

~~SECRET INFORMATION~~

Contract No. W-7401-eng-37

Supplement
to
CC-2636
t-C

Section C-I Group 9

CLASSIFICATION CANCELLED
DATE 12-13-65
For The Atomic Energy Commission
H.F. Canale
Chief, Declassification Branch *ret*

CHEMICAL RESEARCH - EXTRACTION AND PROPERTIES OF U²³³

G. T. Seaborg, Section Chief: F. M. Manning, Associate Section Chief
L. I. Katzin, Assistant Section Chief

REPORT FOR PERIOD ENDING DECEMBER 15, 1944

Photostat Price \$ 6.30
Microfilm Price \$ 3.00
Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

Report received: February 20, 1945
Issued: FEB 24 1945

36p
C-V
MC

8-75-1

~~SECRET INFORMATION~~

Immediately after report CC-2636 was issued, it was discovered that incorrect concentrations had been ascribed to key $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ solutions, and it became necessary to recheck certain salting and extraction experiments in which they were used. The following changes in the original report will bring the discussion into agreement with the experimental findings.

- Page 14: Paragraph 3, line 1: delete "except $\text{Mg}(\text{NO}_3)_2$ "
 Paragraph 3, line 2: Read "The most effective salting agent was $\text{Mg}(\text{NO}_3)_2$ "
 Paragraph 4, line 4: Read "at the nitrate concentration giving 60% extraction of uranium"
 Paragraph 5: Read " $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_3 > \text{Al}(\text{NO}_3)_2 > \text{LiNO}_3 > \text{Cu}(\text{NO}_3)_2 > \text{Mn}(\text{NO}_3)_2 > \text{La}(\text{NO}_3)_3 > \text{HNO}_3 > \text{NH}_4\text{NO}_3$."
 Page 15: Sentence 1: Read " $\text{Mg}(\text{NO}_3)_2 > \text{Ca}(\text{NO}_3)_2 > \text{Mn}(\text{NO}_3)_2 > \text{La}(\text{NO}_3)_3$, $\text{Al}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2 > \text{Th}(\text{NO}_3)_4$, $\text{NH}_4\text{NO}_3 > \text{HNO}_3$, LiNO_3 "
 Sentence 2: Read " $\text{Cu}(\text{NO}_3)_2 > \text{Mn}(\text{NO}_3)_2 > \text{HNO}_3 > \text{La}(\text{NO}_3)_3$, $\text{LiNO}_3 > \text{Al}(\text{NO}_3)_3 > \text{Th}(\text{NO}_3)_4 > \text{Ca}(\text{NO}_3)_2 > \text{Mg}(\text{NO}_3)_2 > \text{NH}_4\text{NO}_3$ "
 Paragraph 2: Read "As judged by these data $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ and to a lesser degree, NH_4NO_3 would be very suitable"
 Page 16: Table 5: Replace the portions of this table on $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ with the following revised figures:

Salting Agent	Total Nitrate Normality	Thorium Normality	% Uranium Extracted	% Thorium Extracted
$\text{Ca}(\text{NO}_3)_2$	7.50	1.0	96	1.2
	5.25	1.0	59	0.1
	4.0	1.0	25	0.0
	2.75	1.0	11	0.0
	7.50	0.0	99	0.0
	4.87	0.0	63	
	3.62	0.0	32	
	2.37	0.0	13	
$\text{Mg}(\text{NO}_3)_2$	5.5	1.0	99	0.31
	4.14	1.0	44	0.00
	3.15	1.0	18.	0.0
	2.17	1.0	9	0.0
	5.5	0.0	99	
	3.60	0.0	38	
	2.58	0.0	18	
	1.50	0.0	3	

8-72-2

Replace

Replace Figs. 10 and 11 (salting effectiveness of $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$) with the attached corrected versions of the figures.

Erratum. CC-2636

Page 2, 4th and 7th lines from bottom: instead of "x-ray count" read "Geiger count."

