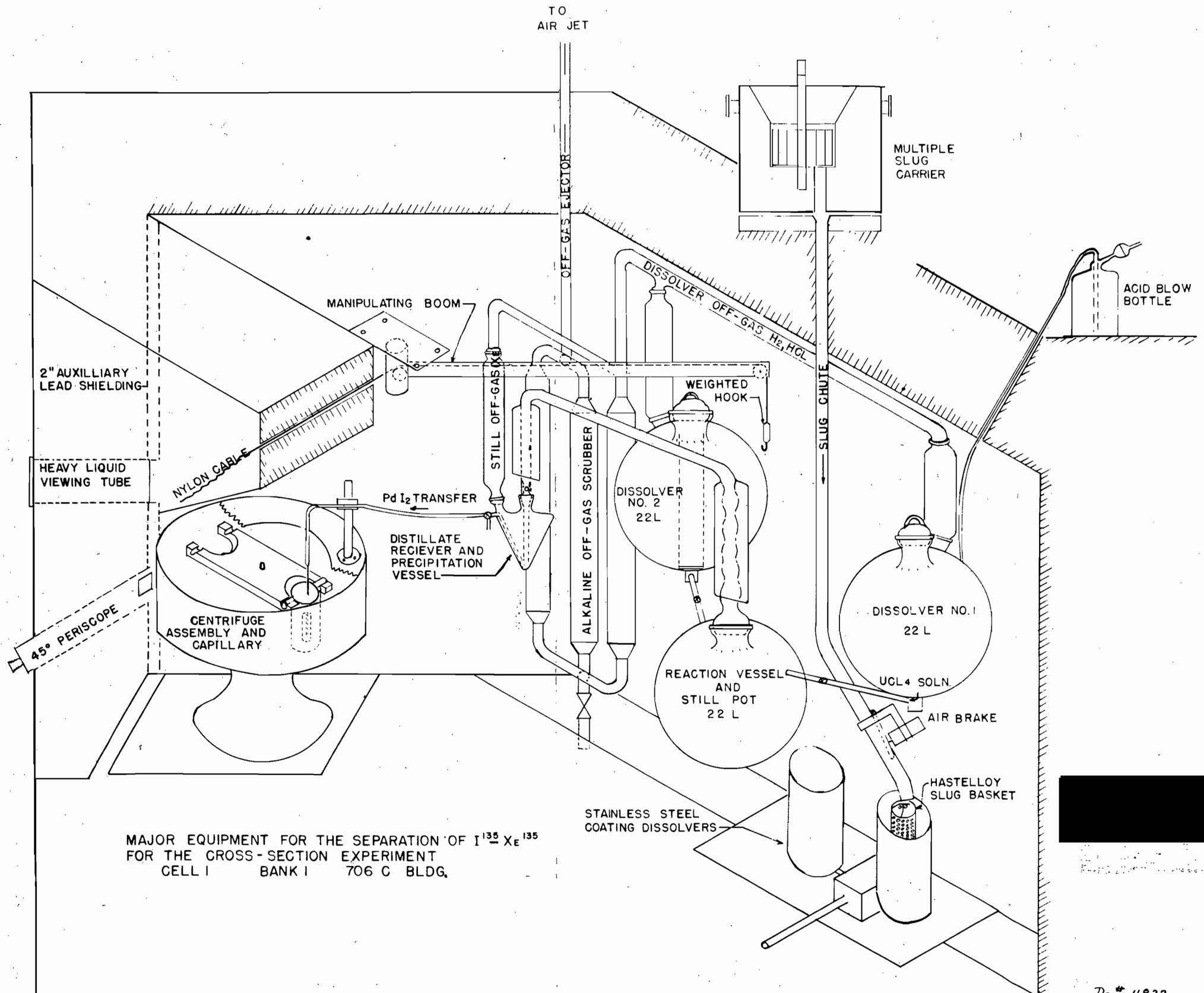

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2. Slug Discharge Mechanism

A special revolver-magazine type slug carrier is used in conjunction with a bent-tube chute which oscillates between two discharge receivers (Decoating Vessels) for quick operation. An air brake stops the slugs before they are dropped into the baskets.

3. Stainless Steel Decoating Vessels

Fach decoating vessel contains a special 3-compartment Hastelloy-B (HCl resistant) perforated cylinder into which the slugs are dropped by rotating 120° between slugs. While the slugs are being dropped, hot caustic solution will be added to these vessels to dissolve the aluminum coatings.

4. Boom Manipulator

It is apparent that only the most precise method of placing a heavy metal container (10# Uranium and Hastelloy) in a fragile glass vessel would be desired; therefore the somewhat doubtful looking but well-tried method of using a weighted grappling hook on a nylon cable combined with a swinging boom under whose arc all vessels are centered is being used.

5. All-Glass Equipment for HCl Process

Three major glass vessels (22 liters, round bottom) are involved. Two are U dissolvers, and the third an oxidizing and distillation vessel. The method of heating this vessel requires six 1,000 watt drying lamps (not shown in the drawing). A fourth, smaller vessel, the distillate receiver and precipitation vessel, is designed with gold-metallized unlubricated joints to expose no organic material to the iodine distillate. In this vessel $PdCl_2$ is added to the reduced iodine solution and the PdI_2 precipitated.

6. The Centrifuge Assembly and Capillary

The development of the centrifuge unit for packing a few milligrams of highly radioactive PdI_2 (30 curies) into a 1-2 mm glass capillary, mounted in a metal block (wafer) with its blank twin, drying it completely and being capable of having the filter plug entirely removed and replaced with leak-proof, thin window plugs is probably the most involved and most important part of the process. Some of the remote-control devices associated with this phase have not yet been completed. Preliminary operation will be largely manual.

7. Need for an Elaborate Off-Gas System

During the dissolving operation most of the 9.2 hr. Xe in equilibrium with the 6.7 hr. Iodine, after 24 hrs. pile bombardment and 1-2 hrs. processing time, and probably a large number of curies of other Xenons and Kryptons of appropriate half-life will be expelled from the hot solution with the large quantity of Hydrogen evolved. It is proposed to keep all vessels under slight negative pressure and considerable air-flow in order to sweep all active gases into the alkaline scrubber (4" pyrex pipe) for

[redacted]

absorption of all acidic active and inactive constituents. Hydrogen and most of the noble gases must be expelled. Since the normal cell ventilation system is not convenient to shield, a special off-gas line is used which is adequately shielded to the building roof. From this point it may be possible to eject this gas into one of the existing stack lines.

XENON PROCESS

OUTLINE OF TIME LAPSE FOR PdI_2 PREPARATION

Estimated Time Required for Step		
1/2-1 hr.	1.	Procure Six Slugs Push slugs from pile center channel after 20-24 hrs. exposure. Load into multiple slug carrier and deliver to top of cell in 706-C.
1/4-1/2 hr.	2.	Dissolve Aluminum Coats Load 3 slugs into each of two coating dissolvers, remove aluminum and wash.
1-1 1/4 hr.	3.	Dissolve U in HCl Load and cap each dissolver vessel; add HCl and dissolve U (90% complete dissolution).
1/2-3/4 hr.	4.	Transfer UCl_4 and Oxidize with $Fe_2(SO_4)_3$ and $Li_2Cr_2O_7$. Transfer UCl_4 slurry to reaction vessel and add $Fe_2(SO_4)_3$ and $Li_2Cr_2O_7$ to predetermined e.m.f. on Pt-Tungsten electrodes. UCl_4 is oxidized to UO_2Cl_2. Add more $Fe_2(SO_4)_3$ for oxidation of I^- to I_2.
1/2-3/4 hr.	5.	Reflux One-half Hour and Distill I_2 Start heating and reflux until most of the Iodine is held in the reflux condenser. Drain condenser and start collecting Iodine in distillate received while admitting SO_2 to distillate.
1/2-3/4 hr.	6.	Reduce I_2 with SO_2 and Precipitate PdI_2 Stop distillation and SO_2. Start heating while agitating with air and continue until SO_2 is expelled. Add $PdCl_2$ for precipitation of PdI_2.

[redacted]

Total:

3 1/4-5 hrs. (Approximate Zero Time of Trapping Xe in PdI_2 Crystals)

3/4-1 1/4 hrs. 7. Centrifuge PdI_2 and Dry with Anhydrous Solvents.

Transfer the PdI_2 slurry to the prepared centrifuge and capillary assembly and centrifuge out the solid PdI_2. Decant the aqueous supernatant and centrifuge with alcohol and ether to remove water and HCl. The PdI_2 should be as nearly pure and free of water as possible and (1) should fill the capillary for even distribution across the beam of neutrons.

1/2-1 hr. 8. Dismantle Assembly: Plug Capillary and Load into Shield.

Total: 4 1/2-7 1/4 hrs.

"Before Releasing Time".

Dismantle the centrifuge assembly by remote methods; place in holding device and insert sealing plugs. Load into carrying shield.

(1) Results to date on the drying and packing of the PdI_2 into a uniform target have not been satisfactory. The precipitate has tended toward flocculence and has been impervous to flow of drying solvents. After prolonged drying the solid also tends to shrink to a thread about 1/2 the cross-section of the capillary. More research is indicated.

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Note on Radiation Shields of Dense Transparent Liquids: (G. W. Parker, G. M. Hebert), P.A. CXI-9.

In typical hot-laboratory design use may be made of dense clear liquids for shielding where water alone will not suffice and direct vision is desirable.

This condition has often arisen in the 706-C Hot Laboratory but only recently has much use been made of even the most readily available heavy solutions or organic liquids.

Some general information on dense liquids is available from mineralogical applications to specific gravity measurements; however, in their list (Table I from Bureau of Mines Tech. Paper No. 381) are many substances which for shielding are undesirable because of cost, toxicity, corrosion or even availability.

Table I

Heavy Liquids for Mineralogical Analysis

Specific Gravity Range	Heavy Liquid
1.6-2.95	Acetylene Tetra bromide (solv. chloroform)
2.95-3.3	Stannic Bromide (solv. CCl_4)
3.5-4.9	Thallous Formate-Malonate (solv. Water)
4.9-5.2	Eutectic of $HgCl_2$, $SbCl_3$ (Solv. Aniline followed by Alcohol)

In Table II a study of some readily available materials is reported including type of solution and approximate cost which is most important for large installations. Presently, use is made in this laboratory of $ZnCl_2$, $ZnBr_2$ and Tetra-bromethane (Acetylene Tetrabromide).

[redacted]

[redacted]

TABLE II

Some Readily Available Dense Liquids

SOLUTION	SP. GR. OF SOLUTION	ESTIMATED COST/GAL.	REMARKS
Bismuth Nitrate	1.85	$16	Dissolved in 2N HNO_3
Calcium Chloride	1.54	$1	Cp chemical not available, technical grade used.
Calcium Nitrate	1.64	$3	Solution crystallized overnight after weighing.
Mecuric Nitrate	1.86	$28	H_2O Solution
Mecurous Nitrate	1.61	$25	H_2O solution was clear and colorless although crystals were yellow. Crystals lost color on standing in solution.
Mercurous Nitrate	1.79	$29	1N HNO_3 solution. Solution was colorless and yellow crystals did not change color on standing.
Zinc Chloride	1.94	$6	H_2O solution.
Zinc Nitrate	1.7	$5	H_2O solution.
Zinc Bromide	2.7	$15	H_2O solution. Approaches density of ordinary concrete.

ORGANIC LIQUIDS - NEXT PAGE.

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Organic Solvents

SOLUTION	SP. GR. OF LIQUID	ESTIMATED COST/GAL.
Carbon Tetra-Chloride	1.59	$1.60
Perchloro-ethylene	1.62	$1.00
Tetrabrom-ethane	2.59	$73.00
Trichloro-ethylene	1.47	$1.00

In Table III is a summary of some radiation measurements thru glass-end, two-foot long cylinders 6 inches in diameter inserted in a two-foot concrete barrier. The energy of the gamma radiation is known only approximately (1 mev.).

Table III on next page.

[redacted]

[redacted]

TABLE III

Shielding Effect of Dense Liquids

	Specific Gravity	Register Readings (1) (Scalers/Min)	Background (2) (Scalers/Min)	Corrected Counts/Min (B.G. Subtracted)	Approximate mr/hr-(from counts/min (3)	Cutie Pie No. 404 (mr/hr) (4)	Cutie Pie No. 415 (mr/hr) (5)	Victoreen Readings (mr/hr)
Water	1.0	jammed register	30	---	---	70	48	65 (6)
Zinc chloride (70%)	1.9	261	22	15,233	4.9	7	1	4 (7)
Tetra Brom-ethane (Acetylene tetra-Bromide)	2.9	46	19	1,728	0.6	0.5*	0.5*	0.5*

* Too small to read.

(1) Average of two readings.
(2) Background taken with slugs lowered well below the window. General activity level of cell and possible contamination on outside of cell could give background.
(3) One mr/hr/ assumed to equal 3100 counts/min.
(4) Reading taken from side of Cutie Pie #404.
(5) Reading taken from end of Cutie Pie #415.
(6) Victoreen with range of 200 mr/hr used.
(7) Victoreen with range of 40 mr/hr used.

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C^{14} from Beryllium Nitride (A. J. Weinberger, J. A. Swartout) P. A. CXI-10

I. Introduction:

The decision to test the H_2SO_4 - CrO_3 process [1] for obtaining C^{14} from Be_3N_2 on a larger scale was indicated in the report for the previous quarter (MonN-370, pgs. 14-16) on the basis of a comparison of the three methods developed to-date. In addition, to an initial experiment at a four-fold greater scale than previously tested, work was continued on the analysis of gas produced in the Be_3N_2 cans during irradiation.

II. Present Status of the H_2SO_4 - CrO_3 Process:

A. Equipment: The present equipment consists of a gas train similar to that used for the NaOH-H_2SO_4 - CrO_3 process [2] with modifications as listed below.

1. The water bath used to heat the pot was replaced by a core type, nichrome element heater controlled by a variac.

2. A hot CuO tube was placed in the inlet air system before the Drierite-Ascarite tube to oxidize any organic vapors in the incoming air.

3. A condenser was placed in the line at the top of the pot to prevent the escape of water.

4. The sulfuric acid trap was removed for reasons discussed below.

B. Problems Arising from Scaling-Up the Process: Several problems appeared when 4 gms. of 69 day Hanford irradiated Be_3N_2 was dissolved which were not present in operation at 1/4 this scale.

1. It was necessary to control the addition of H_2SO_4 more closely since there was a tendency for the solution to froth.

2. The H_2SO_4 trap, included to prevent water vapor from reaching the Drierite-Ascarite trap, was found to remove activity when kept cold. Two alternate solutions were apparent, (a) to remove the trap or (b) to leave it in the line and heat it. Of these, the former was adopted for the initial experiments. However, experiments with the hot H_2SO_4 trap will be made to establish the better procedure.

3. A brass ionization chamber, Drierite protected, was used in conjunction with a Beckmann amplifier to follow the evolution of activity from the pot. This chamber became appreciably contaminated in the larger scale experiment. The contamination was not removed upon long aeration. There are three possible methods for correcting this; (a) the chamber can be decontaminated after each experiment, (b) it can be gold plated, or (c) a CuO furnace can be introduced ahead of the chamber. Decontamination is undesirable and will be done only as a last resort. Gold plating is only a possible solution, so will be tried only if introduction of the hot CuO is ineffective.

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III. Larger Scale Operation of the H_2SO_4 - CrO_3 Process:

A run with 4 gms. of Argonne prepared, 69 day Hanford irradiated Be_3N_2 was made. Approximately one-half of the dissolver solution was turned over to the Organic Chemistry Group for extraction of formic acid as such, since the preliminary work on this extraction was encouraging. The remainder of the solution was oxidized with CrO_3; the CO_2, HCN, CH_3OH and HCOOH was therefore included in one fraction. The analytical work on this experiment has not been completed.

It was in this experiment that the hold-up of activity in the cold H_2SO_4 trap was discovered. Since hold-up may also have occurred in the preceding run and since the activity thus held was recovered in this run, the apparent yield may turn out to be high.

IV. Yields and Isotopic Abundances:

The yields of C^{14} obtained from Be_3N_2 by different chemical extraction processes have been determined and compared with the results of Fries.(1)

His data for the yields of C^{14} obtained by the H_2SO_4 - CrO_3 process for different samples of Be_3N_2 are given in Table I.

Table I

Yields of C^{14} from Be_3N_2: H_2SO_4 - CrO_4 - CrO_3 Process

Sample of Be_3N_2	Irradiation	μcC^{14}/gm Be_3N_2	μcC^{14}/gm Be_3N_2/mo.
(a) Argonne prepared	- Hanford for 1 mo.	~ 84	~ 84
(b) Berkeley prepared	- Hanford for 2 mo.	211	106
(c) Berkeley prepared	- Hanford for 3 mo.	340	113

The Argonne preparation was irradiated in the Hanford pile at a position of maximum flux. For comparison, it is assumed that this was also the case for the Berkeley material and that the Hanford maximum flux did not change appreciably during the irradiations.

The large increase in yield resulting from the increase in irradiation time from one to two months is probably only apparent. It may result from differences in the nitrogen content of the impure Be_3N_2 used since Argonne prepared Be_3N_2 has been shown here to contain only 88% Be_3N_2. Nevertheless, a real increase of several percent in yield of C^{14} per gram of Be_3N_2 per month on continued irradiation seems indicated. Since there is no apparent basis for this, a yield of 113 uc of C^{14} per gm. of Be_3N_2 per month will be considered a maximum unless further work verifies an increase.

For the Argonne preparation (Table I-(a)) this laboratory obtained 79 uc C^{14} per gram Be_3N_2 using the NaOH-H_2SO_4 - CrO_3 process.(2) This is in good agreement with the value of Fries considering the differences in chemical methods, equipment, scale of operation and counting techniques.

[redacted]

Additional comparison between the chemical methods is offered by results of extracting C^{14} from 1 gm. of Argonne prepared, 69 day Hanford irradiated Be_3N_2 using both the $NaOH-H_2SO_4-CrO_3$ and $H_2SO_4-CrO_3$ procedures. Data for the former which were given in the last quarterly report are included in Table II as well for comparison.

Table II

Comparison of Chemical Processes for Extracting C^{14} from Be_3N_2

Chemical Process	Amount of Be_3N_2	μc C^{14} Recovered	$\frac{C^{14}}{C^{12} - C^{14}}$	
			CH_4-CO Fraction	Overall
$NaOH-H_2SO_4-CrO_3$	1 gm.	104	--	0.005
		106	--	0.003
$H_2SO_4-CrO_3$ (a)	1 gm.	73-75	0.013 (b)	--

Notes: (a) Since this dissolver solution was given to the Organic Chemistry Group for extraction of formic acid, a good yield figure and a value for isotopic abundance in the other fractions could not be obtained. If the amount in the HCN fraction which was not determined is assumed to be 5%, the yield is 75 uc C^{14} per gram of Be_3N_2.

(b) The low isotopic abundance is disappointing. However, the Ba CO_3 recovered on the disc weighed only 4.4 mg and contained 16.5 μc C^{14} whereas 39 μc was recovered from the trap walls and the Ba $(OH)_2$ filtrate. The isotopic abundance should, therefore, not be considered conclusive. Normally a major portion of the activity appears on the disc.

V. Analysis of Gas Produced in Be_3N_2 Cans During Irradiation:

A large amount of time was spent this period in setting up and testing gas analysis equipment. The equipment now functions satisfactorily and a chemical analysis of the gas can be made. Sample gas tubes containing approximately the same amount of air as in the gas in the Be_3N_2 can and small amounts of the suspected constituents of the gas have been made and found to be acceptable for spectroscopic analysis. Sample tubes containing the Be_3N_2 gas will be prepared and analyzed spectroscopically.

A gas density analysis was made of the Be_3N_2 gas. This analysis showed the average molecular weight of the gas to be less than 2. Since the gas had been diluted with a large amount of air because of a leaking stopcock, and since some of the pressure and volume measurements were rough, work was not too exact. However, the results, in conjunction with other results (3) indicate that the gas is essentially hydrogen.

VI. References.

(1) Fries, B.A., "The Recovery of C^{14} from Irradiated Beryllium Nitride". BC-43, March 7, 1947.
(2) Anthony, D.S. and Weinberger, A.J., "The Distribution and Specific Activity of C^{14} from Be_3N_2." Part of MonN-311.
(3) "Tests on Beryllium Nitride Slugs", memorandum from R. B. Briggs to M. C. Leverett, November 11, 1946.

[redacted]

Experimental Use of C^{14} (W. G. Brown (to September 26), G. C. Bell, C. J. Collins, O. K. Neville, R. F. Nystrom, W. J. Skraba, A. R. Van Dyken) - P.A. CX4-4

Studies on the Synthesis of Organic Compounds containing Carbon-14

Summary

The hydrogenation of carbon dioxide with lithium aluminum hydride in diethyl carbitol has been shown to produce methanol. A method for the isolation of the methanol in 75% overall yield has been worked out. It is expected that the high pressure hydrogenation of carbon dioxide-C^{14} to methanol-C^{14} will be replaced by this new convenient method.

The preparation of sodium cyanate by the thermal decomposition of sodium urea in yield of 97% is described.

Formic acid has been produced in high yield by the hydrogenation of a potassium carbonate-bicarbonate solution. The isolation of formic acid-C^{14} from beryllium nitride slugs which have been bombarded with neutrons is also under investigation.

Studies are being conducted on the preparation of chemically pure barium carbonate-C^{14} prior to standardization of the various counting techniques used for the determination of carbon-14.

The synthesis of o-phthalic acid-1,2-C_2^{14} from acetylenedicarboxylic acid-2,3-C_2^{14} is under investigation.

The rearrangement of α,α-dibromoacetophenone to mandelic acid is being studied with the aid of carbon-14. Carbonyl-labeled dibromoacetophenone has been synthesized and allowed to rearrange to mandelic acid. Radioactive assays are expected to determine whether a rearrangement of the side chain has occurred.

The Synthesis of Methanol and Sodium Cyanate (R. F. Nystrom)

Introduction

A study of the reduction of carbon dioxide by lithium aluminum hydride has been undertaken with the chief emphasis placed on the isolation of the reaction product, methanol.

The preparation of sodium cyanate by the thermal decomposition of sodium urea is described.

Exploration

Sodium cyanate containing carbon-14 would be a valuable intermediate in the synthesis of organic compounds of interest to biologists. The proposed scheme of preparation is:

[redacted]

[redacted]

1. $C^{14}O_2 + NH_3 \longrightarrow C^{14}\equiv O\begin{matrix} NH_2 \\ ONH_4 \end{matrix}$ (1)

(ammonium carbamate)

2. $C^{14}\equiv O\begin{matrix} NH_2 \\ ONH_4 \end{matrix} \rightleftharpoons H_2NC^{14}ONH_2 + H_2O$ (2)

(urea)

3. $H_2NC^{14}ONH_2 + Na \xrightarrow[\text{ammonia}]{\text{liquid}} H_2NC^{14}ONHNa + H_2$ (3)

(sodium urea)

4. $H_2NC^{14}ONHNa \xrightarrow{\text{heat}} NaC^{14}NO + NH_3$

(sodium cyanate)

The first three steps take place in an overall yield of 79%. Step 4 is a new reaction and the yield for this process is 97%.

The isolation of methanol from $LiAlH_4$-CO_2 reaction mixtures has been accomplished. The equations for this procedure are:

1. $4\ CO_2 + 3\ LiAlH_4 \longrightarrow LiAl(OCH_3)_4 + 2\ LiAlO_2$

2. $3\ LiAl(OCH_3)_4 + 4\ n\text{-}C_6H_{13}OH \rightleftharpoons 3\ LiAl(OC_6H_{13})_4 + 4\ CH_3OH$

In the latter reaction the more volatile alcohol, methanol, is removed by distillation. Hence, the desired alcohol is obtained in anhydrous condition. It should be noted that this new process is simpler, more economical, and less dangerous than the present catalytic method.

Experimental

Preparation of Sodium Urea[3] A 500 cc, three-necked flask was equipped with a dry-ice condenser and a mechanical stirrer. To a well-agitated solution of 0.1 mole (6 grams) of urea in 150 cc of liquid ammonia, 0.1 gram atom (2.3 grams) of sodium was added in small portions. As the sodium was utilized the characteristic blue color of sodium dissolved in liquid ammonia disappeared. After the reaction was complete the liquid ammonia was evaporated and the last traces of ammonia were removed by evacuation.

Thermal Decomposition of Sodium Urea. Slow heating. A 0.5 gram sample of sodium urea was placed in a flask which was connected to a mercury bubbler. The flask was heated by an oil bath. At 140° C a slow evolution of gas, which turned moist red litmus blue, was observed (presumably ammonia).

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(1) Brooks and Audrieth, Inorg. Synthesis, II, 85 (1946)
(2) Hendrichs, J. Am. Chem. Soc., 52, 3088 (1930)
(3) Jacobson, Ibid., 58, 1984 (1936)

[redacted]

At 152° C the gas evolution became more vigorous. The temperature of the oil bath was gradually increased to 205° C and held there until the decomposition was complete. After the flask cooled to room temperature, 20 cc of water and a solution of cobaltous chloride were added. A purple-blue color appeared immediately which is a positive, qualitative test for cyanate ion(4).

The quantitative determination of cyanate was carried out by decomposing 0.38 gram (4.6 millimole) of sodium urea as described above. To the solution of the residue in 20 cc of water, 50.0 ml of 0.1 N silver nitrate were added. After a few minutes the silver cyanate precipitate was filtered off and washed several times with water. Then 5 ml of 1:1 nitric acid and 1 ml of indicator solution (saturated solution of ferric ammonium sulfate in 1 N nitric acid) were added to the filtrate including the washings. The excess silver nitrate was titrated with potassium thiocyanate solution. Hence, the yield of sodium cyanate determined in this manner was 83%.

Rapid heating. The same technique as mentioned above was employed with the exception that the flask containing the sodium urea was heated with a free flame for five minutes. Under these conditions the yield of sodium cyanate was 97%.

Reduction of Carbon Dioxide by Lithium Aluminum Hydride. Isolation of methanol from an aqueous solution. A one liter, three-necked flask was equipped with a gas inlet tube, dropping funnel, mechanical stirrer, and a dry-ice condenser. Two hundred cc of ethyl ether, previously purified by distillation from a lithium aluminum hydride solution, were added to 0.129 mole of $LiAlH_4$ in 130 cc of ether. Then carbon dioxide, generated by adding 30% perchloric acid to 1.992 grams of barium carbonate, was diluted with nitrogen and passed into the hydride solution. Four hours after the last addition the excess hydride was decomposed with 9.6 cc of water. The ether was removed at room temperature in vacuo and then 150 cc of 10% sulfuric acid and 400 cc of water were added. Upon fractionation two 100 cc portions of distillate were collected. These fractions were combined and refractionated with 0.8 cc of material being taken for analysis. On the basis of the weight and freezing point of this material a 50% yield of methanol was obtained.

Isolation of methanol by an exchange reaction. A study was undertaken to determine if methanol added to a slight excess of $LiAlH_4$ in diethyl carbitol could be recovered by the following reaction:

$$LiAl(OCH_3)_4 + 4\ n\text{-}C_6H_{13}OH \rightleftharpoons LiAl(OC_6H_{13})_4 + 4\ CH_3OH$$

The reagents for this experiment were dried and then fractionated. Five cc (0.125 mole) of methanol (b.p. 64.2° C/750 mm) in 50 cc of diethyl carbitol (b.p. 80° C/13 mm) were added to 0.041 mole of $LiAlH_4$ dissolved in 150 cc of diethyl carbitol. Next, 50 grams of n-hexanol (b.p. 77° C/39 mm) were added.

(4) Scattergood, Inorg. Synthesis, II, 89 (1946)

[redacted]

The reaction mixture was then heated with a Glas-col mantle and 4.5 cc of methanol were collected. Hence, the recovery of methanol was 90%.

In view of these results the reduction of carbon dioxide by lithium aluminum hydride and subsequent isolation of methanol was carried out. A one liter, one-necked flask was equipped with a gas inlet and a gas outlet tube. The former was attached to a carbon dioxide generator and the latter to a trap at -80°, ascarite tube, drierite tube, and bubbler, respectively. Dry carbon dioxide, diluted with nitrogen and generated by adding 30% perchloric acid to 0.06 mole of barium carbonate, was passed through a solution of 3.8 grams of $LiAlH_4$ in 500 cc of diethyl carbitol (b.p. 80° C/13 mm). The time required for the addition was sixty minutes. Ten minutes after the last addition the ascarite tube was reweighed and it was found that 2% of the carbon dioxide escaped from the reduction mixture. Next, 100 cc of n-hexanol (b.p. 77° C/39 mm) was added dropwise while the flask was cooled externally with ice-water. The reaction mixture was then heated and 1.9 cc of methanol boiling at 65° C (uncorr.) were obtained. This corresponds to a 75% yield.

It is believed that the yield of methanol can be increased by modifying both the apparatus and technique. Further work will be done along these lines.

C^{14} Labeled Formate Preparation (G. C. Bell)

Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$ and $BaCO_3$ have been utilized as starting materials for the synthesis of their respective formates by hydrogenation in dilute aqueous solution over catalysts at moderate temperatures. Best results have been obtained by hydrogenation of a K_2CO_3-$KHCO_3$ mixture obtained by absorbing CO_2 in 1 N KOH using palladium black as a catalyst with 100 atmospheres H_2 at 70° C[1]. 92% of the theoretical HCOOK has been obtained after twenty-four hours hydrogenation. An appreciable amount (5-10%) of the CO_2 generated is unabsorbed in 1 N KOH, and must be precipitated as $BaCO_3$. An apparatus has been constructed, providing for agitation of the CO_2-KOH solution to facilitate absorption of the CO_2.

Hydrogenation at 100° C of a 5% suspension of $BaCO_3$ was attempted using palladium black as a catalyst. A 22% yield of $(HCOO)_2Ba$ was obtained. The unreacted $BaCO_3$ can be recovered. Work is in progress to improve the yield.

Sodium Formate-C^{14} from Beryllium Nitride (G. C. Bell)

Previous work[2] has shown that oxidizable fractions of C^{14} activity induced in powdered beryllium nitride by neutron bombardment have possessed appreciable formic acid.

The residue from H_2SO_4 dissolution of 1 gram of Be_3N_2 powder[3] was transferred to a flask, saturated with $MgSO_4$, and placed on a steam distillation apparatus, the steam being generated from boiling 0.1 N NaOH. The

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(1) Melville, Nachele and Keller, J. Biol. Chem., 69, 419 (1947)
(2) Yankwich, P. E., BC-36, February, 1947
(3) Cohn, Anthony and Weinberger, Mon N-311, 1947

[redacted]

vapors off the acid solution were condensed in an Allihn condenser and the condensate returned to the NaOH solution. The rate of boiling for each solution was adjusted so that the NaOH solution diminished in volume only slightly over a six hour boiling period. The solutions were allowed to cool to room temperature, and a fresh 0.1 N NaOH solution was put in place. Three such runs were made. At the end of the third cycle, the acid residue was removed, its volume was recorded, and the residue was bottled.

The NaOH-$HC^{14}OONa$ solution was oxidized in the pot with a chromic-sulfuric acid mixture, and the ionization current of the evolved $C^{14}O_2$ was determined with a Beckman micro-ammeter. The $C^{14}O_2$ was then absorbed in NaOH solution and diluted to 100 ml. The acid residue was of such a volume that only one-third the total volume could be added to the pot at one time.

Aliquots of each cycle were taken and the $BaC^{14}O_3$ was precipitated in the usual manner, weighed and counted.

The following results were obtained:

Cycle	μc C^{14} as $BaC^{14}O_3$
1	2.03
2	.58
3	2.89
Acid Residue	4.13
Total	9.6

It is possible that some material containing C^{14}(CO, CO_2, CH_3OH, HCOOH) was lost by volatilization through the condenser. It is planned to modify the condenser to effect complete recovery of C^{14}. Further work on these organic fractions is indicated.

Analytical methods for 1-carbon compounds have been investigated. Permanganate oxidation, calomel reduction and colorimetry methods have proved satisfactory for semi-micro analysis. Colorimetric analysis has shown that 10 γ formaldehyde can be estimated visibly by use of chromotropic acid.(4) Work is now in progress on spectrophotometric analysis of formic acid.

Tracer Studies in the Rearrangement of α,α-Dibromoacetophenone to Mandelic Acid (O. K. Neville)

The mechanism of the reaction of α,α-dibromoacetophenone with aqueous alkali to give mandelic acid is being studied with the aid of carbon-14. The results of this investigation may be compared with those previously obtained in the phenylglyoxal reaction, in which conversion to mandelic acid has been shown to occur without rearrangement of the carbon skeleton. The carbonyl-labeled acetophenone previously prepared was brominated in the presence of light to give α,α-dibromoacetophenone.

(4) Feigl, F., Qualitative Analysis by Spot Tests, 397 (1946)

This, when treated with 10% aqueous NaOH, was converted to mandelic acid. The determination of the specific activities of the benzoic acid and carbon dioxide fractions from the chromic acid oxidation of mandelic acid will show whether rearrangement of the carbon chain has occurred.

Following is a brief description of the experimental work which has been completed.

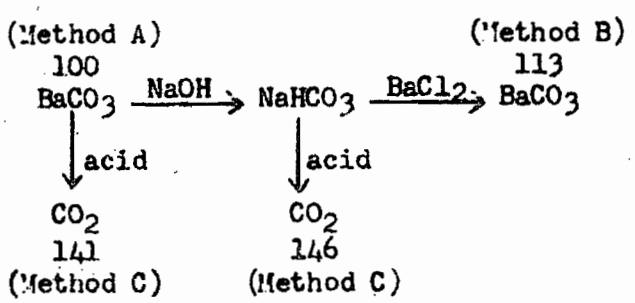
To 1.2 g of acetophenone dissolved in 1.5 ml of carbon disulfide, was slowly added 3.2 g of bromine under strong illumination from a photoflood lamp; after the absorption of bromine was complete, the solution was frozen in a dry ice-acetone bath until crystallization occurred. The product was recrystallized once from a carbon disulfide petroleum ether solution and washed by decantation twice with petroleum ether. The yield of α,α-dibromoacetophenone was 2.55 g or 91.8%.

To this product was added 15 ml of 10% NaOH and the reaction mixture was allowed to stand at room temperature with stirring over night. The slightly brown solution was extracted twice with chloroform and neutralized with HCl. The mandelic acid was precipitated as cadmium mandelate, which was washed with ether and dried. The yield of cadmium mandelate was 1.81 g or an overall yield of 87.5%.

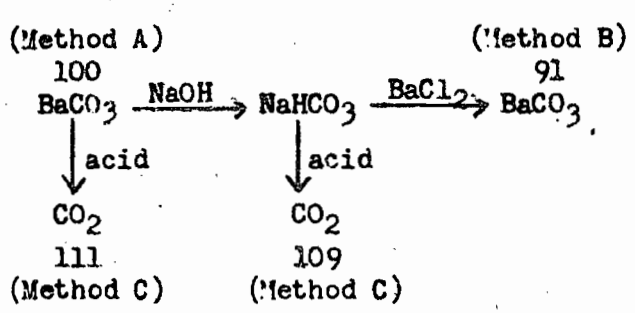
Preparation of Pure $BaC^{14}O_3$ and Standardization of Counting Techniques (W. J. Skraba)

Considerable discrepancy exists among the solid and gaseous counting methods employed at Clinton Laboratories for the determination of carbon-14. Following are preliminary data in chart form showing the anomalous values obtained. The numbers are arbitrary but show exact relations among the results by the different counting methods:

Sample I



Sample II



The methods consist of: method A - packing dry barium carbonate-C^{14} in an aluminum well and counting through an absorber in a mica window counter; method B - precipitating barium carbonate-C^{14} from solution, collecting the precipitate on a sintered porcelain disk and counting in a mica window counter; method C - generating carbon dioxide-C^{14} from barium carbonate-C^{14}, sweeping the gas into a chamber and measuring the ionization current by means of a dynamic condenser electrometer.

Various samples of barium carbonate-C^{14} have been analyzed for carbonate content. The method consisted in acid decomposition of the barium carbonate-C^{14} followed by a direct weighing of the carbon dioxide evolved in a gas weighing bottle. The results indicate that these samples have contained from 18-98% of theoretical carbonate.

The purpose of the present research is to prepare chemically pure barium carbonate-C^{14} containing approximately 100 millicuries of radioactive carbon. The material will then be used as a standard material for calibrating the solid and gaseous counting methods.

Model experiments with inactive barium carbonate have been conducted to determine the optimum conditions for precipitation of barium carbonate in chemically pure form. Barium carbonate samples (500-600 mg) have been decomposed with 5 M perchloric acid and the evolved carbon dioxide has been swept through a dry ice trap and frozen in liquid nitrogen prior to introduction into barium hydroxide solutions of varying concentrations. The precipitated barium carbonate has been analyzed spectrographically and chemically.

Preliminary results indicate that satisfactory precipitation of barium carbonate occurs from dilute barium hydroxide solution. Traces of impurities, such as copper and iron, may be excluded by the use of carefully prepared distilled water and chemically pure barium hydroxide. Other factors, such as aging of the precipitate and the effect of heat and pH on the precipitation, are under investigation.

C^{14} Methanol

The procedure for preparation of methanol has changed in that carbon dioxide-C^{14} is now directly hydrogenated to methanol instead of silver carbonate-C^{14} as previously reported. The yields have increased to 80-83%.

The Synthesis of C^{14} Labeled Compounds (C. J. Collins)

Derivatives of benzene labeled in the nucleus

Introduction

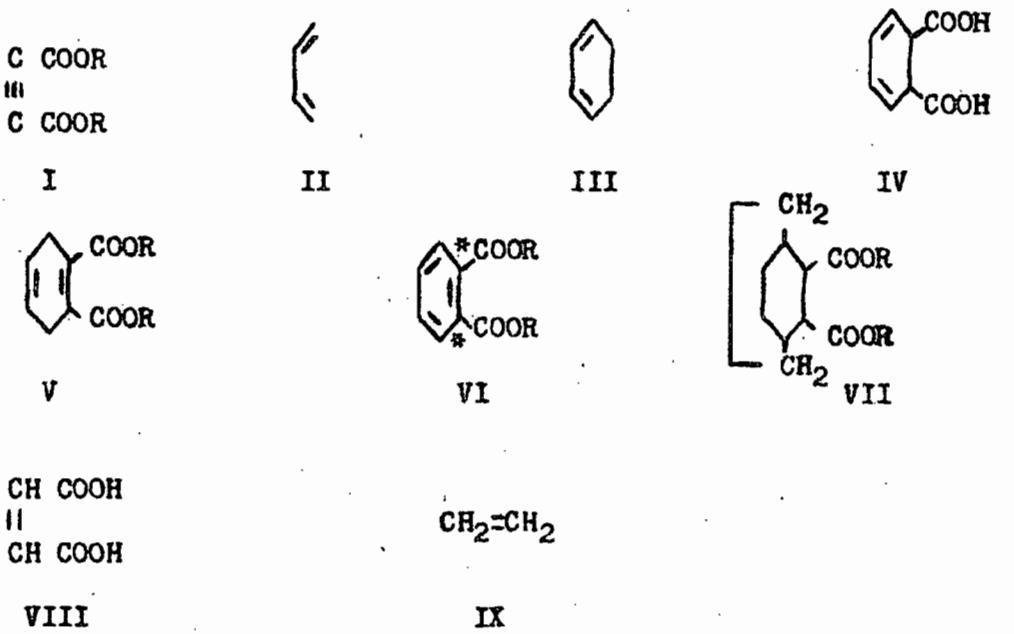
The synthesis of benzene derivatives containing carbon-14 in specific nuclear positions has been undertaken. The prospective syntheses involve the following steps:

1. The conversion of $C^{14}O_2$ to $HC^{14} \equiv CH$ by the action of $C^{14}O_2$ on barium metal followed by aqueous decomposition of the barium

carbide-C^{14}[1].

2. The conversion of acetylene-C^{14} to propiolic acid-2,3-C_2^{14} or to acetylene dicarboxylic acid-2,3-C_2^{14} by the action of one or two moles of carbon dioxide on acetylene-Grignard[2].

3. The "Diene Reaction" between the acetylene-C^{14} acid and a conjugated diene to yield an adduct which may be converted to a benzene derivative labeled in the ring with carbon-14. The first such synthesis attempted will be the preparation of o-phthalic acid (VI, R = H) labeled as shown by asterisks. This synthesis will involve the addition of acetylene dicarboxylic acid dimethyl ester-2,3-C_2^{14} (I, R = CH_3) to either cyclohexadiene (III) or 1,2-dihydrophthalic acid (IV) followed by thermal decomposition of the adduct to o-phthalic ester-1,2-C_2^{14}(VI, R = H).



The reaction between acetylene dicarboxylic acid diethyl ester (I) and butadiene (II) has been reported to yield the diethyl ester of 3,6-dihydro-o-phthalic acid (V) in less than 50% yield[3]. Alder and Rickert[4] state that I and 1,3-cyclohexadiene (III) yield VI with the evolution of ethylene (IX). This reaction probably proceeds through the intermediate adduct VII. These same authors state that I and 1,2-dihydro-o-phthalic acid (IV) produce maleic acid (VIII) and phthalic ester (VI) in unspecified yields.

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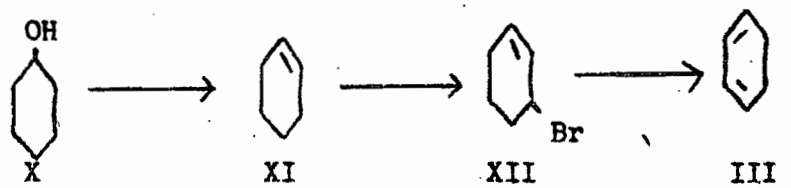
(1) Arrol and Glascock, Nature, 159, 810 (1947)
(2) Jozitsch, J. Russ. Phys. Chem. Soc., 34, 242-44 (1902); Grignard, Lapayre and Tcheou Faki, Compt. Rend., 187, 517 (1928); Oddo, Gazz. chim. ital., 34, 429 (1904); ibid, 38, 625 (1908)
(3) Alder and Backendorf, Ber., 71B, 2199 (1938)
(4) Alder and Rickert, Ann., 524, 180 (1936)

Discussion of Results

An apparatus has been constructed for the preparation of acetylene dicarboxylic acid-2,3-C_2^{14} starting with $BaC^{14}O_3$.

Cyclohexadiene (III) has been prepared by conventional procedures, starting with cyclohexanol (X), dehydration with phosphoric acid to cyclohexene (XI), treatment with N-bromosuccinimide to yield 3-bromocyclohexene (XII), and dehydrohalogenation with quinoline to produce III.



Acetylene dicarboxylic acid has been prepared[5], converted to its dimethyl ester (I) and allowed to interact with cyclohexadiene (III). A small yield of material which may be phthalic acid (VI, R = H) was obtained. At present work is being directed toward improving the yield and purity of this product.

The procedure of Baeyer[6], and of Neville[7] and of Pasquinelli[8] has been followed for the preparation of 1,2-dihydro-o-phthalic acid (IV). At present the interaction of this compound and acetylene dicarboxylic ester (I) is being studied.

Experimental

Cyclohexadiene (III). Cyclohexanol (X) (81.5 gms) was converted to cyclohexene (XI) (47.3 gms boiling 82°; 78.5% yield) by the method of Dehn and Jackson[9]. Next, 60 cc cyclohexene and 21 gms N-bromosuccinimide were heated under reflux twenty-five minutes[10]. The succinimide was collected on a filter, and the filtrate was distilled, yielding 9.58 gms 3-bromocyclohexene (XII) (50-55% yield based on N-bromosuccinimide). This material was redistilled, and the fraction, boiling at 50-52° at 1-2 mm, was collected (3.9 gms). The 1,3-cyclohexadiene was obtained by heating a mixture of freshly distilled quinoline (10 cc) and 3.9 cc XII in an oil bath at 180°. The colorless cyclohexadiene slowly distilled from the mixture (2 cc obtained).

Acetylene Dicarboxylic Acid (I, R = H). Fumaric acid (67 gms) was converted to α,β-dibromosuccinic acid[11] and subsequently acetylene dicarboxylic acid[12].

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(5) Org. Synthesis, Coll. Vol. II, p. 10
(6) Baeyer, Ann., 269, 145 (1892)
(7) Neville, J. Chem. Soc., 89, 1743-1748 (1906)
(8) Pasquinelli, Anales a. soc. quim. argentina, 31, 181 (1943)
(9) Dehn and Jackson, J. Am. Chem. Soc., 55, 4285 (1933); Org. Synthesis, Coll. Vol. II, p. 152
(10) Ziegler et al, Ann., 551, 80-119 (1942)
(11) Org. Synthesis, Coll. Vol. III, p. 177
(12) Org. Synthesis, Coll. Vol. II, p. 10

Acetylene Dicarboxylic Acid Dimethyl Ester (I, R = Me). Acetylenedicarboxylic acid (3.64 gms) was heated under reflux for eight hours with 100 cc methanol containing 1.0 cc acetyl chloride. The mixture was then concentrated and desiccated several days. Yield, 3.90 grams.

1,2-Dihydrophthalic Acid (IV). Twenty grams of o-phthalic acid, 19.7 gms fused sodium acetate and 200 cc H_2O were cooled to 14° C. The mixture was stirred vigorously. To this mixture was added 400 gms 3% sodium amalgam and 60 cc 50% aqueous acetic acid. These reagents were added in one-tenth aliquot portions at a time. When hydrogen was no longer evolved the next portions were added. When all of the sodium amalgam and acetic acid had been added the mixture was stirred an additional twenty minutes, and the mercury was drawn off in a separatory funnel. Next, 200 cc 20% sulfuric acid was added. After standing three hours the white crystals were collected on a filter and crystallized from water yielding 8.0 grams of white needles melting at 210-211° C (corrected). The identity of this material as trans-1,2-dihydro-o-phthalic acid has not yet been established.

Diene Reaction Between Acetylene Dicarboxylic Acid Dimethyl Ester (I, R = Me) and Cyclohexadiene (III). Acetylene dicarboxylic acid dimethyl ester (I, R = Me) (1.0 cc) and 10.0 cc III heated under reflux on steam bath twelve hours. The mixture was then allowed to stand six days and the excess cyclohexadiene was removed by distillation. The residue was then heated to 180° for two hours and 10 cc acetic acid and 2.0 cc concentrated hydrochloric acid were added and the mixture was heated under reflux one hour. The mixture was poured into excess water, filtered and desiccated overnight. Yield, 1.20 gms dark material melting below 100° C over a 15° range. This material was insoluble in water, soluble in benzene, dioxane, acetic acid, and aqueous sodium hydroxide. When precipitated by addition of acid to the sodium salt, a dark brown material melting between 145° and 160° C was obtained. All attempts to obtain a crystalline material were unsuccessful. The use of an alumina chromatograph was also unsuccessful. Further attempts with milder conditions of reaction are indicated.

Phenanthrene-9-C^{14} (13)

It was previously reported that model experiments for the synthesis of phenanthrene-9-C^{14} had been worked out. Phenanthrene-9-C^{14} has now been synthesized at two levels of activity:

1. 72.5 milligrams of phenanthrene-9-C^{14} containing 10.78 millicuries carbon-14 per mole. The activities of the barium carbonate-C^{14} starting material and 9-fluorenecarboxylic acid-10-C^{14} intermediate are respectively 11.65 and 11.62 millicuries per mole.

2. Approximately 70 milligrams of phenanthrene-9-C^{14} containing approximately 1 millicurie of carbon-14 has been prepared.

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(13) For previous work see Mon N-311, p. 9

[redacted]

3. SUPPORTING RESEARCH

Thermodynamics of Coprecipitation (F. Vaslow and G. E. Boyd) P.A. CX3-5

Fairly extensive studies during the past quarter on the distribution of Ag^+ ion between aqueous electrolyte solution and solid TlCl has shown that the coprecipitation observed in this case resulted from an adsorption mechanism. Since the object of this study has been to investigate the behavior of systems wherein solid solution formation was responsible for "carrying", further efforts with (Ag + Tl)Cl have been discontinued.