8-72-3

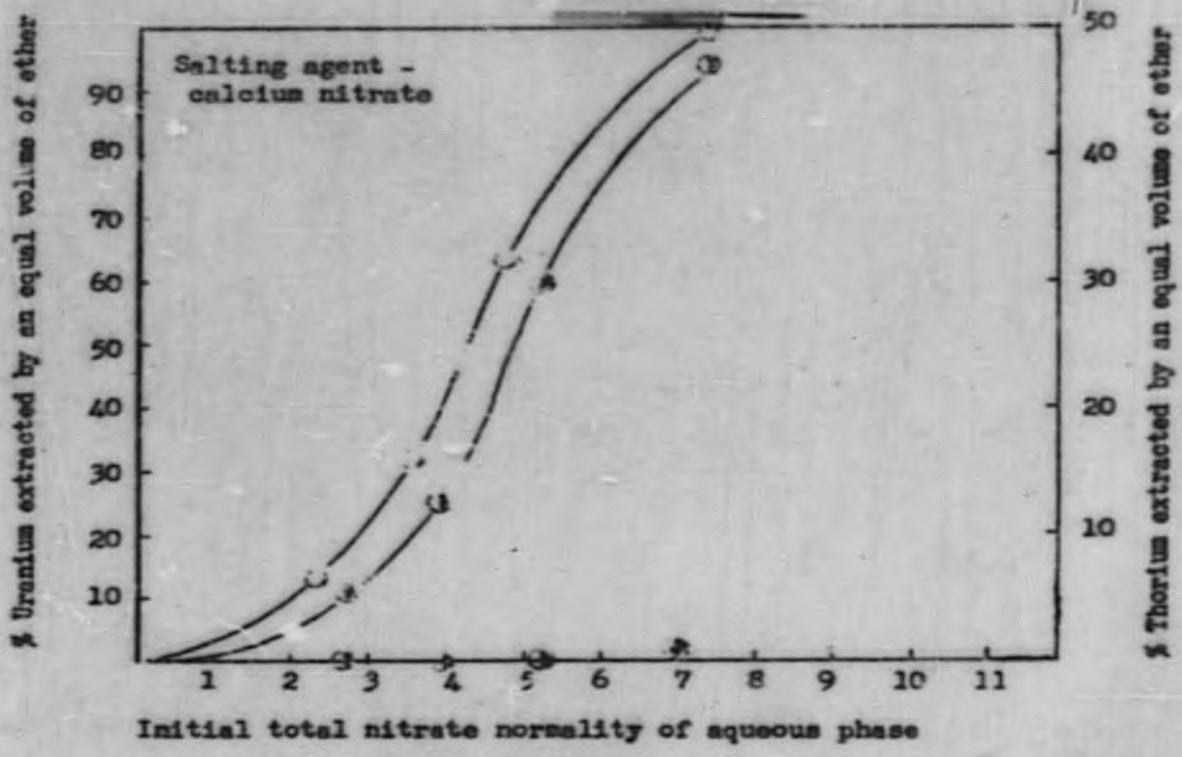
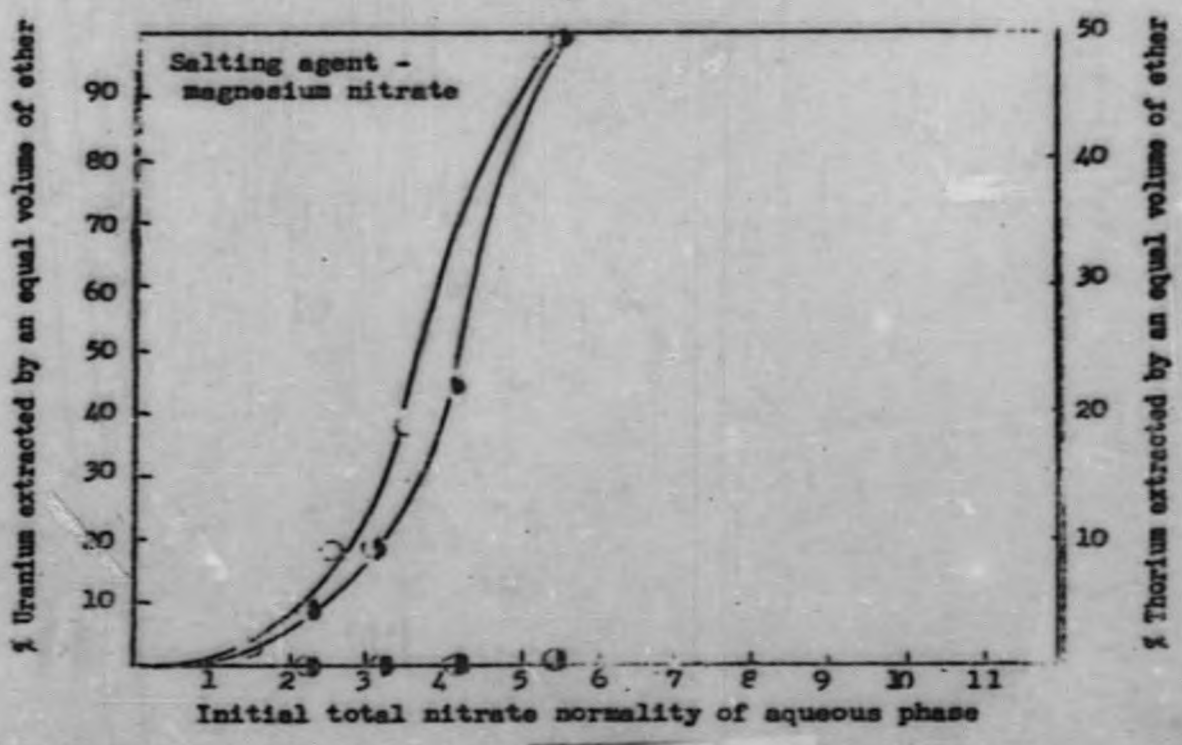