Measurements of the distribution of Br^- ion between aqueous 1 M NaCl solutions and solid AgCl have continued. Much effort has been spent to refine the procedures so as to obtain an experimental accuracy to within 0.5%. This limiting accuracy appears to be set by the statistics of the activity measurements which have been made throughout with a high-pressure, Argon-filled gamma ionization chamber. The great importance of temperature control to within $\pm 1^{\circ}$ was remarked upon previously. Further, attention must be given to the purification of all reagents employed. Particular care must be exercised in the preparation of the 34 h Br^{82} tracer to insure that a known amount of inactive bromide carrier be present. In connection with this last point it has been found that the value of D, the distribution coefficient, depends on the mole fraction of bromide in the AgCl even down to the lowest concentrations attainable. Thus, values of D for 0, 50, 100, 200 and 500 gamma of added Br^- were found to be: 130.6, 131.9, 132.5, 134.3, and 133.3, respectively. This variation is consistent with the formation of either a "regular" or a non-ideal solid solution of AgBr in AgCl.

Ion-Exchange Separations: Theories of Adsorption Column Performance (S. W. Mayer, E. R. Tompkins, G. E. Boyd)

L. A. Matheson, among others, has pointed out that the breakthrough curve was the integral of the elution curve. On that basis, an expression for the former in terms of the plate theory may be written as:

$$c/c_o = 0.5000 + 1/\sigma\sqrt{2\pi}\int_0^t e^{-t^2/2}\,dt$$

where

$$t = \frac{\sqrt{p}\,(F - K_d')}{[K_d'(1 + K_d')]};$$

$$\sigma = [pK_d'(1 + K_d')]^{\frac{1}{2}};$$

c = concentration of the solute in the effluent; c_o = concentration of solute in the influent; p = number of plates in the column; F = number of free-volumes of liquid passed through the exchanger bed; and K_d' = distribution ratio of solute in the exchanger to solute in the solution in any portion of the bed.

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Ion-Exchange Separations: Purification of the Rare Earths (D. H. Harris, E. R. Tompkins and G. E. Boyd) P.A. CX3-5

Effort during the quarter now completed has been directed in the main towards improving the ion-exchange separation of the middle group rare earths, including Sm, Gd, Tb, Dy and Y. Owing to the relatively large abundance of yttrium in the naturally occuring mixtures of these elements, the problem of the separation was in many respects the most difficult yet undertaken. The heavier earths including Lu, Yb, Tm and Er may be separated in good purity as was demonstrated in MonC-361 (cf. Er-1). A repetition of this last experiment (Er-2) showed the same excellent resolution of the heavy earths, but no, or, at best, only a very poor, separation of Ho, Dy, Tb and Cd. Two additional experiments (Er-3 and Er-4) confirmed this. An upflow elution was employed in Er-3.

More recently, however, a satisfactory resolution has been completed of a crude rare earth mixture (Er-5) on a considerably larger scale than with previous separations of this kind. The starting material was 31.3 g. of a partially concentrated yttrium earth fraction resulting from Na_2SO_4 and $K_4Fe(CN)_6$ precipitations of a commercial yttrium oxide. The sulphate precipitation was used to eliminate all the cerium-terbium earths (except for a trace of Tb) and the ferrocyanide served to reduce the yttrium content. In spite of this latter, the analytical results showed as much as 70% of the preparation to consist of yttrium. Judging by the appearance of the elution curve obtained in the ion-exchange separation of this mixture, the exchanger bed was overloaded with yttrium by three or four-fold. By virtue of the very low flow rate (0.025 to 0.05 cm/min) employed, an unusually high rare earth concentration was observed in the effluent solutions. For example, the yttrium gave a plateau at a concentration level of 2.5 g. Y_2O_3/liter. Roughly 85% of the Y was collected at this concentration. When this solution was evaporated, yttrium citrate crystallized out. A solubility of about 3.8 g/l (as Y_2O_3) was determined.

The approximate composition of the initial rare earth mixture was reconstructed from the results accumulated. The data of the following table serve to illustrate the composition of the type of concentrate obtainable using the chemical method described.

Approximate Composition of Er-5 Earths

Lu_2O_3	2-3%
Yb_2O_3	12-13
Tm_2O_3	1-2
Er_2O_3	4-5
Ho_2O_3	2-3
Dy_2O_3	5-10
Y_2O_3	~70

None of the earths was obtained pure, although fractions suitable for a final purification were obtained. All of the earths, excepting the dysprosium, were free of yttrium. The yttrium contained no other earth than Dy (and possibly a trace of Tb) as shown by a faint yellow tinge in the Y_2O_3 preparation.

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Two additional yttrium earth separations are in progress. One (Er-6) is being conducted as was Er-5 using the same bed of exchanger and a starting mixture presumably high in Dy. A companion fractionation (Er-7), which is closely similar to Er-6, is being carried out using a smaller bed and sodium citrate at a pH = 3.00 as elutriant. Incomplete results on this latter have revealed that the sodium coprecipitated extensively with the rare earth oxalates which are precipitated from the effluent solutions. This may render the use of sodium citrate impractical.

An attempt to separate a Sm-Gd mixture has been completed (Sm-1) since a material balance of over 97% has been reached. No separation was observed in this preliminary experiment which employed a pH of 3.20 and a flow rate of 0.05 cm/min. Evidently, the lowered flow rate was insufficient to compensate for the increased rate of movement of rare earth through the bed resulting from the increased pH.

The separation and purification of ca. 15 g of scandium from thortveitite has continued. Also, small scale operations have accumulated considerable amounts of worked-over earths, both in the yttrium and in the terbium groups. These are being produced faster than they can be purified with the ion-exchange columns presently available.

Radiochemistry of Element 43 (E. E. Motta, G. V. Larson and G. E. Boyd)
P.A. CX4-3

The following table serves to summarize some of the information on the radioisotopes of element 43 accumulated both within and outside the project during recent months.

Half-Life	Radiations	Mass	Comments
52 m	β^+ 2.5 K γ 2.84	(94)	Mo(p,n)
52 ± 3 d	K γ 0.25 & 0.84	(95)	Previously known 60 d activity
4.2 d	K β^+ = 0.64 γ = 0.92	96	Mo(p,n); Mo(d,n) Cb(α,n)
88 d* 15 y	I.T., e^- γ 0.097	97	Previously known 90 d activity
6.0 h* 9.4×10^5 y	I.T., e^- γ 0.136 β^- 0.32	99	
20 m		(100)	Tc(n,γ); Rh(n,α)
15 m	β^- 1.3 γ 0.3	101	Previously known 14 m activity

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The characterization and mass assignment of a number of isotopes which may occur in fission either through chain decay or by independent formation has been aided greatly recently by the availability of the calutron enriched isotopes of stable molybdenum. These preparations are being irradiated with 20-22 Mev deuterons at the 60-inch cyclotron at Berkeley through the kind assistance and cooperation of Dr. J. G. Hamilton. Thus far, three molybdenum targets have been irradiated, and the previously known 4, 60, and 90 d periods have been produced in good yields. The one irradiation of Mo^{97} has indicated that our previous assignment of the 90 d activity to mass 97 was probably correct.

A determination of the half-life and energy of the beta radiations emitted by the long-lived element 43 isotope produced by the prolonged exposure of molybdenum metal to pile neutrons has been carried out. Measurements of the specific activity were conducted as follows: After extensive purification by means of chemical and ion-exchange techniques to remove an initial rhenium and molybdenum contamination, about 100 microgram amounts of Tc metal were electroplated on polished copper discs, which then were weighed on a semi-micro balance and counted. Uncertainties as to counting efficiency, scattering, etc. were minimized by electroplating a standardized Co^{60} preparation which was counted under identical conditions. The best average value for the half-life of the Tc activity obtained thus far has been 9.4×10^5 years. A careful comparison of the aluminum absorption curves for the beta radiations of the Tc and the Co^{60} activities showed the former to possess an energy slightly in excess of that for the latter (i.e., 0.31 Mev) in agreement with the Feather extrapolated range-energy determination.

Several attempts to prepare and characterize Tc^{100} by neutron irradiation of a purified sample of Tc^{99} were made. A series of short irradiations has indicated that the half-life of this isotope is probably less than 20 minutes in agreement with the recent cyclotron observations made by Glendenin (M-3866), 26).

Irradiation of the enhanced Mo isotopes with pile neutrons has confirmed the assignments of the 67 h and the 15 m periods to masses 99 and 101, respectively. Irradiation of Mo^{92} has given preliminary indication of a molybdenum activity of several hours half-period.

Chemistry of Technetium (G. V. Larson, E. E. Motta and G. E. Boyd) P.A.CX4-3)

The extraction of pile produced element 43 from thirty cans of molybdenum metal powder which had been irradiated for one year has commenced. The first ca. 195 g aliquot gave a yield of 0.39 mg of Tc^{99}, a value slightly less than was expected. As in previous extractions, an appreciable amount of the 90 h Re^{186} was present in the first distillates as a radiochemical impurity. It was observed, however, that the Re_2O_7 was distinctly more volatile than Tc_2O_7 so that some purification was effected even in the first sulfuric acid distillation step. Rhenium contamination was removed exhaustively from Tc by the use of anion exchange column techniques. Earlier studies (MonN-243) had shown technetium to undergo anionic exchange from dilute hydrochloric acid solutions when the anion exchanger, Amberlite IR-4, was employed. Further determinations during the past quarter of the equilibrium distribution coefficients, K_d, for both tracer Tc and Re initially present in 0.1 N HCl gave values of 1200 and 590, respectively. The ratio of these values, 2.03, showed that a column separation could be effected. Accordingly, a bed of 140/170 mesh IR-4, 88 cm x 1.0 cm^2, was prepared. A mixture of Re and Tc activities was then adsorbed and differentially eluted using 0.1 N HCl and a flow rate of 0.5 ml/sq/cm/min. The rhenium appeared first in the effluent as was expected, and an excellent symmetric peak of activity was observed. However, contrary to expecta-

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tions, the element 43 activity was eluted in a broad diffuse peak much later than the rhenium. The consequence of this behavior was that, although a good separation of the Re and Tc was achieved, it was possible to realize only a 50% recovery of the Tc activity. Conceivably this behavior resulted from the reduction of the heptavalent oxidation state of the Tc.

Long-lived Fission Product Rare Earth Radioisotopes (D. H. Harris, E. R. Tompkins and G. E. Boyd) P.A. CX4-3

Observations on what may be a new long-lived fission product rare earth isotope have continued during the past period. Presently, this activity which was collected in the tail fractions of the yttrium peak during an ion-exchange separation of a fission product sample has shown a decay of approximately 420 d. Its radiations appear to consist of soft electrons (E_β = 0.23 Mev), a soft gamma of roughly 0.1 Mev (0.3 g Pb/sq cm) and a harder gamma of 0.5 Mev (4.2 g Pb/sq cm). The position of the activity peak in the ion-exchange column effluent supports the assignment to Tb^{161}. However, the possibility of its being Eu^{155} has not been excluded.

General Radiochemistry: Heavy Rare Earth Radioisotopes (B. H. Ketelle and G. E. Boyd)

In the previous quarterly report (Mon N-370) were summarized the half-life values for two erbium isotopes and preliminary results from the study of these activities with the beta ray spectrometer. The completed study is reported in the following abstract.

"Two erbium activities were produced in ion-exchange[1] separated erbium, by n,γ reactions, and were studied with beta ray spectrometer and coincidence techniques. (1) A 9.4 ± 0.2 d β^- emitter has been found. It emits no gamma rays and has a beta ray end point of 0.33 ± 0.01 Mev. (2) A 7.5 ± 0.2 h β^- emitter has also been found. It has three alternate modes of β^- decay. 71 ± 5% of the betas have an energy of 1.05 ± 0.03 Mev and are followed by two gammas of 0.305 ± 0.010 and 0.113 ± 0.005 Mev in cascade. The 0.113 Mev gamma ray is highly converted and has a half-life of 2.5 μsec (McGowan and DeBenedetti). 6 ± 1% of the betas have an energy of 1.49 ± 0.05 Mev and decay directly to the ground state of Tm. 22% of the betas have an energy of 0.67 ± 0.03 Mev and are followed by a 0.805 ± 0.025 Mev gamma.

From the disintegration energies it appears that the 7.5 h period should be assigned to Er^{171} and the 9.4 d period to Er^{169}.

A Tm activity of 500 ± 100 d was shown to grow from the activated Er samples; this is probably Tm^{171} daughter of 7.5 h Er^{171}."

On the basis of the fact that an erbium sample decayed almost to the background of the mica window counter, Tm^{171} was reported to have a half-life of about 170 y (Mon N-370). Aluminum absorption curves taken on very thin mica window tubes indicated that a soft radiation might be present in thulium activity separated from neutron activated erbium. A number of samples of thulium obtained from erbium bombardments and from thulium bombardments were measured on the vibrating reed electrometer and on the Simpson proportional beta counter. These measurements showed the presence of a large amount of soft radiation from the thulium obtained from erbium bombardments. This radiation decays with the above reported half-life of 500 ± 100 d and appears

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

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to be of the order of 100 kev β^-. It is absent in neutron activated thulium.

Measurements of old samples of erbium from which thulium had been separated showed that this soft activity was also present, though it could not be efficiently measured through mica window tubes.

Further study is in progress to definitely indicate the genetic relationship of the erbium and thulium activities.

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Hard Gamma Measurements (H. A. Levy, M. H. Feldman)

A method similar to that of S. Bernstein[1] for counting γ of energy greater than 2.2 Mev, has been developed. The apparatus is composed of a cylindrical tank 16" high and 16" in diameter filled with D_2O. The tank has a 3/4" well on top and a slot half way down the side which contains a uranium fission chamber 6" in diameter. A long test tube inserted in the well will rest upon the upper surface of the slot. The fission chamber differs from previously used fission chambers only in being larger in area and in having a substantially heavier deposit of U^{235} on its median plate. It is hoped that this chamber with a one mg U^{235} per cm^2 deposit will be more sensitive as a neutron detector.

When a sample inserted in a test tube through the top well emits a hard γ a (γ,n) reaction may occur,

$$(1)\quad {}_1D^2 + \gamma \longrightarrow {}_0N^1 + {}_1H^1$$

followed by moderation of the neutron in the heavy water and finally a fission in the chamber.

$$(2)\quad U^{235} + n \longrightarrow [U^{236}] \longrightarrow \text{fission}$$

The fission pulse is fed to a preamplifier, an A_1 amplifier[2], and is counted on a scale of 1024. This counting equipment allows for accurate pulse height selection.

Since the cross section for production of reaction[1] by γ's above 2.2 Mev is known only in one case and since the efficiency dependence on the constants of our apparatus was not known and not easily determinable, a comparison method was used. This method consisted in the use of Na^{24} as a standard. The decay scheme of Na^{24} is well known[3] and it is known there is one 2.7 Mev γ per disintegration and no other γ above 2.2 Mev.

Manganese

A hard γ of energy greater than 2.2 Mev has been found in the radiations from 2.6 hr Mn^{56}. Its energy has been determined as 2.7 Mev[4]. This is in agreement with previously known decay energies[5] if it is a crossover γ.

A sample of Mn^{56} and a sample of Na^{24} produced in the Clinton Pile were compared for absolute disintegration rate in the calibrated high pressure ionization chamber of Clark and Zumwalt[6] and then compared

(1)S. Bernstein. Report # MonP-172, 9/24/46.
(2)P. R. Bell. Report # MonP-323, 7/28/47.
(3)Elliot, Deutsch and Roberts, Phys. Rev., 61, 99 (1942).
(4)Wattenburg, Phys. Rev. 71, 497 (1947)
(5)Elliot & Deutsch, Phys. Rev. 63, 321, (1943)
(6)Clark & Zumwalt. To be published shortly as an CNL report.

[redacted]

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in our heavy water tank setup. It was found that the efficiency of the γ from the Na^{24} for giving neutron counts in our apparatus was 0.6×10^{-7} per disintegration. Then, the total number of disintegrations being known for the Mn^{56}, and the number of neutrons counted in our apparatus being known, the 0.6×10^{-7} factor was used to determine the factor

$$\frac{\text{Number of 2.7 Mev } \gamma \text{ from } Mn^{56}}{\text{Total number of disintegrations of } Mn^{56}}$$

It was found that the γ occurred in .23% of the disintegrations. The γ did come from Mn^{56} disintegrations as was shown by the half life curve [Fig. 1] and the fact that it originated in a sample of Mn irradiated in the pile.

Radium

An attempt has been made to duplicate the experiment in the case of Ra and its descendents. Definite evidence was found for hard γ emission in a series of radium samples purchased from the Radium Corporation of America. See Table I. This table represents counts made on different days on a series of radium sources. It is obvious that the inconsistencies are greater than statistical fluctuations would warrant. On the other hand no trend is discernible except that the lighter samples gave higher counts. This might be explained on the basis of the "microphonic character" of the counting arrangement(2). Or, it might be attributed to impurities. The presence of Thorium C in the samples as a likely impurity would account for some high counts.

However, there seems no doubt that a hard γ is present and has resulted in neutron counts from radium and its descendents. If we take all the values for the counts from the radium sample MSA 154 (10 mg Ra) + some later counts, the average result is:

$$37.0 \pm 2.6 \text{ /counts per 100 sec/per 10 mg Ra}$$

No absolute fractional value can be assigned to these hard γ because they are not separable as to energy and efficiency if there are two or more occurring with energies greater than 2.2 Mev. According to various workers(7), the γ emission goes no higher than 2.2 Mev. Some Russian workers(8), however, find that there are at least two γ's [actually emitted by RaC], one of 2.2 and one of 2.4 Mev and the extent of these two is 10.9% of all γ emitted in the series.

If we attempt to ascertain an absolute number of hard γ per decay, we are unable to do so because no absolute measurement can be made in our apparatus; there is no way of distinguishing the two γ's postulated and there is no reliable comparison γ emitter as there was for Mn^{56}.

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(7) R. D. Evans, J. Ind. Hyg. Tox., 25, 266 (1943) gives a review of these results.

(8) Alichanov and Latyschev, Jour. Phys. USSR 3, 263 (1940)

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Dwg.#4855 MonN-432

Fig 1 Decay of Hard β From MnO_2 Sample CI 1205/p 69 (6)

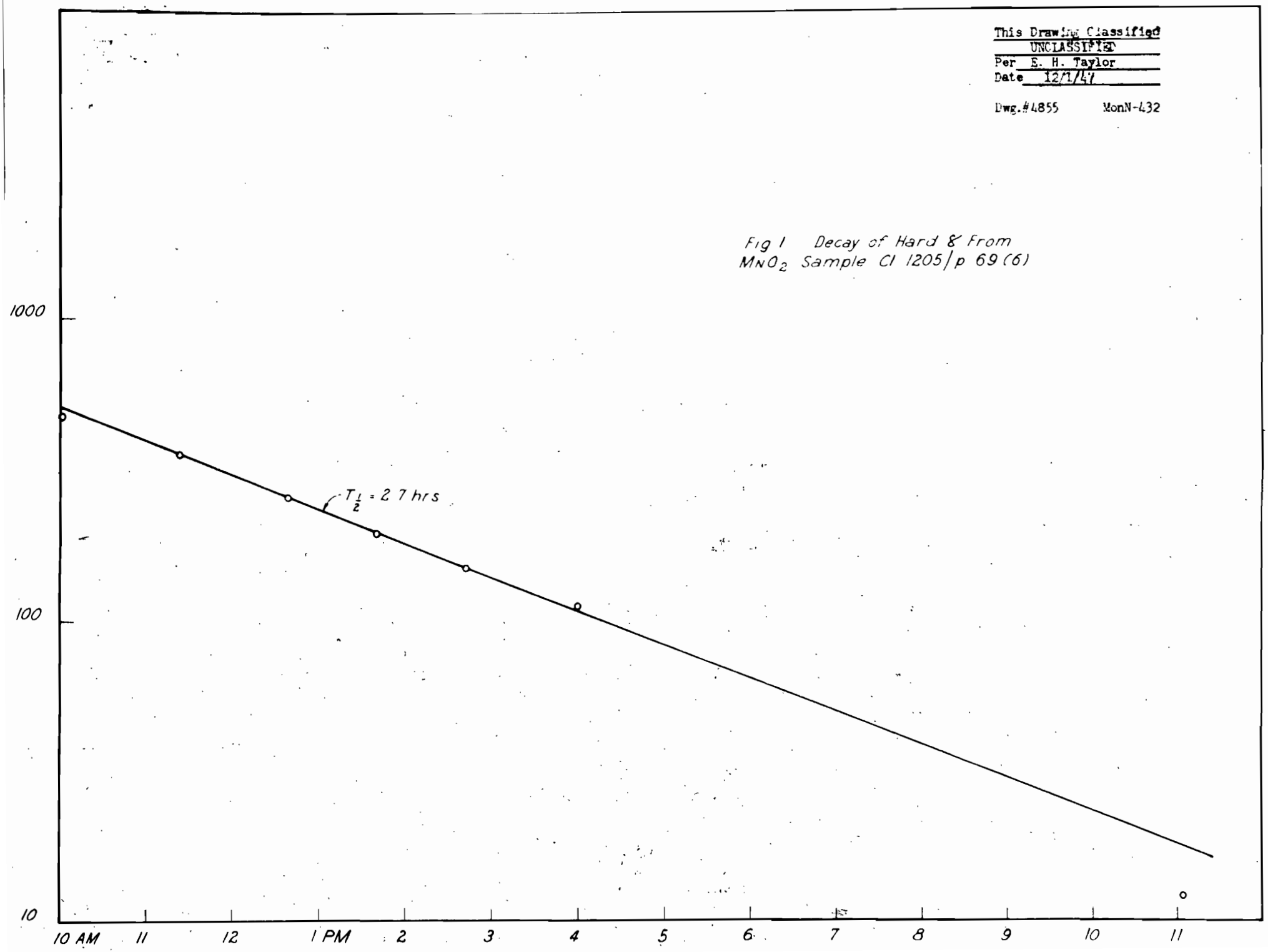

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Table I

Sample No.	Size of Sample	Total No. Neutron Counts	C/100 sec/10 mg Ra
21620	1.72 mg	328	54.8
21619	.897	67	82.9
MSA 154	4.87	297	46.2 (Sealed by Radium Corp. 2-18-44)
MSA 149	10	639	41.0 (Sealed 2-11-44)
Cl-C	23.35	984	40.1
Hart	48.2	2173	36.2
21619	.897	625	197
21620	1.72	675	74.8
MSA 154	4.87	1028	49.5
MSA 149	10	1030	35.8
Cl-C	23.35	1046	39.3
Hart	48.2	1200	41.2
21619	.897	2433	226
Cl-C	23.35	2464	37.3
21620	1.72	1050	65.6
Hart	48.2	4997	35.6
MSA 154	4.87	1792	42.0
MSA 154	4.87	1952	51.0
Cl-C	23.35	2057	38.1
Hart	48.2	2672	40.1
MSA 154	4.87	2344	53.0
Hart	48.2	4130	39.1
Cl-C	23.35	4197	39.6
MSA 149	10	4566	40.7
MSA 154	4.87	8590	59.1

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An approximation can be made, however, if we use the 10^{-7} factor determined for Na^{24} in our apparatus. We can assume that the efficiency factor for the 2.2 and 2.4 Mev γ found by Alichanov would be the same in our apparatus as a 2.7 Mev γ. This is a reasonable assumption as shown by the relative flatness of the curves of Breit and Condon(9) who calculated the cross section of D for the (γ,n) reaction as a function of the energy of the γ. It will at least give information of the correct order of magnitude.

Since the Ra capsule was sealed in 1944, the series members are in equilibrium through C' and C''. So, if RaC is the descendent that is emitting the hard γ, it is in equilibrium with the parent.

Then, using the efficiency factor 10^{-7} and making the assumptions described in the previous paragraph, the number of hard γ per RaC decomposition, when in equilibrium with 10 mg of Ra, is obtained from these data: The 10 mg Ra source, sealed in a gas tight capsule gave 37 neutron counts per 100 sec and must therefore have had $.37 \times 10^7$ hard γ emissions per sec. Since the number of disintegrations in 10 mg Ra is $10 \times 3.7 \times 10^7$/sec, the fraction in which a hard γ occurred is 1/100.

Other Substances

Similar attempts to find hard γ in other substances gave the following results.

Substances	No. Neutron Counts	Sample Size or Activity
Co^{60}	None	5 rd
Natural K	None	1 gm
S^{37}	Slightly above background	1 R*
Spent Rn tube	Slightly above background	10 tubes
Pu	None	1.4 mc
Cl^{34}	None	1 R
Au	None	6 R
Sb^{124}	None	4 R
Ga^{72}	Above background	6 R

It was our intention to obtain a series of γ emitters which had energies from 2.2 to about 5 Mev so that an experimental determination of the shape of the cross section curve for comparison with the theoretical curves of (γ,n) cross section in the case of deuterium could be made. This would give definite information as to the shape and depth of the potential well as well as type of forces in the deuterium nucleus.

(9)Breit and Condon, Phys. Rev., 49, 904 (1936)

*The R values are Roentgens/hr. at 10 cm measured through 2 mm Al + 10 cm air + 1.5 cm bakelite.

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So far, a suitable series of activities has not been found. But there are several hard γ emitters /of fairly short life as is to be expected/ in fission products and an attempt to identify these will be made. If they prove useable, then the above program of experiments will become possible.

Selenium 81 Mass Assignment (H. A. Levy, H. W. Feldman)

The 57 m Se activity has been assigned tentatively to mass 79 or 81[1][2]. Theoretical considerations indicate the mass 81 as the more probable of the two. Mass yield curves in uranium fission indicate this activity is 81. In addition Bohr-Wheeler calculations indicate Se^{79} should be long-lived[3].

Since stable isotopes of Selenium, enriched respectively in Se^{78} and Se^{80} were available to us, an experiment to determine the correct mass assignment was planned. Samples of stable isotopes Se^{78} and Se^{80} were irradiated in the Clinton Pile and the resulting activities studied by means of a standard Geiger-Muller thin window counter. It was expected that one of the two samples would give the characteristic 57m activity with β energy of 1.5 Mev.

Actually, both samples gave only the 57 m 1.5 Mev beta activity. (See Figures 1, 2, 3, 4 for half life and radiation characteristics). This, of course, is due to the fact that the enrichment is not perfect.

However, the 57 m 1.5 Mev specific activity resulting from irradiation of Se^{80} was about 200 times greater than that resulting from Se^{78}.

It is concluded from this ratio of activities that the correct mass assignment is 81. Also, the additional conclusion is possible that the Se^{79} activity is either very short or very long compared to 57 m, with the latter more probable[3].

(1)Snell, A. H. Phys. Rev. 52, 1007 (1937)
(2)Seaborg, G. T. and I. Perlman - BC-59
(3)Way, K. - Private communication

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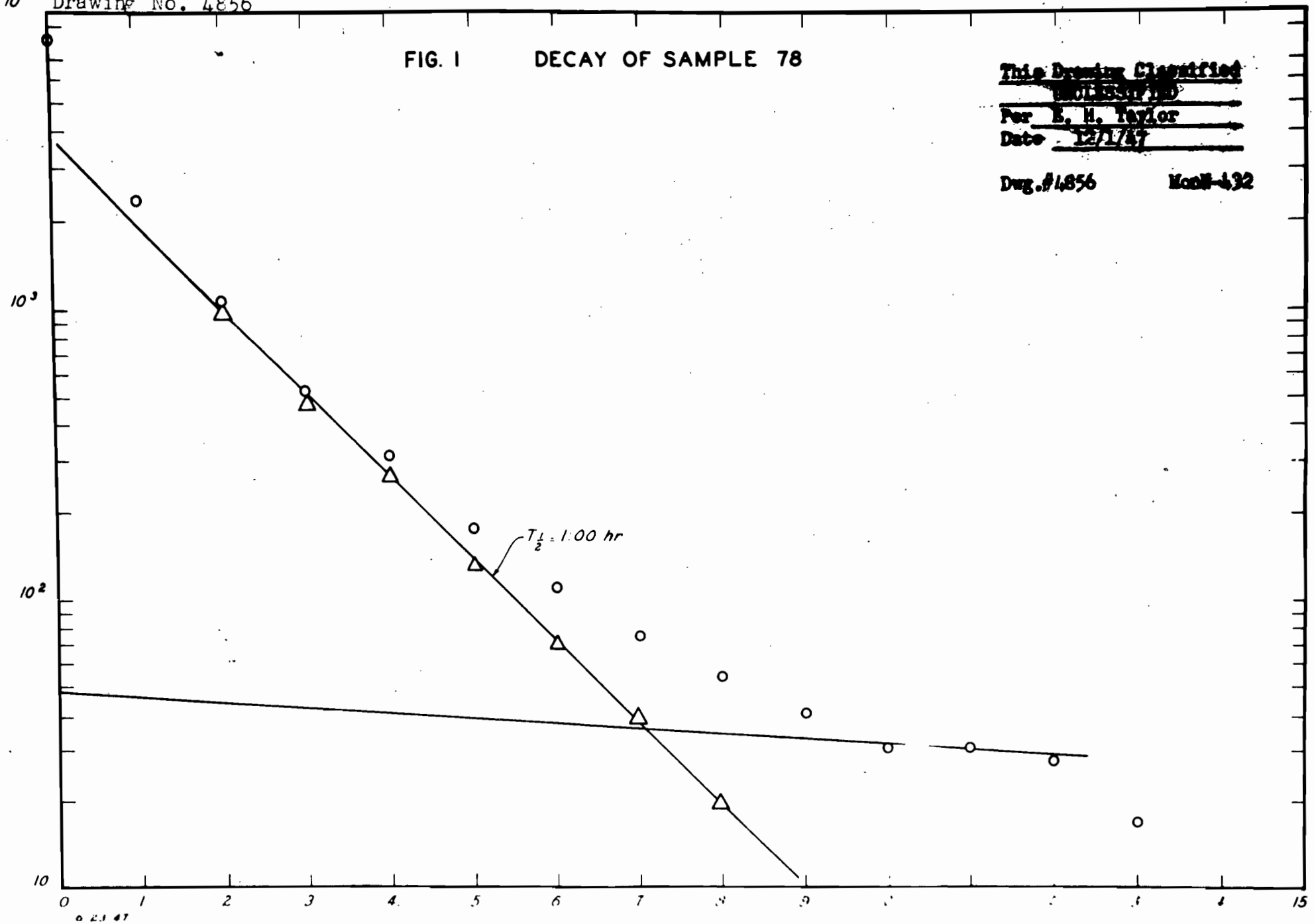
Drawing No. 4856

FIG. I DECAY OF SAMPLE 78



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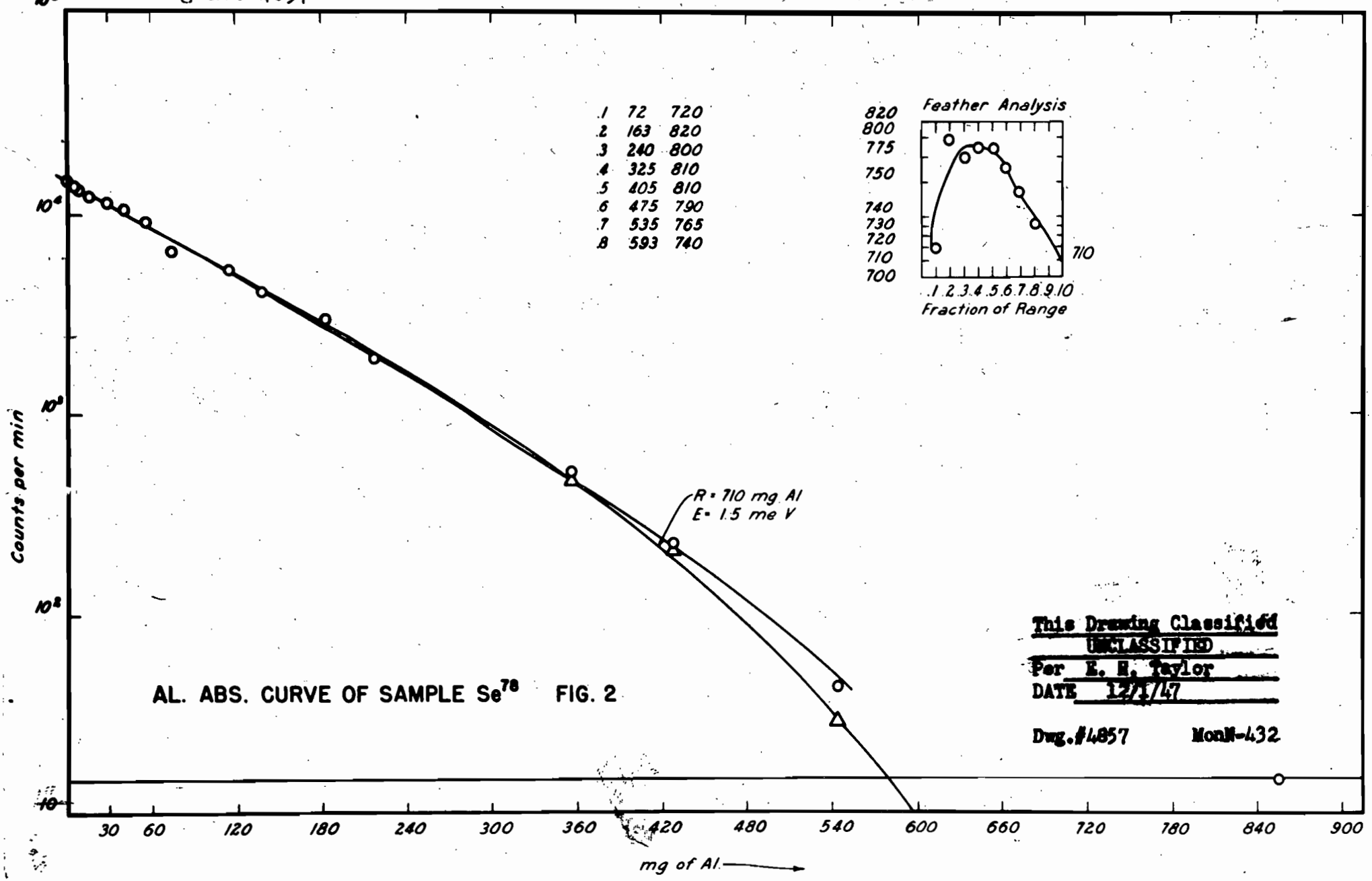

AL. ABS. CURVE OF SAMPLE Se^{78} FIG. 2

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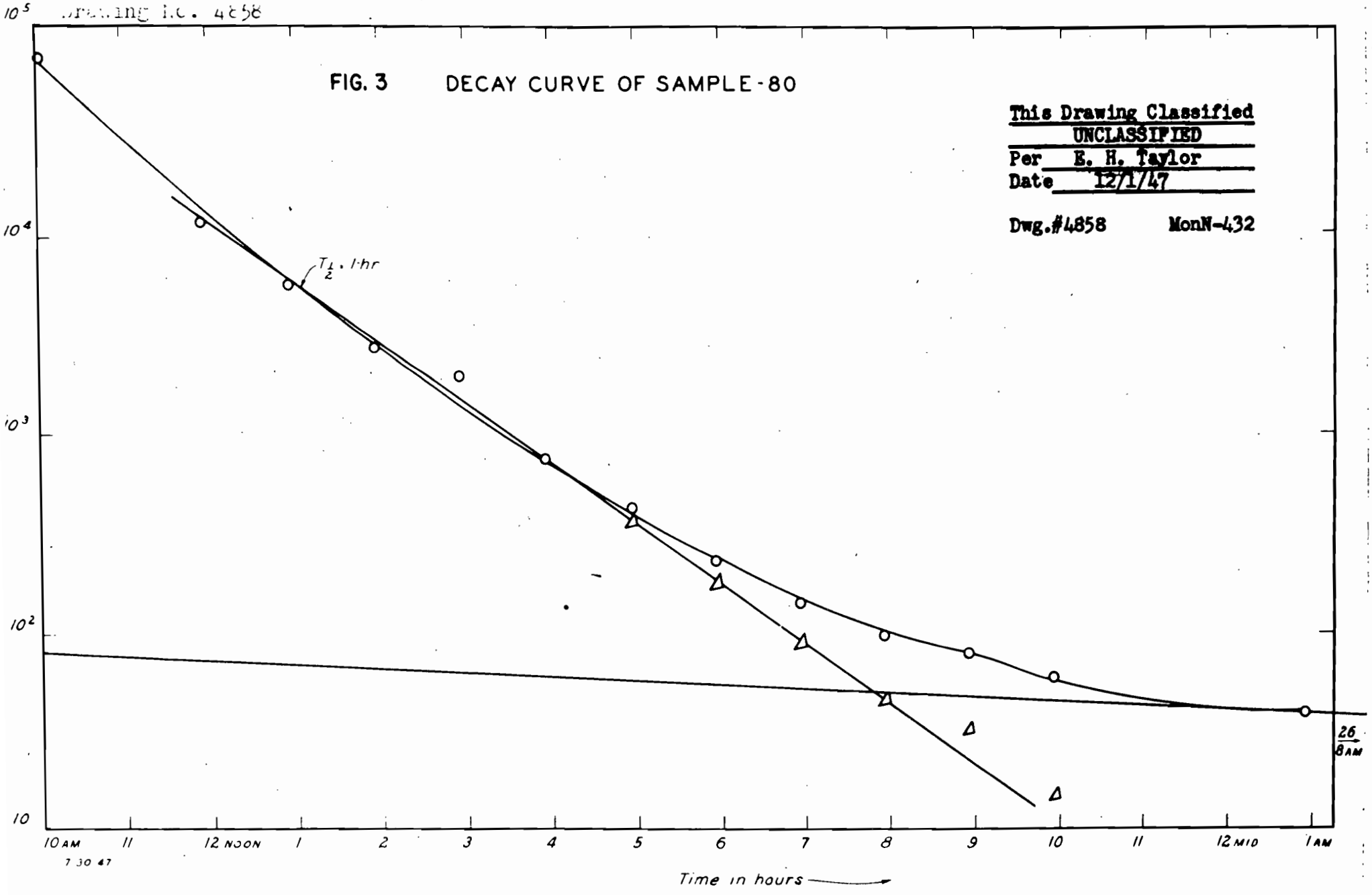
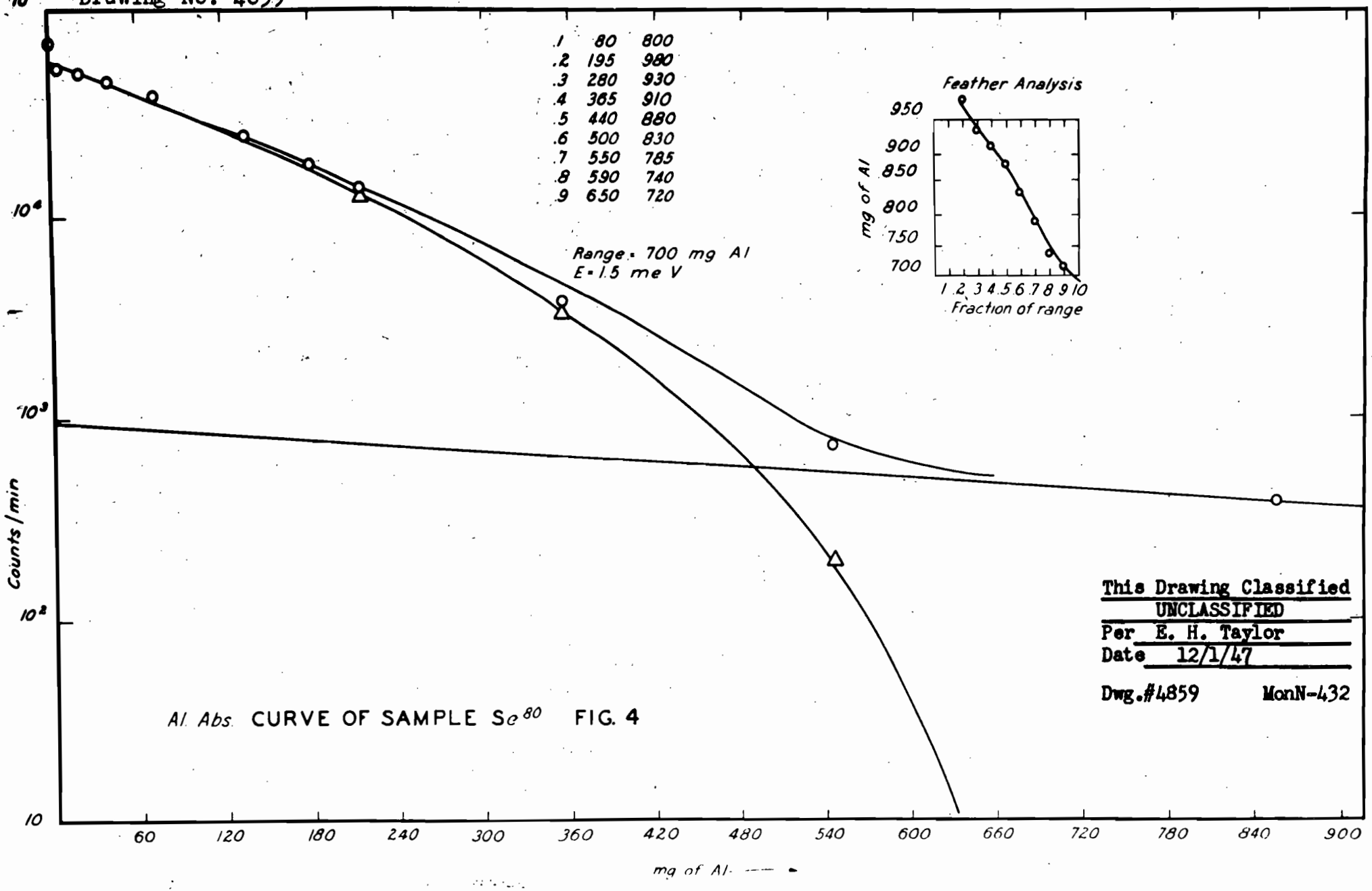


Drawing No. 4859



Al Abs. CURVE OF SAMPLE Se^{80} FIG. 4

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

I. Introduction:

Experimental work on the fundamental chemistry of ruthenium, initially reported in MonN-370, is being continued. In general, emphasis is now being placed upon a study of the higher valence states (VI, VII and VIII). Included in this work are the preparation of pure compounds and their identification and characterization by spectrophotometry.

II. Preparation and Characterization of Ruthenates and Perruthenates:

Considerable difficulty was encountered in the preparation of pure K_2RuO_4 and $K\ RuO_4$ according to the directions in the literature.[1,2] These salts contain water of crystallization and are very hygroscopic. Both are crystallized from a strongly alkaline media by evaporation under vacuo. In preliminary experiments pure salts were not obtained in either case. However, what appeared to be a pure ruthenate was obtained in the form of the barium salt, $Ba\ RuO_4$. This was prepared in the following manner. $RuCl_3$ was heated with dilute H_2SO_4 until the distillate no longer gave a test for chloride. $KMnO_4$ was added and the mixture heated on a water bath. The crystals of RuO_4 which distilled over were collected in an ice-cooled receiver. A saturated solution of $Ba\ (OH)_2$ was added to the tetroxide and a fine red crystalline precipitate of $Ba\ RuO_4$ was obtained. This precipitate was filtered, washed with distilled H_2O and dried over Drierite. Preliminary results from an X-ray diffraction determination indicated that the compound might be isomorphous with $Ba\ MoO_4$ or $BaWO_4$. The composition of $Ba\ RuO_4$ is being checked by a barium analysis and the density of the salt is being determined. Subsequent experiments indicated that it was unnecessary to eliminate chloride ion in the preparation of $Ba\ RuO_4$; $RuCl_3$ is oxidized directly with H_2SO_4 and $KMnO_4$. The RuO_4 formed, although containing some HCl, reacts readily to form the insoluble $Ba\ RuO_4$.

III. Spectrophotometric Data:

Previous work had shown the existence of an absorption peak for $RuO_4^{=}$ at 4650Å. The curve obtained for a 0.0002M solution of $RuO_4^{=}$ in 0.5M KOH is shown as Curve A on Figure I, which is a plot of optical density $\log\left(\frac{1}{\%\ \text{Transmission}}\right)$ versus wave length. A solution of pure RuO_4 in H_2O was prepared by the first method given above and its absorption spectrum was determined with a Beckmann spectrophotometer. The results are plotted as Curve B. Two absorption peaks in the near ultra-violet appear to be present for Ru(VIII), a primary (or higher) one at 3150Å and a secondary peak at 3850Å. Curve C was obtained for a solution of $Ba\ RuO_4$ in 0.05N HCl; the formation of this dark greenish-colored solution is ascribed to the formation of perruthenate, RuO_4^-, as a result of the following disproportionation:

$$RuO_4^{=} \xrightarrow{H^+} RuO_4^- + RuO_2\downarrow$$

The perruthenate ion is unstable and also disproportionates:

$$RuO_4^- \longrightarrow RuO_4\uparrow + RuO_2\downarrow$$

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The green color of the solution disappears with time at a rate which is accelerated by heating and black RuO_2 precipitates from solution. The tetroxide which is formed is easily identified by its characteristic ozone-like odor. These results will be further checked and extinction coefficients determined for $RuO_4^{=}$, RuO_4^{-} and RuO_4 solutions.

IV. Program:

Future work will include the determination of the reversibility of the $RuO_4^{=}$, RuO_4^{-} system (potentiometric titration) for setting up an E.M.F. cell to obtain thermodynamic data.

Other methods of preparing a pure perruthenate are being investigated.

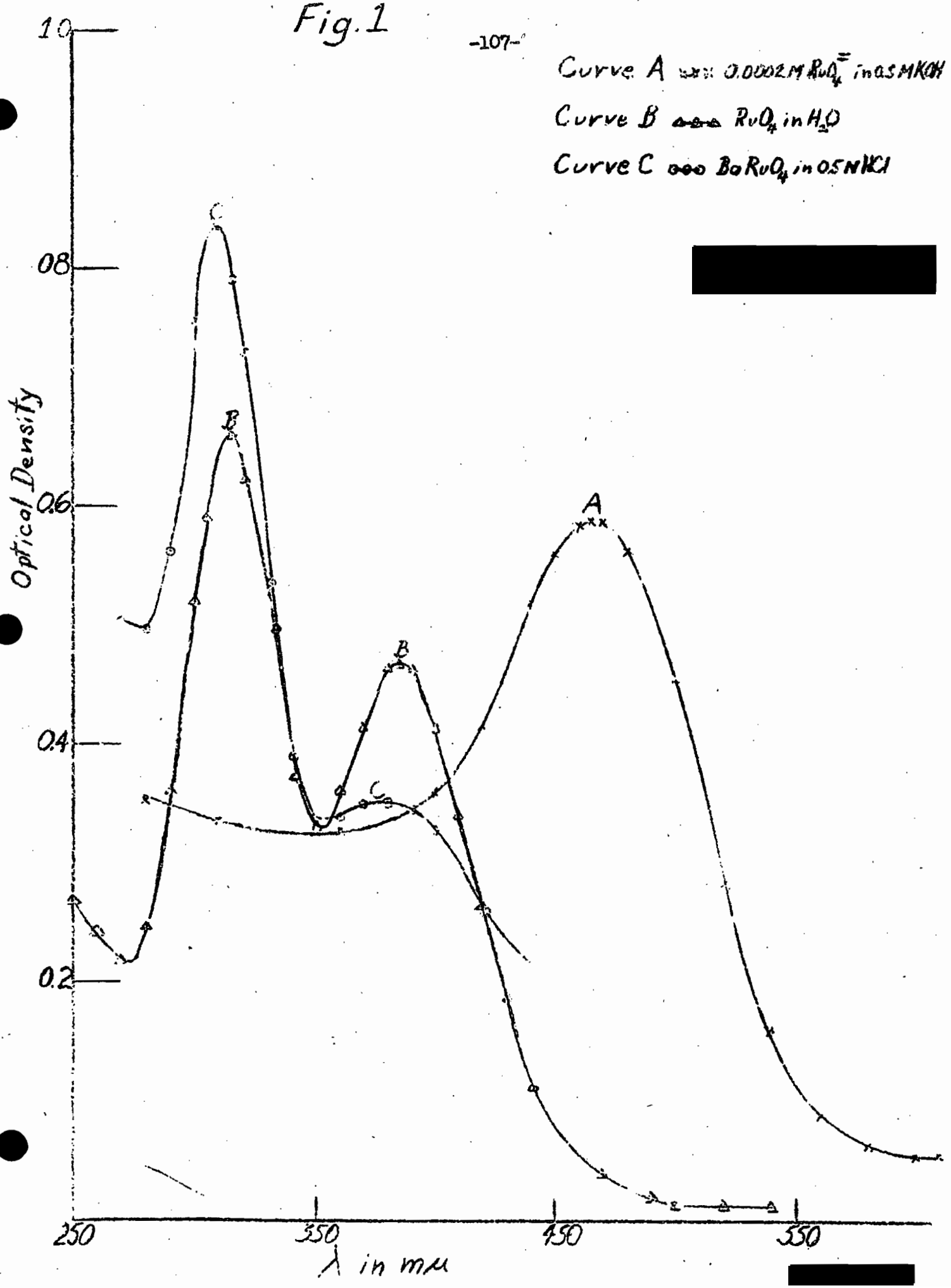
V. References.

1. Debray and Joly, "Compt. Rendu" 106, 1494 (1888).

2. Krauss. Z. Anorg. Chem. 132, 301 (1924).

[redacted]

Fig. 1



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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.

Decomposition of Pure Water Under Pile Radiation

Effect of state of aggregation of water and material of container. By repeated distillation in fused silica, water of specific conductivity 3×10^{-7} mho/cm was obtained. Specimens of this water in sealed fused silica ampoules were irradiated in Hole 12, as water at 23°C, and as ice at -60°C (ampoules packed in dry ice). After irradiation, the ampoules were opened and the water analyzed for dissolved gases and peroxide. The water ampoules were practically full of water, with negligible vapor space; the ice ampoules, about 2/3 full. Results are given in Table 1 in terms of micromoles of product per kilogram of water present.

Table 1

Decomposition of Pure Liquid Water and Ice
In Silica Ampoules Under Clinton Pile Radiation

State	Irradn. Time	Product Concentrations, μM			
		H_2	O_2	H_2O_2	CO_2
Ice	2 min.	8.8	1.1	6.4	0.5
	"	13.2	0.15	18.4	1.1
	30 min.	-	-	33.7	-
	1 hour	196.	75.	102.	1.7
	"	-	-	111.	-
Liquid	1 hour	24.2	5.1	19.6	0.8
	"	28.3	8.7	10.8	5.5
	22 hours	377.	145.	116.	5.
	"	333.	120.	152.	3.

The initial rate of decomposition of ice is less than for aqueous solutions (see previous quarterly reports) but the back reaction in ice is much less pronounced than in liquid water, so that much more decomposition is found in the ice after an hour's exposure.

Reproducibility and material balance are poor in all cases. Since the water is carefully purified, these bad effects are to be ascribed to the action of the material of the containing vessel. It is noteworthy that the effects are as bad in ice as in liquid water. Since radiation activation occurs throughout the material, and the active molecules or

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radicals cannot be supposed to migrate readily through the ice to reach the wall, the perturbing impurity must be distributed throughout the body of the water in the form of colloidal particles or motes. The photochemical decomposition of hydrogen peroxide in aqueous solution in glass vessels has been shown by several investigators to be greatly influenced by the presence of motes, which come out of the glass walls.

It was thought that silica ampoules might be replaced by aluminum containers, if the metal were suitably treated so that it would give little reaction with water. Tests were made in which rods of aluminum, treated in various ways, were sealed with water in silica ampoules. Three metal rods, 3/16" in diameter and about 2" long, were sealed with a few cc of water in each ampoule. Anodized Al yielded in 6 days only 3 micromoles of hydrogen per liter of water; Al boiled in distilled water gave 40-60 micromoles; Al treated with HNO_3 gave much more. (In Pyrex ampoules, more hydrogen was always evolved than in silica.) The corrosion resistance of either the anodized or boiled Al was thus fairly satisfactory. On irradiation, however, the aluminum was found to give considerably more radiation decomposition of water than occurred in its absence. Thus in 2 hours' irradiation, 597 and 947 μM hydrogen were formed in the presence of anodized Al, and 1130 and 1230 μM with boiled Al, together with comparable amounts of oxygen and peroxide. Al is, therefore, a worse surface than glass for study of radiation effects in water.

Other materials and surface treatments are being investigated.

Temperature effects. To determine the effect of temperature on the steady-state level of products in water decomposition, a small furnace was placed in Hole 12. Temperature of the furnace, measured by a thermocouple connected to a Brown recording controller, was maintained within 1° of any desired value. Water was irradiated in the furnace in ampoules of the "direct-reading" type, in which the pressure of gas over the water is determined without opening the ampoule, by means of a boiling-point measurement. The ampoule was kept at one temperature until a steady value of the pressure was reached, as shown by successive pressure readings giving little change; then the temperature was changed and held at the new value until a new steady-state pressure was attained.

The pressure history of the ampoules is shown in Figure 1. Ampoule "A" had been irradiated above the furnace at about 36°C, and had attained a pressure of about an atmosphere. On being placed in the furnace at 110°C, the pressure dropped to about 6 cm and remained constant, except for a continual rise of about 0.05 cm per day which was presumably due to ageing of the walls. Ampoule "B", introduced later than "A", attained a steady state at 2.6 cm. When the temperature was increased to 150°C, the pressure in "A" dropped to 4 cm and in "B" to 2.0 cm. Then the temperature was dropped to 42° and the pressure rose markedly, to 31.6 cm in "A" and 19 cm in "B". Although the pressures attained in the two ampoules are different as usual, owing to adventitious impurities, the temperature effect on the two was similar. Thus high temperature promotes the back reaction and reduces water decomposition by radiation. The result is of interest in connection with proposed use of high-pressure high-temperature water-moderated reactors for power production.

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Drawing No. 4823

This Drawing Classified
UNCLASSIFIED
Per A. O. Allen
Date 12/1/47

Dwg.#4823 MonM-432

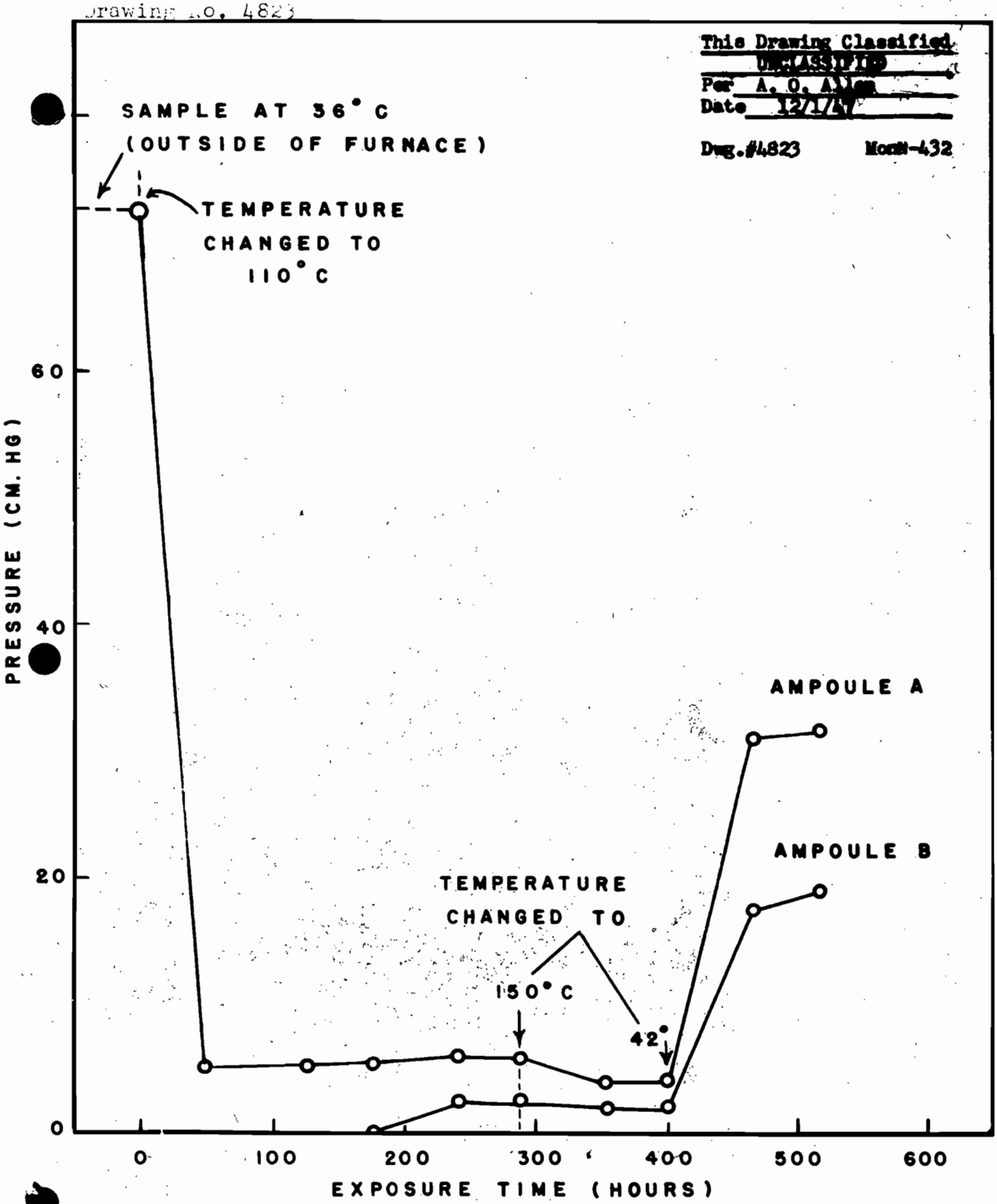

FIGURE 1. EFFECT OF TEMPERATURE ON WATER DECOMPOSITION BY PILE RADIATION

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An attempt was made to verify the temperature effect by exposing sealed ampoules, full of water, for various times at different temperatures, then determining the amount of decomposition by analysis. The results were inconclusive, because of the usual irreproducibility.

It could be argued that the increase in back-reaction rate at higher temperatures in the direct-reading ampoules was not occurring in the water at all, but rather in the gas phase. Such gas phase reactions are unlikely to be important, since the gas absorbs very little energy compared to the liquid. Moreover, the temperature coefficient of the H_2-O_2 reaction produced by alpha rays is not very great (Lind). However, a test of the rate of back reaction in the gas phase was thought desirable. Ampoules, connected to a manifold by narrow capillaries, were filled with electrolytic H_2-O_2 mixture, the capillaries were plugged with ice by freezing a small drop of water in each one, the manifold flushed with air, and the ampoules sealed off above the ice plug. The amount of water in each ampoule was so small that it completely vaporized at room temperature. Unfortunately, exact results were not obtained, since the initial pressure in any series of ampoules was not exactly the same (probably because the ice plugs were not quite tight). Of six ampoules, exposed in the pile for 20 or 56 hours at 110° or 150° C, five showed no significant drop in pressure; the sixth contained no gas, probably because of an accidental explosion. It may be fairly concluded that reaction in the gas phase is not an important factor in fixing the steady-state level in water decomposition.

Decomposition of Water in Solutions Under Pile Radiation

The existence of a real steady-state pressure over 1 N H_2SO_4 solutions was demonstrated by approaching the steady state from both sides. A number of ampoules, 90% full of 1 N H_2SO_4, had been kept for a long time in Hole 12 at "Position -3" (24" below the center plane of the pile). Some of these were opened and analyzed, and showed a partial pressure of 25 atm. of hydrogen. The remainder were put back in the pile for a week in the more active "Position -1" (6" below center) surrounded with 3/4" of lead, which by reducing the intensity of gamma radiation tends to raise steady-state pressures in the pile. Two of these ampoules were opened and analyzed, and showed hydrogen pressures of around 29 atm. The remaining ampoules were replaced in "Position -3" for two weeks, and on opening again showed hydrogen pressures of 25 atm. This is considerably lower than the pressure of 45 atm. which had previously been found on long exposures in Position -1, and which appeared to be still increasing. Since the previous measurements, the pile loading has been changed, and it may be that the character of the radiation has changed in the direction of leading to lower steady-state pressures.

A comprehensive study of the kinetics of reactions occurring in chloride solutions is planned. With sufficient solute present, reproducible results can be obtained, since the effects of the solute ions overwhelm those of the "motes" or other adventitious impurities. Chloride is chosen in preference to any other solute because its possible reactions are relatively simple, giving some hope of detailed interpretation of the reaction mechanism, and the water decomposition is not so sensitive to its

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presence as to the presence of bromide or iodide, so that reasonably high concentrations of chloride may be used without suppressing back-reaction entirely. Because of the pronounced effect of bromide, the chloride solutions must be as free as possible from bromide impurity. Some potassium chloride has been purified by repeated chlorination and recrystallization, and apparatus for deaerating the solutions and sealing them in an atmosphere of pure helium has been set up.

Monitoring the Radiations in Hole 12

Energy is imparted in two ways to material placed in a pile--absorption of gamma rays, and moderation of fast neutrons. To understand the chemical reactions occurring, it is essential to know how much energy is being given to the material in each of these ways. The theory of the pile does not give an exact account of either the gamma-ray intensity or the fast neutron spectrum at any particular point in the pile. It is, therefore, desirable to measure these quantities at the same point at which chemical experiments are conducted.

The total energy absorbed by a material can be measured calorimetrically. A measurement of this kind was mentioned in a previous report, but the result is not believed to be very reliable because of numerous possible sources of error. Calorimetry in the pile is difficult because not only the material of interest but also the calorimeter walls, thermocouples, etc., evolve heat at different rates, so that temperature gradients are all abnormal. Also, the calorimeter must be made entirely of materials which do not decompose badly under pile radiation. Considerable time is being spent on designing a calorimeter that will give reliable results on energy absorbed by different materials under pile radiation.

As a first step in examining the fast neutron picture, a comparison of the "fast flux" was made at the three positions in Hole 12 which had been used for exposure of H_2SO_4 solutions, and which had shown such different results in the amount of gas evolved by these solutions. Fast neutrons were measured by the S^{32} n,p P^{32} reaction. Identical samples of concentrated C.P. H_2SO_4 were irradiated simultaneously in the three positions, and the phosphorus activity was counted without separation. The irradiated acid was diluted with 9 volumes of water, and 15 λ aliquots of this solution were neutralized with NH_4OH and mounted for counting in a standard way. The chief extraneous activity present was S^{35}, a relatively weak β-emitter (0.107 Mev) which could readily be shielded from the counter by a 55.5-mg. Al absorber. Both S^{35} and P^{32} are pure β-emitters, and the absorption curve showed the virtual absence of any γ radiation in the samples, indicating the absence of impurity activities. Each sample was followed for one half-life (14.3 days) or longer, with counts being taken every 2-3 days, and the activity at the start was determined by the method of least squares. Any sample which showed a half-life differing from the true value more than allowed by the statistical counting error was discarded. The absolute counting rate was determined by comparison with Dr. Zumwalt's P^{32} standard. The absorption curves were found to agree exactly with those of the standard.

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Another sample of H_2SO_4 was exposed on another day, shielded by a 24-mil cadmium foil. Comparison of shielded and unshielded results should show if any large part of the activity arose from thermal neutron activation of phosphorus impurity in the H_2SO_4.

A thermal-neutron-flux determination for the entire length of Hole 12 has been obtained by Miss Arnette. Table 2 gives the results of the fast neutron monitoring in the three positions, with the ratios of the thermal fluxes at these positions included for comparison.

Table 2

"Fast flux" at Three Positions in Hole 12

Position (inches below center)	No. of samples counted	(Normalized to 100 Mw-hr, 1 mg. S, at time of removal from pile) Counts per min.	Dis. per min. at zero absorber	Active atoms	Ratio to activity at highest position "Fast Flux"	Thermal flux
6	4	10600[a]				
6	5	11300	2.19×10^5	6.52×10^9	100	100
16	3	11100	2.15×10^5	6.38×10^9	98.2	96.9
24	5	10900	2.11×10^5	6.27×10^9	96.5	93.1

(a) Cd shielded

The Cd-shielded sample gave a count only a few per cent less than the others, showing phosphorus impurities to be of small importance. The "fast flux", as measured by n,p on sulfur, is seen to vary little with position--less in fact than the thermal flux. This makes it harder than ever to explain the difference in behavior of H_2SO_4 solutions on long exposures in the three positions. It may be that the fast flux varied more as between these positions when the experiments were performed (last spring), and has since been evened out by changes in pile loading.

Decomposition of Water Containing Tritium

As mentioned in the previous report, the walls of the silica ampoules used for containing tritium water are permeable to helium, which is formed by decay of the tritium atoms present. As the tritium decays, the helium pressure builds up within the ampoule to a point at which the helium is diffusing out as fast as it is formed. The activity of the tritium within the ampoule can then be determined accurately by measuring the rate at which helium comes out. The rate can be determined by placing the ampoule in a system of soft glass, which is not permeable to helium, allowing the

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gas to accumulate for some time in this system, then transferring the gas to a system which contains a calcium getter for removing any contaminating gas and a Pirani or McLeod gauge for measuring the quantity of gas. Measurements of this kind have been made on two ampoules, and it was found that the rate of helium formation was constant after about two weeks in an ampoule containing tritium of the order of a curie. Only helium diffuses through the walls of the silica ampoules; the quantity of tritium coming out was undetectable in an ionization gauge, indicating the rate of escape of tritium to be less than 10^{-10} curie per day.

This is the most reliable method known at present for determining the activity of a sample of tritium. Measurement of the heat production from the same ampoule in Dr. Jenks' calorimeter will give an accurate measure of the average energy per disintegration for tritium. By combining this figure with the heat production from another sample, which will contain a known weight of tritium as determined by gas density measurement (Sweeton and Jenks) a value for the half-life of tritium can be obtained. An independent half-life value can also be obtained by noting over a period of many months the drop in the rate of helium production from a tritium water ampoule. This research should yield the most accurate values yet obtained for the radioactive disintegration constants of tritium.

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Adsorption (T. W. DeWitt)

The general outline of a research program on the removal of fission product rare gases has been proposed.

Adsorption seems to offer the best possibilities at the moment. This is particularly true since heats of physical adsorption may be as much as doubled over the usual values on such materials as charcoal, with consequent increases in adsorbent capacity of one to two orders of magnitude, by employing adsorbents with pores of molecular dimensions. Such materials exist naturally and might be made artificially.

Further consideration of data on adsorption on materials of very fine pore size, leads to the conclusion that they might be used as molecular sieves, permitting the passage of small carrier gas molecules and screening out larger molecules such as Kr, Xe, I_2 and Br_2. Continuous and effective removal of the radioactive rare gases and halogens might thus be achieved rather simply. While the production of suitable membranes for such an operation might pose some difficult problems, materials with such properties do exist and their preparation with suitable properties cannot be considered hopeless. The comparative simplicity and effectiveness of such a removal should justify considerable research effort devoted to its study.

The proposed program envisages three simultaneous lines of attack: (1) a study of the adsorption equilibrium and kinetics on materials of fine pore size, (2) study of the diffusion of gases through membranes with pores of molecular dimensions and, (3) a study of the preparation and properties of materials with pore sizes of molecular dimensions both for adsorbents and diffusion membranes. A sample of the natural zeolite chabazite has been obtained through the courtesy of Dr. P. H. Emmett. This material when dehydrated has pores of the order of 5 Å in diameter. It will be used in exploratory adsorption studies with krypton and xenon.

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A Comparison of Methods of Estimating Surface Areas of Crystalline Solids by Gas Adsorption (S. Ross)

A previous report[1] gave the adsorption isotherms of ethane at -183° C on cube crystals of NaCl and KCl. The results obtained were there interpreted as indicative of a two-dimensional phase transition of ethane. The nature of these isotherms makes it possible to compare some of the methods that have been proposed for estimating the surface area of crystalline solids by means of gas adsorption.

The following table gives the results of these comparisons. The values used for the incompressible area per molecule for the gaseous and condensed phases on NaCl and the condensed phase on KCl were obtained from the crystallographic unit cells of these substances. It is postulated that the ethane molecules would be at sites of maximum adsorption energy on the surface lattice and that the condensed phase is represented by a configuration of less entropy than the gaseous phase. From these conditions it is possible to visualize models for the phases and derive therefrom the incompressible area per molecule, as given in the table.

Comparison of Surface Areas Obtained by Methods Proposed by Various Authors from the Vapor Adsorption Isotherms of NaCl and KCl Crystals at -183° C

Author	Portion of Isotherm Used: Description	Lower limit of p/p_0	Upper Limit of p/p_0	Monolayer Capacity in cc-mm/gm at 0°C	Incompressible Area per Molecule in $Å^2$	Specific Surface in cm^2/gm
#1 - Cube Crystals of NaCl						
Gregg[2]	Gaseous Phase	0.007	0.027	20.0	31.7	2250
Gregg[2]	Condensed Phase	0.07	0.165	43.5	15.8	2433
BET[3]	Condensed Phase and Multilayers	0.06	0.22	27.8	23.0	2260
Harkins and Jura[4]	Multilayers	0.11	0.77	----	----	2350
#2 - Cube Crystals of KCl						
Gregg[2]	Condensed Phase	0.04	0.11	49.0	19.7	3416
BET[3]	Condensed Phase and Multilayers	0.04	0.14	42.2	23.0	3430
Harkins and Jura[4]	Multilayers	0.08	0.38	----	----	3930

(1) S. Ross, Mon N-311, pp. 99-103
(2) S. J. Gregg, J. Chem. Soc., (1942), 696
(3) S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 60, 309 (1938)
(4) W. D. Harkins and G. Jura, J. Chem. Phys., 11, 431 (1943); Idem, J. Am. Chem. Soc., 66, 1366 (1944)

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A detailed account of the methods of calculation and a discussion of the significance of the results is in progress of preparation as a report from the Chemistry Division.

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

Cloud Chamber Operation

A large number of cloud chamber pictures were made with a 5.4 curie polonium beryllium source. In a rapid study of the pictures, only two fission tracks were found.

In order to get a higher neutron flux, the decision was made to move the chamber to the pile.

A number of pictures were taken of uranium alphas in order to improve the chamber operation. Tetrachloro-β-butane gave good results for the first few days of operation, and it will probably be used in the first work at the pile. A moderate supply is available.

Arrangements have been made with K-25 to obtain a supply of 816-Cl_2. This material may be used for later work.

Pile Facilities

The installation of equipment at the pile is essentially complete. A collimated neutron beam, about 1/4 inch x 2½ inches is taken from the pile and the chamber so positioned that the beam enters one of the slit shape windows. A barricade in back of the chamber stops the beam. Provisions have been made to later install a thermal neutron beam shutter so that the chamber will be in a thermal neutron flux only at the time of expansion. The control circuits, lights, etc. have also been installed. The radiation background with the chamber in place and beam on gives about four hours working time near the chamber.

The chamber has been cleaned out and is now being refilled. The twin lens stereo-camera has been completed, and the mirror system for use with it is nearing completion.

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

I. Measurement of the Average Energy of the Betas from Tritium Decay

For this determination, samples of tritium already available at this laboratory will be measured in the β-calorimeter after purification and analysis for the protium-tritium ratio.

It is planned to purify the gas sample by passing it through palladium and to handle the purified gas in a system in which it will come into contact with only glass and mercury. The protium-tritium ratio will be measured by determining the density of the sample with a gas density balance.

At the present time, most of the components of the glass system have been constructed and are ready for assembly. Electrical controls for two automatic Topler pumps have been assembled and the mercury for the system purified. A gas density balance made entirely of quartz except for the fulcrum which consists of two tungsten tips cemented to the beam with silver chloride has been constructed. Preliminary test of the balance show it to be sensitive to about 0.1 μg which is sufficient for this work.

II. Modifications of Calorimeter

The reproducibility of gas evolution rates with the β-calorimeter described in report MonC-410 became fairly erratic recently. The cause of this trouble was traced to a partial loss of vacuum in the calorimeter head shown in Fig. I of that report. A new head was built with some modifications which caused the tube connecting the calorimeter with the pressure system to be cooled in the outer bath. Satisfactory sensitivity of the calorimeter has resulted.

The calorimeter Dewar shown in the drawing mentioned above had a neck with an internal diameter of 6.5 mm. and samples were limited to that diameter. In order to carry out some measurements on gold which were planned, it was necessary to use samples of larger diameter than 6.5 mm. and a new calorimeter Dewar was required. The new calorimeter was built exactly like the old one except that a larger tube (9.0 mm. I.D.) was used for the neck. A ground glass adapter was made so that the new calorimeter could be fitted to the existing calorimeter head. The adapter increased the length of the joint by 7 mm. Calibration of this larger calorimeter has shown it to have the same background heat evolution and sensitivity as the smaller one.

III. Search for a 65 Kev Gamma in the Decay of Au^{198}

A 65 Kev γ in cascade with the 0.412 γ in the decay of Au^{198} has been reported by Feather and Dainty[1]. If a gamma of this energy does occur in a majority of the disintegrations, it should be possible to

(1) N. Feather and J. Dainty - Proc. Cambr. Phil. Soc. 40, 57 (1944)

detect its presence with the β-calorimeter by using an absorber which selectively absorbs the gamma in question.

Procedure

Approximately 15 mg. of gold foil (10 mg/cm^2) were encased in one mil. aluminum foil and rolled into a cylinder of about 2 mm. diameter and 2 cm. long. After irradiation, this sample was placed in a graphite cylinder with the following dimensions: 7.5 mm. O.D., 3.5 mm. I.D., 2 cm. in length. This sample was then placed in the large calorimeter Dewar described above and the absorbed energy measured(2). Following this measurement, the calorimeter was disassembled and the graphite, including the ends, was covered with a 0.147 g/cm^2 silver absorber and the energy again measured. The results of four repeated energy determinations are shown in the table.

Table I

Run No.	Absorber	Time, Hours (Middle of run)	Rate (Arbitrary units)	Watts x 10^4 (At time of measurement)	Watts x 10^4 (Zero time)
1	Calorimeter	3.1	0.972	1.83	1.90
2	Calorimeter	4.4	0.955	1.80	1.86
3	Calorimeter + 0.147 g/cm^2 Ag	23.8	0.789	1.47	1.90
4	Calorimeter + 0.147 g/cm^2 Ag	25.6	0.778	1.45	1.90
5	Calorimeter + 0.147 g/cm^2 Ag	27.3	0.761	1.41	1.90
6	Calorimeter	51.2	0.617	1.13	1.96
7	Calorimeter	53.4	0.605	1.11	1.96
8	Calorimeter + 0.147 g/cm^2 Ag	72.6	0.490	0.882	1.88
9	Calorimeter + 0.147 g/cm^2 Ag	75.3	0.477	0.857	1.92

Discussion

Since the disintegration rate for this sample has not yet been determined, the energy absorbed per disintegration is not known. However, using the mass absorption coefficients for the components of the calorimeter and for silver, it was calculated that when the silver absorber is added, the measured energy should increase by approximately 2% due to increased absorption of the high energy gammas. If a gamma of about 60 Kev, energy occurs in every disintegration, the absorbed energy should increase by about 8%. The last column of the table of data shows that within $\pm$ 2% no increase in the absorbed energy occurred when the silver was added.

(2) For details of the measurement, see report MonC-410

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

Absorption spectra of crystalline $AmCl_3$ kindly furnished us by Sherman Fried of the Argonne National Laboratory were taken on a grating in Wadsworth mounting having a dispersion of 5A/mm. in the first order. (The quantity of the material available was several micrograms.)

The spectrum consisted for the most part of sharp lines even at room temperature, comparing very favorably with the sharpest of rare earth spectra. The lines varying from about 1A to 5A wide were at 3160, 3350, 3380, 3640, 3670, 3770, 3780, 3800, 4400, 4570 and 4630A. In addition there is a doublet at 4050A and regions of absorption at 4250A and 5090A whose structures have not as yet been resolved.

Preliminary observations at the temperature of liquid nitrogen indicate a partial resolution of the absorption at 5090A with a line at 5120A appearing above the background.

Our results may be accepted as excellent verification of analogies drawn between the electronic structures of the ions of the heavy elements and those of the rare earths. In fact the analogies, in the light of these sharp spectra, extend not only to the electronic configurations of the ions in their basic states but also to the configurations of the excited electronic states.

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Polarography of Ions Encountered in Pile Process Solutions (H. H. Miller, L. B. Rogers)

The applicability of the stationary platinum electrode for semi-quantitative work in polarography has been investigated with several ions. The ions investigated were those which might be found as major constituents or impurities in pile process solutions. Because various anions might be present in such solutions it was desirable to study the half-wave potentials in different background media. The backgrounds selected were 0.10 M HF, HNO_3, H_2SO_4 and HCl.

The polarographic technique was that described in MonC-236. The solid electrode was a bright platinum wire, 1 mm. long and 0.5 mm. diameter, sealed in a glass tube.

The half-wave potentials are listed in the following table. A comparison of the potentials for different ions in a given medium indicates that in most cases the waves would not be separated sufficiently to allow a mixture of these ions to be analyzed.

Half-Wave Potentials
(In 0.1 M Backgrounds)

1.00×10^{-3} M Solution	HF	HCl	H_2SO_4	HNO_3
K_2CrO_4	+0.42	+0.448 +0.113	+0.428 -0.156	*
$CuCl_2 \cdot 2H_2O$	+0.45 -0.02	+0.126 -0.176	+0.095	-0.081
$FeCl_3 \cdot 6H_2O$	No wave	+0.507	*	*
$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 2H_2O$	*	*	+0.421	*
N_2H_4 ($N_2H_5^+$)	+0.457	+0.337	+0.382	+0.324
UO_2Cl_2	No wave	No wave	No wave	No wave

*Not analyzed.

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Electrolytic-Polarographic Studies of Silver and Palladium Complexes (J. C. Griess, L. B. Rogers)

Polarographic Experiments

Since the last report, it has become necessary to obtain more accurate values of the half-wave potentials of silver and palladium in various complexing media. The values previously reported were obtained with an automatic recording polarograph but were not checked with a potentiometer as were those reported below. The half-wave potentials of silver in various concentrations of sodium hydroxide and sodium cyanide were determined in a similar manner.

An attempt was made to examine the reversibility of silver and palladium reactions by means of the polarograph and stationary electrodes. The procedure consisted of plating a micro platinum electrode with a thin coating of the desired metal. The electrode was then placed in a given background solution and a polarogram recorded with the direction of polarization reversed from that used in obtaining a normal curve. Whenever the reaction was readily reversible the dissolution wave began at a potential more positive than that of the reduction half-wave.

The value of the dissolution potential listed in the table below was that where the first indication of a wave appeared on the polarogram. While this manner of choosing a dissolution potential is arbitrary, the values obtained are suitable for the purpose of comparison. It can be seen from the following table that reactions involving silver are readily reversible whereas the palladium reactions are irreversible with the exception of the one in cyanide solution. Since the silver reactions are reversible, it is possible to calculate formal potentials, (E_f^o) from the half-wave values of silver (1) which agree within about 0.1 V. of the E^o values reported by Latimer (2). In the case of palladium it would be difficult, if not impossible, to calculate the E^o's.

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Polarographic Half-Wave and Dissolution Potentials Using a Micro Platinum Electrode and Millimolar Solutions of Silver and Palladium (II) in Several Complexing Media

Background Solution	Ag $E_{\frac{1}{2}}$	Ag Dissolution Pot.	Pd $E_{\frac{1}{2}}$	Pd Dissolution Pot.
0.1 M $Na_2S_2O_3$	-0.41	-0.45	>-0.7*	+0.07
0.3 M KCNS	-0.22	-0.23	-0.43	+0.25
0.1 M NH_4OH	-0.02	-0.01	-0.50	+0.39
0.1 M NaCN	-0.84	-0.89	>-0.8*	-0.71
0.05 M NaCN 0.0 M NaOH	-0.85	-0.92	>-1.2*	-0.90
0.1 M NaCN 1.0 M NaOH	-0.79	-0.76	>-1.3*	-0.85
0.5 M NaCN 1.0 M NaOH	-1.03	-0.87	>-1.1*	-0.88

All potentials were measured against a saturated calomel electrode and were obtained using millimolar concentrations of metal ions and a micro platinum electrode.
*Hydrogen evolved at this potential.

(1) See "onC-236 and Kolthoff and Lingane's "Polarography" for more details concerning this type of calculation.
(2) Latimer, W.M., "Oxidation Potentials", Prentice Hall, New York (1938).

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Electrolytic Data

In order to check the validity of the data obtained polarographically concerning the reversibility of the reaction $Pd^{o} \rightleftharpoons Pd^{+2} + 2e$, cathodes containing palladium activity were electrolyzed at potentials above and below the dissolution potential to see if any palladium was removed during the electrolysis. These electrolytic studies at potentials near the dissolution wave are analagous to studies near the polarographic reduction wave which were reported previously. The procedure was as follows: Four millimolar palladium tracer solutions were prepared, each one containing one of the following as supporting electrolyte: 0.1 M NaCN; 0.1 M NH_4OH; 0.3 M KCNS; 0.1 M $Na_2S_2O_3$. Two aliquots from each solution were electrolyzed (3) for a period of time long enough to plate a measurable amount of palladium on the cathodes. The cathodes were removed, counted, and then reinserted in their respective cells. The electrolyte from which the cathode was originally plated was returned to each cell. One cathode was electrolyzed at about 0.1 V. more positive than the polarographic dissolution potential and the other about 0.1 V. more negative than the dissolution potential. At the completion of a three hour electrolysis, the cathodes were removed and counted.

The results below indicate that the electrolytic behavior in the neighborhood of the dissolution wave is characteristic of that for a reversible reaction, i.e. plating occurs at potentials more negative than the dissolution potential and dissolution at more positive potentials.

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Checks of the Polarographic Dissolution Potential by Removal of Activity from Cathodes.

Background Solution	Dissolution Potential*	c/m on Cathode before Elect.	Cathode pot.* during Elect.	c/m on Cathode after Elect.
0.3 M KCNS	+0.25	7,020	+0.100	16,900
		31,000	+0.380	11,700
0.1 M $Na_2S_2O_3$	+0.07	7,100	+0.200	3,490
		4,140	-0.100	7,290
0.1 M NH_4OH	+0.39	34,500	+0.200	40,200
		35,000	+0.530	24,500
1.0 M NaOH 0.1 M NaCN	-0.85	3,310	-1.150	11,300
		26,900	-0.700	6,200

*All potentials measured against a saturated calomel electrode.

Determination of Separation Factors

The value of a separation factor has been found to depend very heavily upon the amount of silver that can be plated out. In the last report (4) the rapid and extensive dissolving action of the cyanide ion on thin silver films was mentioned. Therefore, to retain traces of silver on an electrode, it is necessary to remove the cyanide solution from the cell before breaking the circuit. Previously this was carried out by removing the cyanide with suction and, at the same time, adding water to wash the cell. Recently it has been found that even this procedure

(3) The electrolyzing vessel was a cell of the type described by D. B. Ehrlinger, MonN-311, p. 198.

(4) MonN-370, p. 160-163

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allows some dissolution to take place. It is possible to avoid this difficulty, however, if instead of water a solution of an electrolyte is used in which the $E\frac{1}{2}$ of silver is more positive. Many electrolytes were found to be effective. 0.1 M KCl is convenient to use and it has made possible the complete recovery of silver from solutions as dilute as 10^{-13} M.

Separation factors, believed to be more accurate than those given in the last report, have been obtained for the separation of carrier-free Ag^{111} from palladium in thiocyanate, thiosulfate and ammonia media; to date the redetermination of separation factors from a cyanide solution has not been undertaken. The values listed in the table below are felt to be of greater accuracy because: 1) The actual number of Ag^{111} and Pd^{109} atoms as determined experimentally in our laboratory have been used in calculating the separation factors. The previous results were based on theoretical calculations only. 2) New voltage regulators capable of controlling the cathode potential to ± 1 mv. have been obtained. 3) The improved technique described in the preceding paragraph was used for washing the cathodes, thereby minimizing losses of the deposit.

The procedure used in the preparation of the sample and in the electrolysis was the same as that described in the last quarterly report (4). The results listed in the table below are for an electrolysis time of thirty minutes and a solution volume of twenty milliliters.

Separation of Trace Amounts of Silver from Macro Amounts of Palladium Using Thiocyanate, Ammonia, and Thiosulfate Solutions.

Supporting Electrolyte	Cathode* Potential	% Ag Plated	% Pd Plated	Separation Factor
0.3 M KCNS	-0.100	16.0	0.069	230
	-0.220	27.4	0.15	180
	-0.350	43.6	0.80	50
0.1 M NH_4OH	+0.150	8.4	0.008	950
	0.000	15.0	0.007	2000**
	-0.025	29.3	0.006	5400**
	-0.350	47.4	0.14	350
0.1 M $Na_2S_2O_3$	-0.250	4.3	0.016	260
	-0.410	11.7	0.018	660
	-0.500	21.9	0.086	250

*All potentials measured against a saturated calomel electrode.
**This value is being checked.

Multiple Electrolyses

It has been found that pure Ag^{111} activity can be obtained by carrying out multiple electrolyses. Following the first electrolysis, the cathode deposit was dissolved in a fresh background solution and then reelectrolyzed.

Because palladium was plated reversibly only from a cyanide solution, it was necessary to use a cyanide solution in all cases.

The solution was prepared as follows: A 10 mg. sample of palladium was irradiated in the pile for a given period. Upon removal from the pile, the sample was dissolved in a minimum of sulfuric and nitric acids. The excess acid was neutralized and sufficient sodium hydroxide and sodium cyanide added to make the solution 1.0 M in sodium hydroxide and 0.1 M in sodium cyanide when diluted to 100 ml; the palladium and silver concentrations were approximately 10^{-3} M and 10^{-11} M respectively.

A 20 ml. aliquot of the solution was electrolyzed for three hours at a cathode potential of -1.200 V. vs. S.C.E. Then the electrolyte was replaced by 20 ml. of a 1.0 M NaOH - 0.1 M NaCN solution, and the polarity of the cell reversed for thirty minutes in order to remove both the palladium and the silver from the cathode. The cathode potential was readjusted to -1.200 V. vs. S.C.E. for three hours at the end of which time the cathode was removed and a decay curve plotted. In all cases the decay curves have indicated a pure Ag^{111} activity. To date a yield of 73% of the total Ag^{111} has been realized; with an improved technique it should be possible to increase this yield to 90%.

Studies are now in progress to determine electrolytic reduction waves for silver from a cyanide solution where the silver concentrations are either above or below those necessary to give a completely covered cathode. In addition, studies of the rate of deposition are being made from similar solutions.

The Electrodeposition Behavior of Traces of Silver (D. P. Krause, L. B. Rogers)

An attempt was made to duplicate the work of Ehrlinger, published in previous quarterly reports, on the electrolysis of nitrate solutions containing trace amounts of silver. Improved techniques were introduced for: 1) Preparation of active silver solutions of known concentrations and; 2) Washing of the cathode at the end of the electrolysis.

Carrier-free silver was prepared by the multiple-electrolysis method of Griess. (See the preceding section in this report by Griess for the method and the quantitative data regarding the separation of palladium and silver). Cathodes from the multiple electrolysis, having essentially pure silver activity, were stripped into a 0.1 M KNO_3 solution containing a known amount of dead silver. The amount of silver added from the stripping was insufficient to alter the concentration in the range in which the work was carried out.

The data on electrolysis of a 5.0×10^{-4} M Ag^{+} solution indicated that deposited silver was being physically removed from the cathode when washing of the cathode was carried out by the procedure followed by Ehrlinger. Therefore, a different technique was adopted in which the bulk of the electrolyte was removed by suction to the point where the anode and probe were just under the surface of the solution. Then the potential on the cathode was changed to a much more negative value and the cell was flooded with a stream of water. The water was removed by suction at the same rate as it was added. Electrical contact was broken by sucking the cell dry only after the washing had been completed.

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Experimental Details

500 ml. of a 10^{-3} M Ag^{+} solution was prepared by weighing 0.0849 grams of Merck Silver Nitrate (C.P. crystals) and dissolving it in 0.1 M KNO_3 solution. A portion of this was used to strip silver activity from a platinum cathode prepared by multiple electrolysis.

The pH was adjusted to 4 with dilute HNO_3 and KOH. Before the solution was used, it was observed that turbidity developed in the final solution, and on standing overnight a visible precipitate appeared. The solution was filtered and the filtrate used in all electrolyses. Nephelometric analysis of the filtered solution by D. LaValle gave the concentration as 5.0×10^{-4} M in Ag^{+}. This indicates that one half of the Ag^{+} present had been removed by precipitation with Cl^{-} present as an impurity in the KNO_3 and the distilled water.

Controlled cathode electrolyses were carried out on 25 ml. aliquots of the 5.0×10^{-4} M solution at potentials between +.500 V. and -.200 V. (vs. S.C.E.) Duplicate five hour electrolyses were run in each case. The next table is a summary of data obtained. A plot of the ratio $\frac{Ac}{Ao}$ versus potential indicates that the $E_{50\%}$ for the 5×10^{-4} M solution is approximately +.35 V. The plot of $\frac{A_o - A_s}{A_o}$ versus potential gives a value of -.35 V. for $E_{50\%}$.

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The Percentage of Silver Deposited on a Silver Electrode From a 5.0×10^{-4} M Solution as a Function of Electrode Potential.

	Potential (vs. SCE)	Percent on Cathode After Wash $\frac{A_c}{A_o} \times 100$	Percent Plated $\frac{A_o - A_x}{A_o} \times 100$	Material Balance $\frac{A_t}{A_o} \times 100$
1	+.500	.64	6.5	94
2	+.500	.49	13	87
3	+.400	4.4	14	91
4	+.400	.67	10	91
5	+.350	33	44	90
6	+.350	39	46	97
7	+.300	81	93	87
8	+.300	68	95	73
9*	+.300	85	95	91
10	+.250	76	99	78
11	+.250	77	100	77
12*	+.250	82	98	94
13*	+.200	59	82	113
14*	+.200	45	100	100

A_c = Activity of cathode.
A_s = Activity of solution after plating.
A_t = Total activity (cathode plus solution after plating).
A_o = Activity of original solution 5.06×10^5 c/m.

*On these runs the activity of the wash water was measured and included in A_t. If it is assumed that the activity in the wash is from material that had been deposited on the cathode and then physically removed during the washing process, the material balances are as follows: Run #9 - 85%; Run #12 - 92%; Run #13 - 95%; Run #14 - 100%. In these experiments, 100 ± 10% is considered satisfactory.

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A 10^{-5} M Ag solution was prepared in a manner similar to that used for the 5 x 10^{-4} M solution except that 5 ml. of a stock 10^{-3} M solution was diluted to 500 ml. with 0.1 M KNO_3. The pH was again adjusted to 4. No turbidity or precipitation was observed. The solution was stored in a brown bottle to eliminate the possibility of decomposition. Controlled cathode electrolyses were carried out in duplicate for five hour periods on 25 ml. aliquots of the solution. The potential range was from +.500 V. to +.150 V.

In all cases the improved washing technique was used. 125 ml. of distilled water were used for washing. The wash was diluted to 250 ml. and 1000 λ of this evaporated to dryness for counting. A table summarizes the data obtained. The plot of A_c versus potential gives the value +.22 for E50%.

$\overline{A_o}$

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The Percentage of Silver Deposited on a Silver Electrode from a 1.0 x 10^{-5} M Silver Solution As a Function of Electrode Potential.

Potential (vs. SCE)	Percent on Cathode After Wash $\frac{A_c}{A_o}$ x 100	Percent Plated* $\frac{A_o - A_w}{A_o}$ x 100	Material Balance $\frac{A_t}{A_o}$ x 100
-.503	2.6	28	75
-.500	4.4	28	77
-.401	5.7	16	90
-.402	4.4	12	93
-.358	5.7	13	93
-.352	3.6	12	92
-.298	6.8	18	88
-.300	8.0	27	81
-.298	7.2	24	84
-.246	12.5	26	86
-.248	9.4	26	83
-.251	7.2	24	84
-.225	38	50	87
-.223	62	61	101
-.220	60	66	94
-.200	87	86	101
-.200	83	84	98
-.150	97	100	97
-.150	99	100	99

A_o = 2.68 x 10^5 c/m.
*Calculated from the amount of activity found in the wash solution (A_w).

The shift in $E_{50\%}$ between the concentration 5 x 10^{-4} M and 10^{-5} M is in agreement with that predicted by the abbreviated form of the Nernst equation. The calculation shift is .10 V. whereas the observed shift is .12 V.

Ehrlinger did not observe any shift in $E_{50\%}$ values between 10^{-4} and 10^{-5} M solutions. However, his data in the critical region of $E_{50\%}$ is too sparse to allow a definite conclusion to be made. Furthermore, his method for the preparation of the standard active solutions was such that there is a possibility that the concentrations he reported were in error.

Work will be continued along the same lines at decreasing concentrations of Ag^+ ion (10^{-7}, 10^{-9}, 10^{-11}) to check the observation made by Ehrlinger that at concentrations less than that at which a monolayer is deposited on the cathode a positive shift in $E_{50\%}$ is obtained.

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Adaptation of the Hanford-Type Liquid-Liquid Continuous Extraction to the Solvent Extraction of Uranium with Diethyl Ether (W. Davenport, W. Byerly)

Small amounts of uranium must be determined in the samples of the U^{235} recovery process (1). These samples will be radioactive and it would be advantageous to separate the uranium from the interfering ions and from the major portion of the radioactivity. Solvent extraction offers a means of separation and decontamination. On highly radioactive solutions it is necessary to work with small samples at a distance in order to reduce the level of the radioactivity to which the operator is exposed. This may be done effectively with the Hanford-type liquid-liquid extractor (2) if it can be shown that quantitative recovery of uranium will be effected with a reasonable volume of solvent.

Extractions using varying volumes of solvent indicate 98% recovery of uranium is obtained if a volume ratio of 19 to 1 for solvent to aqueous is used.

Aqueous solutions (2.1 ml. of a 2.3 molar aluminum nitrate solution at a pH of 0.1 containing 500 γ of uranium) were extracted with volumes of diethyl ether ranging from 10 to 50 ml. to give the following results:

Extraction Number	Volume Ratios Vs/Va	Percent Recovery
1	4.8	74
2	9.5	90
3	14.3	97
4	19.0	98
5	23.8	95

Fluorophotometry (P. Thomason, U. Koskela, W. Byerly)

In a former quarterly report of the chemistry division (3), a brief statement was made as to the fluorophotometric precision and accuracy in the range of 0.0005 to 1.0 micrograms of uranium. The maximum deviation of a single value from the average of six was listed as about 60% while the maximum deviation of this average from the true value was listed as about ±15%. The first value of 60% has been improved to about 15%, and the second from ± 15% to ± 10%. The higher precision seems to be the result of better distribution of the uranium in the sodium fluoride cake. The later results were obtained by adding the liquid samples to a fused sodium fluoride cake and

(1) "26" Recovery Flowsheet, June 4, 1947.
(2) H.E.W. Laboratory Manual, Apparatus Section, AE-23f.
(3) Byerly, W., Sadowski, G., MonN-311, p. 205.

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fusing again. Heretofore the sodium fluoride was added to the dried sample in a platinum dish and fused.

It is desirable to have permanent fluorescent standards with which to check the stability of the fluorophotometer. As the fused sodium fluoride uranium cake is hygroscopic, it is not suitable to be used as a standard. Three uranium glass discs made by fusing varying quantities of uranium glass (Corning No. 3750) with soft glass to give different intensities of fluorescence are being read as standards. The glass standards have the fluorescent equivalent to approximately 30, 87, and 218 milligamma of uranium, which is the optimum range of the fluorophotometer for the determination of uranium. The maximum deviation of the instrument or standards has been ± 10% from the average reading. When the glass standards read either lower or higher than normal the deviation of all three glass standards agreed which indicated the fluctuation was in the instrument rather than in the standards.

The influence of radioactivity on the photomultiplier tube used in the fluorophotometer will be studied. Methods using this instrument for the determination of other elements also will be investigated in the future.

Colorimetric Determination of Aluminum (E. Hanig, W. Byerly)

The volumetric aluminum method (1) now being used for the samples of the U^{235} recovery process is not adapted for remote control operation and therefore as the radioactivity increases a more suitable aluminum determination must be developed. Several colorimetric methods for the determination of aluminum have been investigated. The chloroform extraction of aluminum quinolate as outlined by Gentry and Sherrington (2) was tried without success. The results were erratic and a standard curve could not be repeated. Purification of chloroform did not improve the precision.

The most promising of the colorimetric methods tried uses quinalizarin as the complexing reagent as recommended by Kolthoff (3). The pH is critical and an ammonium acetate buffer is added to hold the solution to a pH of 5.5 - 5.7. The transmission of the color complex is read at a wavelength of 540 millimicrons with a Beckman DU Spectrophotometer. The method will determine aluminum in the range of 0 - 30 micrograms in the presence of 30 micrograms of iron and 30 micrograms of uranium. This amount of iron and uranium is greater than that expected in the U^{235} recovery process samples.

Remote Control Sampling (H. Hemphill, W. Davenport, W. Byerly)

Four remote control samplers of the revised planograph type (Clinton Laboratory drawing No. 252) have been installed in the analytical laboratory in Bldg. 706-D. These samplers are used to deliver 1 to 500 λ of a radioactive solution. A remote pipette ejector (Clinton Laboratory drawing CD-254-A) which enables an operator to remove a radioactive micro-pipette from the sampler at a safe distance has been designed and is in use.

A mercury column sampler has also been devised and used to deliver 100 λ samples with maximum deviation of ±7%. This sampler may be operated with zero visibility, however, it does not have the desired flexibility.

(1) Lundell, G.E.F., Knowles, H.B., Bur. of Stds. J. of Res. (1929).
(2) Gentry, C.H.R., Sherrington, L.G., Analyst 71, 432 (1946).
(3) Kolthoff, I.M., J. Amer. Pharm. Asoc. 17, 360 (1928).

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Solvent Extraction of Plutonium and Cerium (J. E. Hudgens, F. L. Moore)

Investigations into solvent extraction techniques capable of separating cerium and/or plutonium from other elements contained in samples submitted by the Clinton Laboratories heterogeneous pile program have been continued during this report period. Separations made by extracting cerium from aqueous solutions with nitromethane, nitroethane, nitropropane, chloroform, normal hexyl alcohol, etc. were reported in the quarterly report of the Clinton Laboratories Chemistry Division for the months of June, July and August (1). We were unable with a limited number of equilibrations to extract the cerium quantitatively into these organic solvents.

The extraction of cerium and plutonium with benzene solutions of the chelate complexes thenoyl trifluoroacetone (TTA) and trifluoro acetyacetone (TFA) has been reported by Thomas and Crandall (2). Greenlee and Winner (3) separated the +4 valence state of plutonium from other valence states of this element by extracting with TFA. The extraction of calcium and scandium with solutions of TTA was reported by Tompkins and Broido (4) and calculations to show the dependence of the distribution coefficients on the pH of the aqueous phase were also given. Since TTA was readily available in this laboratory, the principal effort has been expended to determine the conditions best suited to the extraction of cerium and plutonium with benzene solutions of this complex.

Studies of the Extraction of Cerium Activity

Survey experiments have been completed to determine the pH of the aqueous phase and the concentration of TTA in the benzene phase best suited to the quantitative extraction of cerium activity. Since accurate pH adjustments are difficult and time-consuming in routine analytical practice, it was desirable to determine the criticality of the pH adjustment. In these experiments, ceric activity was prepared by heating cerium tracer obtained from the radioisotope group (G. W. Parker) with ammonium persulfate and dilute nitric acid. The oxidation of the cerium was shown to be complete by performing experiments under similar conditions using macro quantities of cerous nitrate. The tracer solution after preparation was then adjusted to the desired pH and equilibrated with 5 M solution of TTA for two minutes. Aliquots of the organic phase were then evaporated and counted for beta activity. The results of these experiments are shown in Table 1. Future work will be concerned with determining the effect of small changes in the hydrogen ion concentration on the distribution coefficients (percent extraction) for the pH range of from 4 to 6.

1. Hudgens, J. E. and Moore, F. L., MonN-370, Sept., 1947.
2. Thomas, J. R. and Crandall, H. W., CN-3733, Dec., 1946.
3. Greenlee, R. W., and Winner, B. M., CN-3676, Feb. 1947.
4. Tompkins, P. C., and Broido, A., MonN-311, June, 1947.

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Table I

Extraction of Ce^{+4} with Benzene Solutions of T. T. A.

Extraction Conditions	pH	Ce Extracted (% of Ce activity added)
Equal vol. of 5 M T.T.A. Soln. 2 Min. Equilibrations	0.16	0.56
"	0.45	1.96
"	0.91	2.46
"	1.46	6.40
"	2.23	52.73
"	2.91	70.10
"	3.41	77.28
"	4.01	89.94
"	4.50	92.24
"	5.04	90.02
"	5.38	94.81
"	5.90	82.58

The effect of the concentration of the TTA in the benzene solution on the distribution coefficient was determined by equilibrating TTA benzene solutions of different concentrations with equal volumes of cerium tracer. The pH of the solution before equilibration was adjusted to 4.5 pH units and the TTA solution equilibrated with the aqueous phase for two minutes. A curve having a relatively small slope was obtained and the greatest extraction (highest $\frac{org}{aq}$ distribution coefficient) was observed at a TTA concentration of 5 M. A more accurate determination of this curve will be made in a forthcoming experiment.

Extraction of Plutonium Activity

The extraction of plutonium from aqueous solutions has been investigated by Crandall and Thomas (2) and these authors have given data and equations from which distribution coefficients can be calculated. The investigations reported here were therefore limited to those necessary to make the extraction methods usable by the personnel charged with the responsibility of performing the analyses. As a first step, oxidation and reduction experiments were performed to determine the concentration of oxidizing or reducing agents necessary to reduce plutonium +6 and to oxidize plutonium +3 to the extractable +4 valence state. In contradiction to the predicted behavior, plutonium tracer which had been boiled vigorously and allowed to stand overnight with 0.01 M potassium dichromate containing 0.5 M nitric acid, was extracted quantitatively. The addition of hydroxylamine hydrochloride (0.2 M) or of hydrazine sulfate (0.02 M) did not reduce the plutonium quantitatively to the non-extractable +3 valence

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state, while the addition of hydrogen peroxide (final aqueous solution 0.90% H_2O_2) reduced the distribution coefficient $\frac{org.}{aq}$ to approximately 0.25. Since sodium bismuthate is a very effective oxidizing reagent for plutonium a solution of plutonium tracer (0.9 M nitric acid) was boiled with this reagent for several minutes and then equilibrated with a 5 M solution of TTA in benzene. The plutonium was quantitatively extracted. From these experiments it can be concluded that under certain conditions the +6 valence state of plutonium is extractable with the TTA complex.

Further experiments to establish the conditions best suited to the extraction of plutonium activity from samples representative of those to be submitted by the heterogeneous pile program will be performed and these results reported in the near future.

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4. TECHNICAL SERVICES TO CLINTON NATIONAL LABORATORY RESEARCH GROUPS

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

1. Corrosion Film on Aluminum

In the experiments of R. Van Winkle (Sec. 2, Tech. Div.) on the heat transfer from aluminum tubes to hot demineralized water it is found that a film is formed on the surface of the aluminum, which lowers the heat transfer appreciably. The film grows rapidly during the first few days, but when it reaches a thickness of the order of 1 to a few microns it becomes reasonably protective and grows very slowly thereafter. It seemed worth while to study the nature and structure of the film, and to investigate the possibility of forming more suitable films by pretreatment, or by altering the conditions, e.g. pH.

Corrosion films can be stripped from aluminum surfaces by immersion in mercuric chloride solution (Keller, J. of App. Physics, 15, 696, 1944) so it is possible to examine the films by optical and electron microscopy and electron diffractbn and, in the case of the thicker films, by x-ray diffraction.

Briefly, the results of such examinations are:

(1) On the tubes as received from the manufacturer there is a film of the order of 0.05 microns in thickness (estimated from resolution obtained in electron micrographs), which appears to consist mainly of amorphous material plus some small crystals, which do not give a sufficiently good diffraction pattern for satisfactory identification. This is in agreement with the literature which says that natural oxide films on aluminum are from 0.01 to 0.1 microns thick according to their age.

(2) During the HF treatment, which has been used in cleaning the tubes for the experiment, the old film is removed, but a thin, amorphous film of the order of 0.01 to 0.02 micron thickness forms quickly on reexposure to air.

(3) After exposure to the hot demineralized water for one day the film is much thicker, approximately 0.10 to 0.25 microns. Since no lines are obtained by electron diffraction it must be presumed to be amorphous.

(4) After exposure to the hot demineralized water for longer periods the films are too thick for transmission electron microscopy or diffraction and, because the films are electrical insulators, it is difficult to examine the tube surface by reflection electron diffraction without a low voltage electron spray. However, experiment showed that these thicker films could be examined by x-ray diffraction and the material has been identified as small crystals of boehmite (see M. Bredig, this report). According to the literature this is the usual corrosion product when aluminum is exposed to hot water.

[redacted]

Some preliminary experiments show that the thickness of these films is of the order of 1 to a few microns.

(5) One tube was given a pretreatment consisting of heating in a steam bath in a weak dichromate solution for three weeks and this tube has given a rather remarkable performance, as compared to untreated tubes, in the heat transfer apparatus (see Sec. 2, Tech. Div. Report, Nox. 15). The film on a tube given this treatment was only about as thick as that which forms naturally in one day in the hot demineralized water. It was amorphous in nature, as judged by the lack of lines in the electron diffraction pattern.

This experiment makes it seem very probable that a more satisfactory film can be formed by pretreatment than that which forms naturally in the hot demineralized water.

(6) A literature survey has shown that there are numerous ways of forming films on aluminum for protection against corrosion, but in many cases the films appear to be too thick for use in this particular application. There is the further consideration as to whether preformed films will stand up for the required time (one month), especially in view of the rapid flow rate. Since a variety of properties are required in a satisfactory film, it will probably require considerable experimentation to get the best compromise.

(7) This work is discussed in more detail in CLM-LN#10.

2. Beryllium Oxide

About a dozen specimens have been examined in connection with the Power Pile Division program. Results will be given at a later date when the experiments, which these specimens illustrate, are completed.

3. Resins Used in Ion Exchange Columns (CLM-LN#9, Sept. 26, 1947)

Since particle size, size distribution, and particle shape are factors which affect the use of these materials, a record of the various resins available is being used - see Fig. 2. Certain other factors, such as colour, surface roughness, etc. are also being recorded since they may be evidence of structural changes which affect the exchange behaviour.

A current theory of the structure of these resins in that they contain coarser channels leading to successively finer channels. Such channels were sought by optical microscope examination of the original particles and of polished sections. No evidence of the existence of such channels could be found, so that if they do exist, the largest of them must be smaller than could be resolved under the conditions of examination (approximately 1 micron). The transparency of the particles and absence of scattered light are also evidence that the presence of such channels is unlikely. Therefore, unless there is good adsorption

evidence to the contrary, it seems best to regard the material as being of relatively uniform structure down to dimensions of the order of 1 micron at least, and probably smaller.

4. Crud Formed in Solvent Extraction Process

In the solvent extraction of uranium, it is found that occasionally there is a tendency for the column to plug on account of the formation of an emulsion at the hexone-water interface.

Micrographs demonstrating the presence of the emulsion and of the film formed by drying the emulsion have been taken. (CLM-LN#7) Aug. 20, 1947 by T. E. Willmarth). From the behaviour of the film on drying it was suggested that the troublesome material was organic in nature, and that the relatively few crystals observed had nothing to do with the trouble. Spectrum analyses of some (not all) samples showing very slight inorganic content confirms this view.

Further work has consisted in the examination of synthetic cruds. F. Bruce produced a synthetic crud which was very dissimilar to the naturally-occurring type. J. Savolainen and A. de Haan prepared a film at a water-hexone interface which was amorphous in nature, about 0.1 micron thick, and with rather good mechanical properties. It is obvious that a small amount of material of this nature could cause a considerable amount of trouble.

Figure 1

Micrographs of Aluminum Tubes and Corrosion Films Stripped From Them

Note:

(1) From the resolution obtainable in the electron micrographs it can be estimated that the film thickness (on the tube as received) is of the order of 500 A.

After HF treatment it is 100 to 200 A, and after one day in the hot demineralized water it is 1000 to 2500 A. These values are not exact, but are certainly of the right order of magnitude.

(2) The magnifications are ½ those given on the print, having been reduced in copying.

ME-30

ME-32

ME-29

EM-49

EM-54

EM-56

Optical micrographs (60x) of the surface of 2 S aluminum tubes - as received (Plate No. ME-29), after HF treatment (Plate No. ME-30), after exposure to demineralized water for 1 day in the heat transfer apparatus (Plate ME-32), and transmission electron micrographs (12000x) of the films stripped from corresponding tubes (Plate Nos. EM-49, 54, 56).

ME-23

ME-24

ME-28

Optical micrographs (125x) of stripped films from tubes in the heat transfer apparatus for periods up to 1 month.

[redacted]

Figure 2

Resins Used in Ion Exchange Columns

Note:

(1) In most cases the samples have been sized for use in exchange columns by sieving.

(2) Particles of Dowex 50 are spherical in shape, with a rather smooth surface. Some are quite transparent, and others opaque. They vary in colour through all the shades of brown to black, with a few being blue-black. The examination of fractured particles has shown that in some cases they are coloured more deeply at the surface than in the interior. In a few cases hemi-spherical shells have been found after fracturing particles. For these reasons they may not be entirely uniform in structure.

(3) The particles of colloidal Dowex 50 shown are aggregates of very small spheres (0.05 micron diameter), which can be seen by electron microscopy.

(4) The Amberlite IR-1 resin consists of irregularly-shaped fragments, probably produced by grinding. They are dark red in colour and coloured so deeply that only the very thinnest fragments transmit any light.

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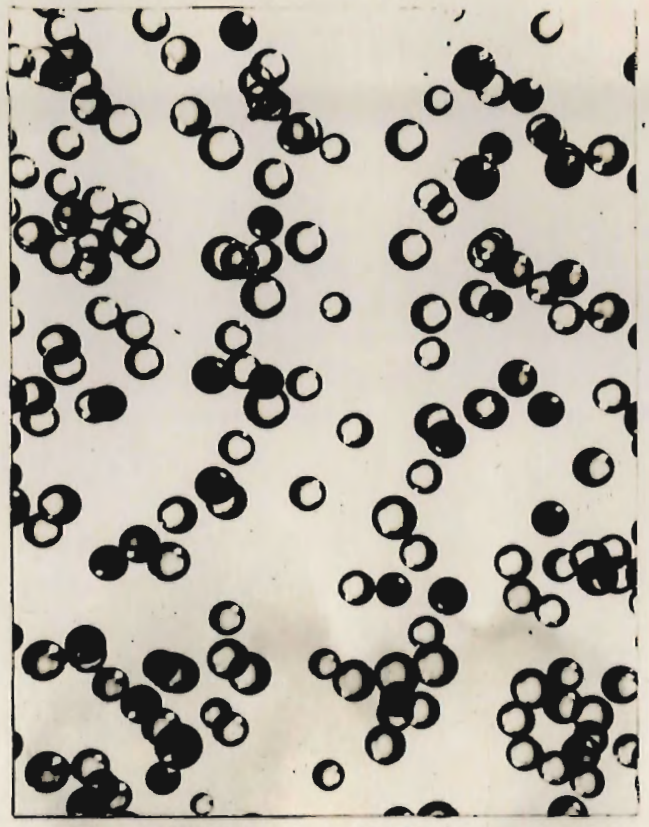

M 125-5 DOWEX 50

MAG. 100 X

M 127-5 DOWEX 50 (H FORM)

MAG. 100 X

M 128-5 COLLOIDAL DOWEX 50 (AGGREGATES)

MAG. 100 X

M 126-5 AMBERLITE

MAG. 100 X

[redacted]

X-Ray Diffraction (M. A. Bredig)

1. The design of the high-temperature oven for the x-ray spectrometer has been receiving increased attention. The Engineering Research Shops are in the process of preparing drawings in which the details of the construction will be brought out. There will be a water-cooled cylindrical metal housing of approximately 5" diameter with two x-ray windows 1/2" high and 2" long, corresponding to a Bragg angle range up to 45°. The housing will turn around the goniometer axis with the same speed as the sample. It can be evacuated, and considerable space will be available to permit the mounting inside of heating elements and sample holders of a variety of shapes and types for various conditions and purposes.

The slit system of the x-ray tube of the spectrometer was slightly altered so as to give maximum room to this heating device.

Because of the large size of the windows, beryllium metal of sufficiently low thickness will probably be mechanically unsuitable, and the attempt will be made to use thin films of cellophane or nylon, or the like, properly shielded from heat radiations by a very thin aluminum foil on one window, and by a thin nickel foil on the other one, which will simultaneously serve to monochromatize the x-ray radiation of the copper target tube. With an indifferent gas filling, instead of the vacuum, at somewhat lower temperatures, beryllium windows may be substituted.

A heating element which simultaneously serves as sample support was constructed (Figure 1). It was made almost entirely of graphite because of the outstanding combination of machining, electrical, and heat conductivity properties of this material. A solid wedge-shaped piece of graphite, 1-1/2" high, 1" long, and 3/8" to 5/8" wide, has an opening through its center, perpendicular to its largest faces, where the flat specimen will be inserted in a vertical position. Three carbon resistor rods are inserted in three cylindrical channels, slightly wider than the rods, penetrating the graphite block vertically. They are electrically connected in series, with the graphite block at the bottom serving as electrical connection for the bottom ends of two of them. The temperature will be measured with an optical pyrometer trained on the specimen. At lower temperatures a thermocouple might also be inserted in the carbon block which was found in preliminary tests, at approximately 1300° C, with an energy input of 500 watts, to glow with a rather uniform heat throughout, when inserted in an alundum tube with openings for the x-ray beams.

It is hoped that by thus using carbon as structural material even higher temperatures may be reached than in a furnace constructed with platinum and ceramic material as recently described by van Valkenburg and McMurdie (Natl. Bur. of Standards Journal of Research 38, 415-418, 1947), who by measurements at 1500° C have just confirmed the actual occurrence, at high temperature, of structural changes in a compound of the type A_2XO_4 (Ca_2SiO_4), that had been postulated from crystal-chemical considerations (M. A. Bredig, Journ. Physical Chem. 46, 747-64 (1942), and 49, 537-53 (1945)).

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Per E. H. Taylor
Date 11/25/47

Dwg.#4832, MonN-432

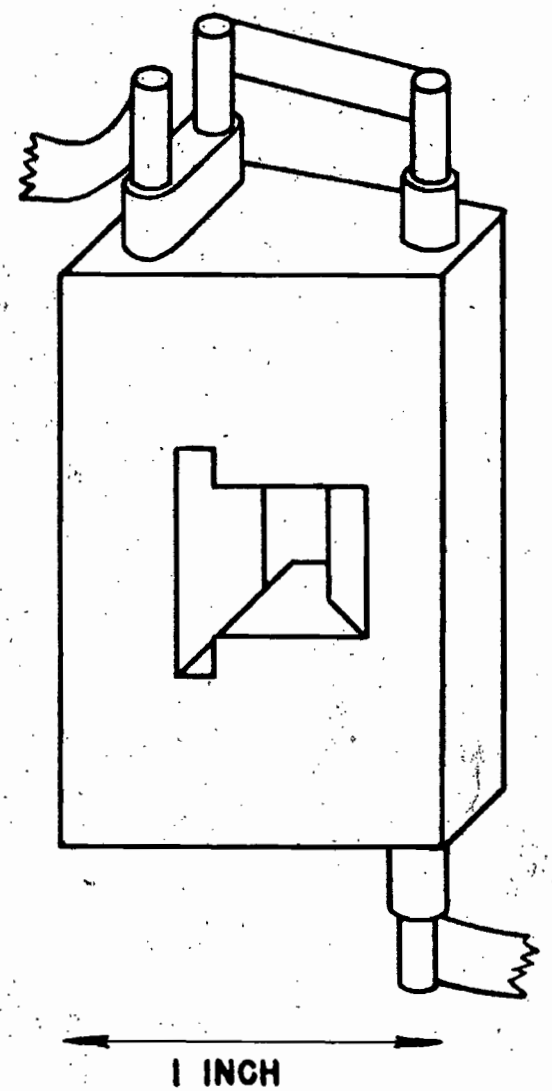

FIG. 1

HIGH TEMPERATURE HEATING ELEMENT FOR X-RAY SPECTROMETER

[redacted]

The use of carbon will also simplify the study of carbides and other compounds which would readily react with either metals or ceramics.

2. A specimen holder for use at room temperature with substances sensitive to components of the atmosphere, or which are to be kept at certain equilibrium vapor pressures of solutions, was designed and made out of lucite, as shown in Figure 2. It consists of three parts, of which the middle one carries the powder specimen in a flat groove, exposing an even, smooth surface of approximately 1 cm^2 to the x-rays. One other part carries a thin film of polystyrene, or nylon, as a window easily penetrable by x-rays even at low angles of incidence. They are joined on a flat circular surface by stop-cock grease, as is the third part covering an opening in the back of the middle part, which can be filled either with a drying agent, or a solution in equilibrium with the solid substance of the specimen.

As an alternative, or additional, arrangement--as the case may require--a cylindrical metal housing of 2-1/2" diameter with two thin polystyrene windows was attached to the specimen post of the goniometer, enclosing the post, and turning with it. It is large enough to receive small open vessels containing either drying agents or equilibrium solutions.

These devices proved useful in obtaining a powder x-ray pattern of extremely hygroscopic potassium ruthenate (submitted by M. D. Silverman), i.e., in a case in which a sufficient amount of material was available to obviate the use, in a Debye-Scherrer camera, of a thin glass capillary which is much more difficult to fill, in a dry-box, with a sticky powder such as this, than the specimen holder described here.

3. Lead sulfate-barium sulfate coprecipitates had been observed by W. H. Baldwin and J. E. Savolainen, Technical Division, to occur in crystals of different habit under different conditions (MonM-330). Samples of lead sulfate precipitated from nitrate solutions containing none, 5, and 25 mole percent of barium nitrate were submitted by J. Savolainen. Table 1 contains the experimental data obtained from Debye-Scherrer films and spectrometer records. The precipitate from the 5 mole percent barium solution did not show any measurable difference from pure lead sulfate, and any could hardly be expected in view of the comparatively small effects observed with the precipitate from the 25 mole percent solution. Measurements were confined to the innermost reflections, because of their greater sharpness, even though for geometrical reasons much greater accuracy is usually obtained with larger Bragg angles. Sodium chloride admixed to the powders served as internal standard.

The precipitate from the 25 mole percent barium solution showed the orthorhombic type of crystal structure common to the pure compounds lead sulfate and barium sulfate, with lattice constants $a = 8.51 \pm .01$, $b = 5.42 \pm .01$, and $c = 6.98 \pm .01 \times 10^{-8}$ cm, molecular volume

$$V = \frac{a \cdot b \cdot c}{4} = 80.49 \times 10^{-24}\ cm^3,$$

slightly larger than those of pure lead sulfate, $a_o = 8.45 \pm .01$, $b_o = 5.38 \pm .01$, and $c_o = 6.93 \pm .01 \times 10^{-8}$ cm, $V_o = 78.76 \times 10^{-24}\ cm^3$. The lattice constants of

[redacted]

D DRYING AGENT
G STOPCOCK GREASE
S SPECIMEN
W WINDOW (i.e. .001" POLYSTYRENE)

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Dwg.#4833, MonN-432

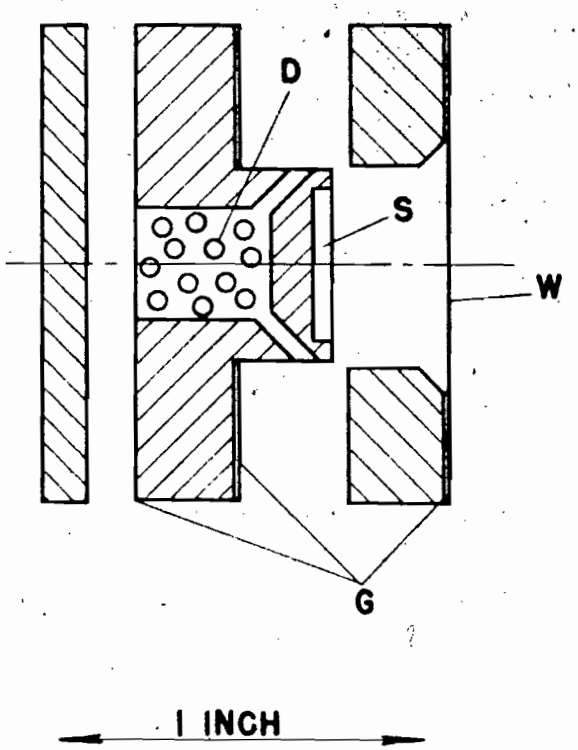

FIG. 2

SAMPLE HOLDER

Table 1

Lattice Spacings of $(Pb,Ba)SO_4$ and $PbSO_4$

hKe	Intensity	$(Pb,Ba)SO_4$ coprecipitate: From spectrometer chart C-101	From film D-15	mean	Lead Sulfate: from spectrometer chart C-122	from literature data	mean	Lattice expansion in coprecipitate
		Å	Å	Å	Å	Å	Å	Percent
(200)	m	4.245	4.250	4.248 ± .003	4.225	4.225	4.225 ± .000	.55
(111)	mw	3.810	3.820	3.815 ± .005	3.790	3.797	3.793 ± .004	.58
(002)	m	3.490	3.480	3.485 ± .005	3.460	3.464	3.462 ± .002	.66
(210)	m	3.340	3.345	3.343 ± .003	3.320	3.322	3.321 ± .001	.66
(102)	s	3.230	3.225	3.228 ± .003	3.209	3.207	3.208 ± .001	.62
(211)	s	3.020	3.024	3.022 ± .002	3.000	2.996	2.998 ± .002	.80
(112)	m	2.775	2.777	2.776 ± .001	2.750	2.754	2.752 ± .002	.87
(020)	m	2.700	2.706	2.703 ± .003	2.688	2.690	2.689 ± .001	.63
(301)	v.w	2.640	2.632	2.636 ± .004	2.620	2.613	2.616 ± .004	.79
				average ± .003			average ± .002	average .69%
				≈ ± .10%			≈ ± .07%	

 [redacted]

pure barium sulfate are known as $a = 8.898$, $b = 5.448$, and $c = 7.170 \times 10^{-8}$ cm, $V = 86.90 \times 10^{-24}$ cm^3. According to Vegard's law, postulating as a first approximation a linear change in the unit cell size with change in composition of solid solutions of isomorphous substances, from which however exceptions have been found, and which may or may not be valid in the present case, the volume change in the precipitate, of

$$\frac{80.49 - 78.76}{78.76} \times 100 = 2.2\%,$$

as compared with the difference in the crystal lattices of the pure sulfates, of

$$\frac{86.90 - 78.76}{78.76} \times 100 = 10.3\%$$

would indicate that approximately

$$\frac{2.2}{10.3} \times 100 = 21.5 \text{ mole percent of } BaSO_4$$

were present in solid solution with the $PbSO_4$.

Since deviations from Vegard's law usually are in the form of a contraction, or of too small an increase in cell size by substituting a larger ion such as Ba^{++} for Pb^{++}, the result of the x-ray measurements indicates that essentially all of the barium of the hydrous solution was precipitated with the lead as a rather homogeneous solid solution.

4. X-ray patterns were obtained from various samples of magnesia cement mixtures submitted by T. Rockwell. A number of different crystal-phases could be distinguished. The results are now to be evaluated in the light of the extensive x-ray diffraction study of the MgO-$MgCl_2$-H_2O system by Feitknecht (helv. Chim. Acta. 27, 1480-1501 (1944)), and shall be discussed in a later report.

5. Among several other, more or less incidental, problems dealt with during this period, a film formed in corrosion and heat transfer tests in the aluminum tubings (Van Winkle) was identified in a Debye-Scherrer x-ray pattern as α-AlO·OH, or böhmite, the usual product of corrosion of aluminum. The significance of this finding is discussed in L. T. Newman's detailed report on this subject.

[redacted]

 [redacted]

Development and Construction of Special Instruments (C. J. Borkowski and R. L. Butenhoff) P.A. CX11-5

Development of Proportional Counters for the Detection of Beta and Gamma Radiation

Counters filled with methane and operated in the proportional region with gas amplifications of the order of 10^4 have many advantages over Geiger counters for detecting beta and gamma radiation. First, they are fast counters having coincidence corrections of only 1.3% per 10^5 counts per minute whereas Geiger counter coincidence correction is about 1.0% per 10^3 counts per minute. Thus it is possible with the proportional counter to count samples at rates of 5×10^5 counts per minute with only small coincidence corrections. This allows one to follow the decay of sources over many more half lifes than is possible with Geiger counters. Second, unlike the Geiger counter, the counting characteristics of the proportional counter are little influenced by cathode surface conditions. Third, due to the relatively low gas amplification compared to the Geiger counter fewer molecules are decomposed in each discharge, consequently the life of a proportional counter with respect to the total number of counts accumulated by it should be at least 100 times that of the Geiger counter. Figure 1 gives the results of a life test on a mica window counter having a 7 mil center wire and filled with methane to a pressure of 20 cm. Hg and operated as a proportional counter. A UX_2 source giving 2×10^5 counts per minute in the counter was used to accumulate a total of 3×10^9 counts. It is apparent from this figure that no significant change in the counter characteristics occurred. Several other counters were tested in a similar manner with the same results. A life of 10^{12} counts for a permanently filled methane proportional counter is not at all unreasonable.

A comparison of counter characteristics in the proportional and Geiger regions was obtained by counting a standard UX_2 beta source with a counter which was operated first as a Geiger counter and the same counter as a proportional counter. An argon - butane mixture at 12 cm. Hg was used as the counter gas for the Geiger region. Methane at 20 cm. Hg was used for the proportional region. counting rates of 7900 c/m and 8900 c/m were obtained in the Geiger and proportional regions respectively. Applying the usual 1.5% per 1000 c/m coincidence correction to 7900 c/m gives 8850 c/m which is in close agreement with the 8900 c/m observed with the proportional counter. From these results we may qualitatively conclude that the proportional counter has the same beta counting efficiency as a Geiger counter.

The operating voltage for a mica end window counter with a one inch diameter cathode, seven mil center wire and filled with methane to a pressure of 20 cm. Hg was 2500 volts. With a 3 mil center wire the operating voltage was 2250 volts; in both cases the plateau length was 200 volts.

The continuous flow methane beta proportional counter which was described previously (Mon M-311), has now been in use for eight months with no change in characteristics. A UX_2 standard has been counted daily in this counter with a day to day reproducibility of 1%, the statistical error. Since the source is placed directly in the sensitive volume of the counter extremely low

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Potential on Wire	Initial Plateau	After 2×10^9 Counts	After 3×10^9 Counts
2200	10.50	10.25	12.50
2300	33.00	27.00	35.50
2400	58.75	55.75	58.75
2450	65.00	62.75	65.25
2500	69.25	68.75	69.00
2550	70.00	69.75	70.25
2600	69.50	70.75	69.25
2650	71.00	72.00	69.75
2700	72.00	71.50	71.75
2750	73.25	73.25	72.50
2800	—	75.75	73.50

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per C.J. Borkowski

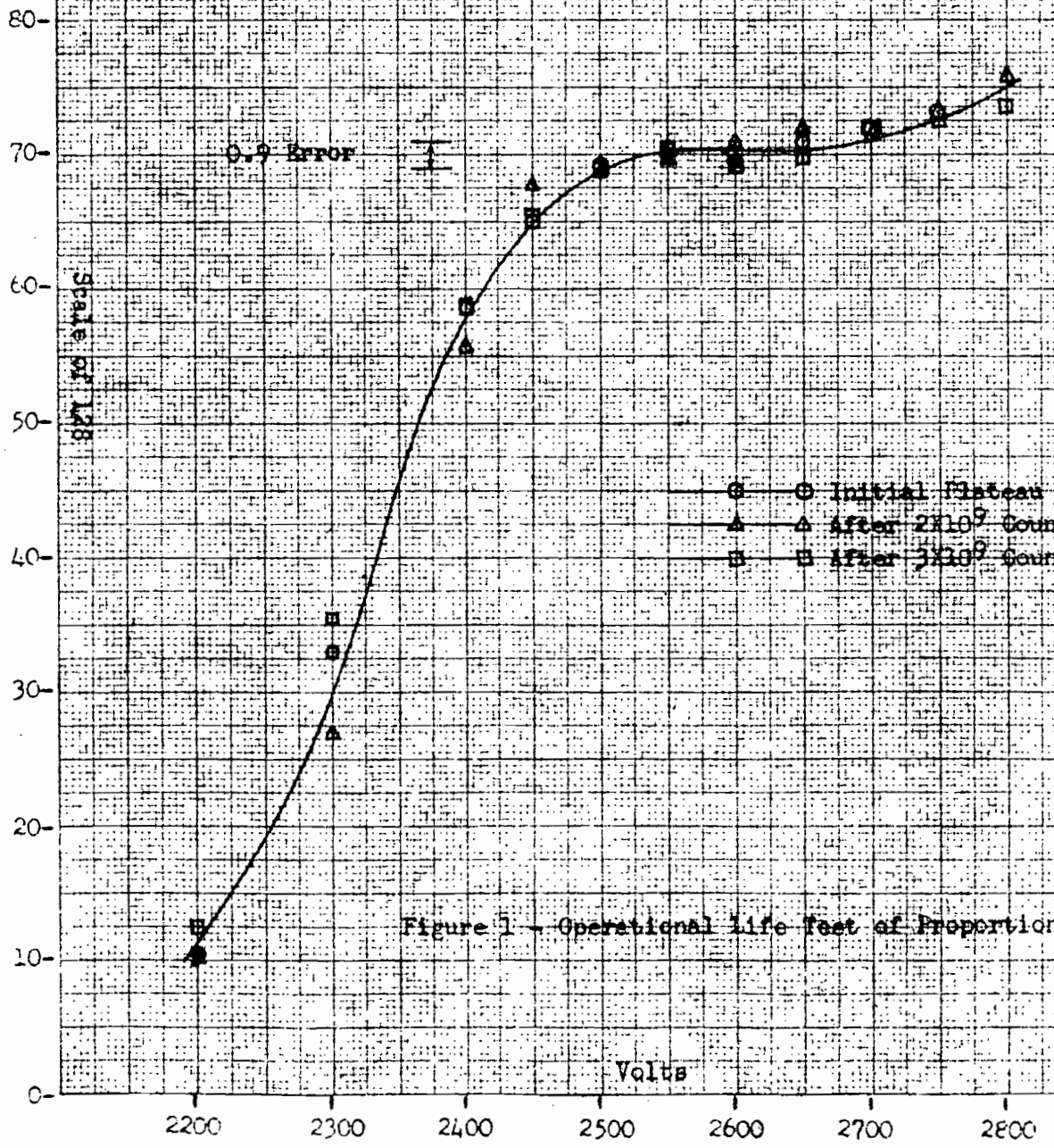

Figure 1 - Operational life test of Proportional Counter

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energy electrons, as well as high, can be counted with a counting yield as high as 70% for thin samples on platinum. This counter has also been used for obtaining aluminum absorption curves for soft electrons and X-rays.

In order to determine the coincidence correction of the continuous flow beta proportional counter the paired sample technique was used.

Three groups of paired samples were used. The members of the sample pairs are called "A" and "B" and are counted in the following manner: "A" separately, "A" and "B" together ($\overline{AB}$), "B" separately. The coincidence correction on C is obtained from the equation:

$$C = \frac{A + B - \overline{AB}}{\overline{AB}^2 - (A^2 + B^2)} \times 10^5$$

C is expressed as the percentage correction per 1000 counts per minute.

Results

Pair	A	AB	B	C
1	37.034	74.384	37.715	0.012
2	19.213	38.019	18.984	0.013
3	12.518	22.217	9.782	0.014

The above data indicate that the coincidence correction for this beta proportional counter is about 1.3% per 100,000 counts per minute and is linear over a wide range of counting rates.

Substanial progress has been made in developing a compact 60 cycle dynamic condenser electrometer which can be easily constructed in the machine shop. Sufficient quantity of these will be made to replace all Beckman and F P - 54 D.C. amplifiers.

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Development and Construction of Alpha-Counting Equipment. (J. H. Parsons)
P.A. CXII-4

Differential Displacement Pulse Analyser

The sweep type differential analyser has been described in reports Mon N-311 and Mon C-416. This analyser was primarily designed for analytical work where the amount of material in the sample can be controlled to have a disintegration rate between 200 and 20,000 alpha's per minute. If samples are encountered whose rate is below this, a multichannel analyser can be used. The multichannel analyser has several disadvantages as shown in the above mentioned reports.

A new type of analyser has been developed that will handle the low rate samples and in addition has the following advantages.

1. Essentially 100% utilization of pulses from amplifier
2. Low coincidence loss
3. Pulse height measurement is very precise
4. A permanent record is obtained

The analyser operation is shown in block diagram in Figure one. The chamber and amplifier are the same

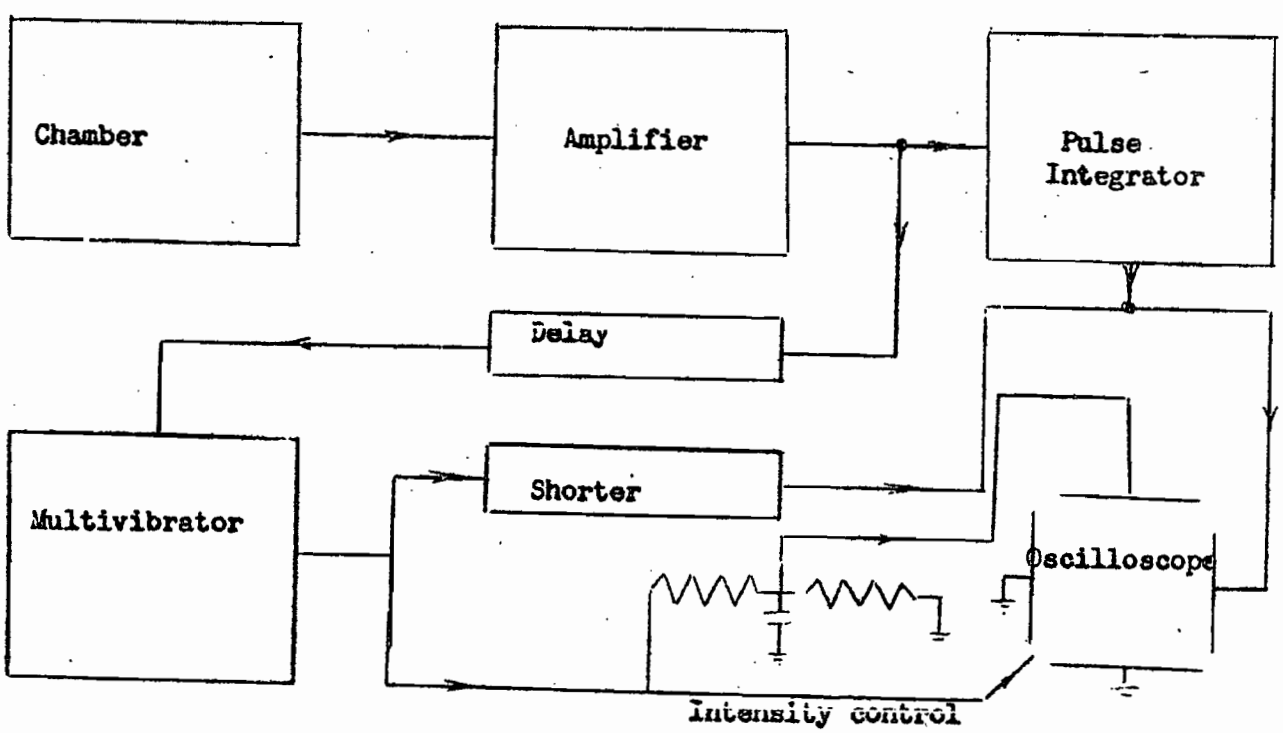

Figure 1

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as in previous units. The pulse integrator supplies a voltage whose magnitude is proportional to the energy of the out put pulse from the amplifier. The duration of this transient is controlled by the multivibrator as shown later. This transient positions the beam of an oscilloscope. The position is a measure of the energy. The multivibrator is tripped after the voltage from the pulse integrator is constant. This generated square wave intensifies the oscilloscope beam, moves the beam in a vertical trace, and in returning to a stable position discharges the pulse integrator, making the system ready for the reset pulse.

A time exposure photograph of the oscilloscope screen would reveal a distribution of energy where position is a measure of energy and density a measure of number. This negative may be read by a densitometer.

One very simple unit of this type has been tried and experiments show that there are no insoluble problems. Detailed design will be studied in the near future.

[redacted]

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Analytical Service Groups

Summary of Analyses Made by Analytical Service Groups
August 15, 1947 to November 15, 1947

Group	Tech.	Prod.	Chem.	Physics	Health Physics	Medical	Misc.	Total
1200 Area Control	4400	-	-	-	-	-	-	4400
1300 Area Control	682	-	456	-	-	-	-	1138
Water Analyses	820	-	9	-	-	-	12	841
Radiochem. Analyses	247	-	132	-	18	-	-	397
General Ionic Analyses	165	-	6	1	-	-	14	186
Radioisotope Anal.:								
Radiochem.	-	3955	205	-	-	-	-	4160
Ionic	-	686	35	-	-	-	-	721
Spectrographic Lab.:								
Qual.	24	57	195	44	-	2	6	328
Quan.	11	-	4	4	-	20	8	47
Totals	6349	4698	1042	49	18	22	40	12,218

1200 Area Control Group (E. J. Frederick, W. T. Mullins, H. A. Parker, J. N. Weeks)

During this quarter the group was expanded to a total of five technical and twenty-eight non-technical personnel to handle the analyses for the 25 pilot plant. This pilot plant started preliminary operations about November 1, 1947 and expects to be in full operation soon. The present personnel seems to be adequate for the expected load from the pilot plant and the semi-works.

1300 Area Control Group (L. T. Corbin, G. R. Wilson)

The present personnel consists of two technical and five non-technical personnel. There has been little change in the analytical load in this period and the present personnel seems to be adequate.

[redacted]

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Water Analysis Group (J. H. Edgerton, F. J. Miller)

Three non-technical people were added to this group in this quarter. These, with the two technical men, seem to be capable of handling the present load which comes primarily from corrosion studies in the Technical Division.

General Radiochemical Analyses (C. L. Burros, O. M. Bizzell, J. D. Gile)

The addition of two laboratory technicians brings the personnel of this group to a total of three technical and four non-technical people. This seems to be adequate for the present load, the major part of which consists of fission product analyses for decontamination studies being made in the various groups working on the 25 process.

General Ionic Analyses (D. E. LaValle, E. W. Milam, W. Wolkowitz)

This group, with a personnel of three technical and one non-technical persons, is considerably understaffed for the number of samples now coming in. This group has the responsibility for routine aluminum-uranium alloy analyses and organic combustion analyses as well as for all types of non-routine ionic analyses.

Radioisotope Analysis Group (S. A. Reynolds, R. H. Powell, G. W. Leddicotte, D. I. Gilbert, J. G. Gill, T. G. Harmon, W. S. Lyon, E. I. Wyatt, C. M. Goolsby)

This group, at present, has eleven technical and twenty-one non-technical people. It is expected that this group will continue to expand as the needs of the radioisotope production program increase.

The group is devoting considerable time to the development of methods and has completed work on the following:

Ca^{45}, ionic calcium, carbonate and moisture on $CaCO_3$ product;
Solubility of $Na_2Cr_2O_7$ in conc. HNO_3.

Work is continuing on methods for the following elements:

Ti, Os, [illegible], Se, Tl, Co, Sr, Ta, Hg,
Ru, Zn, K, Cl, Ag, Ni, Fe.

In addition to analyses for regular production requirements, analytical assistance has been given on the development of the following processes:

Fission-product iodine
Ca^{45} from Sc
Fe^{59} from Co
P^{32} from S (acetic acid extraction) and from P_2O_5
Cb^{95}
Resin column fission-product process

Spectrographic Laboratory (C. Feldman, A. J. Estepp, M. Murray)

The present personnel of this group consists of three technical people. This will be increased by one when clearance for an additional person has been

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completed. In addition to the regular qualitative and quantitative analyses, the following development problems were studied:

1. A sparking chamber of new design for hot samples was put into operation. This chamber makes it unnecessary to handle hot samples in the open, and simplifies optical adjustments.

2. The slit jaws of the Jarrel-Ash instrument, found to be defective, were re-lapped by D. Holcomb. Lens and source poisitions were worked out for obtaining maximum illumination while focussing on slit or mirror, using spherical or cylindrical optics.

3. Sensitivity limits were established for the following elements by the porous cup technique:

Element	Medium	Sensitivity (ppm)
Ce	10% H_2SO_4	25
Zr	" "	3
Li	" "	25

4. A procedure was devised for estimating the concentration of an impurity spectrographically when no base material free of that impurity is available for standards. The procedure is based on the assumption that the exponent n in the equation Intensity $\propto$ (concn.)^n is known.

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REPORTS ISSUED BY THE CHEMISTRY DIVISION

SEPTEMBER, OCTOBER, NOVEMBER, 1947

MonC-347 C^{14} Tracer Studies in the Rearrangement of Phenylglyoxal to Mandelic Acid
O. K. Neville and W. G. Brown

MonC-354 Equations for Column Calculations
F. T. Miles

MonN-370 Report of the Chemistry Division for the Months June, July and August, 1947
J. R. Coe and E. H. Taylor

MonC-378 Quantum Corrections to the Thermodynamic Properties of Liquids, with Application to Neon
O. K. Rice

MonC-380 Electrodeposition of Micro Amounts of Uranium on a Cathode of Small Area
F. T. Bonner

MonC-390 Fixation of Nitrogen by Pile Radiation and Acid Formation in the Argonne Pile
A. O. Allen, T. W. Davis and C. J. Hochanadel

MonC-400 A Table of Radioactive Isotopes Arranged According to Half Lives
J. W. Jones and H. M. Clark

MonC-401 The Determination of Trace Amounts of Elements by Radioactivation Analysis
H. M. Clark and R. T. Overman

MonC-410 A Micro Calorimeter and the Measurement of the Decay Energy of $Phosphorus^{32}$
C. V. Cannon and G. H. Jenks

MonC-417 Separation of Radium from Barium by the Use of an Ion-Exchange Column Procedure
E. R. Tompkins

[redacted]

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PAPERS PRESENTED BY MEMBERS OF THE CHEMISTRY DIVISION

American Chemical Society Meeting, September 15-20, 1947

The Application of Ion Exchange to the Separation of Yttrium Group Rare Earths

B. H. Ketelle

Absolute Beta Counting Using End-Window Geiger-Müller Counter Tubes

L. R. Zumwalt

Determination of Trace Amounts of Elements by Radioactivation Analysis

R. T. Overman and H. M. Clark

Radiochemistry, a Growing Field of Specialization

R. T. Overman and H. M. Clark

The Synthesis of Phenanthrene-9-C^{14}

C. J. Collins and W. G. Brown

Ion Exchange as a Separations Method:

I. The Separation of Fission Produced Radioisotopes, Including Individual Rare Earths, by Complexing Elution from Amberlite Resins

E. R. Tompkins, J. X. Khym and W. E. Cohn

III. Equilibrium Studies of the Reactions of Rare Earth Complexes with Synthetic Ion-Exchange Resins

E. R. Tompkins and S. W. Mayer

IV. A Theoretical Analysis of the Column Separations Process

E. R. Tompkins and S. W. Mayer

Laboratory Handling of Radioactive Material: Protection of Personnel and Equipment

P. C. Tompkins

The Pile Production of Radioactive Isotopes

W. E. Cohn

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PAPERS PRESENTED BY MEMBERS OF THE CHEMISTRY DIVISION

General Information Meeting, October 13-15, 1947

Decomposition of Water and Aqueous Solutions by Pile Radiation
A. O. Allen, J. Boyle, T. W. Davis,
J. A. Ghormley and C. J. Hochanadel

Hydrolytic Behavior of Uranium (IV)
K. A. Kraus and F. Nelson

Some Aspects of the Hydrolytic Behavior of the "Actinide" Series
K. A. Kraus and F. Nelson

The Separation of Heavy Elements by Ion Exchange
S. W. Mayer

Phase Relationships in the System Uranyl Sulfate-Water
C. H. Secoy

s-Diphenylthiourea as a Complexing Agent for Ruthenium
G. D. Calkins

Calibration of Gamma Ion Chamber Used in X Pile Flux Determination
J. W. Jones and R. T. Overman

Activation Measurement of the Epi-Cadmium Flux in the X Pile
J. W. Jones, H. M. Clark and R. T. Overman

The Anomalous Distribution of Ruthenium
G. R. B. Elliott

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