Fig. 10

Fig. 11



3

A-72-

Contract No. W-7401-eng-37

CC-2636
2-C

Section C-I Group 9

* * *

CHEMICAL RESEARCH - EXTRACTION AND PROPERTIES OF U²³³

L. I. Katzin, Assistant Section Chief

* * *

REPORT FOR PERIOD ENDING DECEMBER 15, 1944

* * *

Table of Contents

	Page
Abstract	1
333 MLC 1906 Determination of physical constants for U ²³³ .	1
A. The radiation spectrum of pure U ²³³ . M. Studier	1
B. New half-life determination for U ²³³ . E. Hyde, F. Hagemann, L. I. Katzin	3
333 MLC 1907 Determination of decay chain of U ²³³ . A. Ghiorso, F. Hagemann, L. I. Katzin, M. Studier	4
351 MLC 1901 Extraction of U ²³³ . F. Hagemann, N. Hellman, M. Studier	7
351 MLC 1902 Extracting solvents for uranium. E. K. Hyde, M.J. Wolf	8
351 MLC 1912 Factors affecting the extraction of uranium and thorium by organic solvents, especially ether.	11
A. Extraction of H ₂ O ₂ and thorium by ether from thorium nitrate and ammonium nitrate solutions. M. J. Wolf and N. N. Hellman	11
B. Influence of various nitrates on the extraction of uranium and thorium by ether. N. N. Hellman	14
353 MLC 1909 Analysis of ore samples for protoactinium. Q. Van Winkle and J. Sedlet	18

Report received: January 17, 1945; Figures received: January 17, 1945
Issued: JAN 27 1945

SECRET

A-72-5

Abstract

The Radiation Spectrum of Pure U²³³. Aluminum and lead absorption curves on a 16 mg sample of U²³³ have indicated the presence of gamma rays of 130, 230, and 420 Kev energy and an abundance (uncorrected for counting efficiency or window absorption) of from one to ten per million alpha particles. Lower energy radiations of 90, 19, 14 and 8 Kev range in abundance from about two in 10⁵ alpha particles to about one in ten alpha particles. Magnet experiments have demonstrated the presence of conversion electrons.

New Half-Life Determination for U²³³. The specific activity of the U²³³ sample used by Anderson and May for physical measurements has been re-determined. The isotopic ratio has been measured mass-spectrographically by a dilution method which improves the accuracy of the determination. The results indicate a longer half-life than hitherto assumed, namely, 1.62×10^5 years. The isotopic purity of U²³³, according to these latest measurements, is about 97 per cent, rather than 87.5 per cent.

Determination of Decay Chain of U²³³. The following identifications of members of the 4n-1 series have been tentatively established. RdNp (Th²²⁹), an alpha emitter of probably several thousand year half-life; NpX (Ra²²⁵), an alpha emitter of about one month half-life; NpC (Bi²¹³), an alpha emitter of about 44 minute half-life; NpD (Pb²⁰⁹), a beta emitter of 3.3 hour half-life, whose activity is already known. It is not as yet established whether the radium and thorium isotopes have branching decays. Neither has it been ascertained definitely that the emanation is an alpha activity. The half-lives between NpX and NpC seem to be considerably shorter than ten minutes.

Extraction of U²³³. An unidentified organic compound, which is either an impurity of, or some reaction product of, diethyl ether has been found to complex uranium and to prevent its transfer from ether to an aqueous phase. The compound seems to be extremely stable, as its destruction could be accomplished only with HNO₃-H₂O₂ and aqua regia.

Extracting Solvents for Uranium. Tests on the extraction of uranium, thorium, and in many cases, protoactinium, have been made on solvents of several types. In general, the cellosolve derivatives extracted undesirably large amounts of thorium, together with uranium. The ketones with six or more carbon atoms extracted satisfactorily low amounts of thorium, but too large amounts of protoactinium. Diisopropyl ketone extracted 56 per cent of uranium and 63 per cent of the protoactinium, with only 0.3 per cent of thorium from the standard test solution (3 N Th(NO₃)₄, 2 N NH₄NO₃ and 1 N HNO₃). Of the esters, ethyl acetate showed the most desirable characteristics of high uranium extraction and low thorium and protoactinium extraction.

Extraction of Nitric Acid and Thorium by Ether from Thorium Nitrate and Ammonium. The extraction of nitric acid by ether follows approximately the same pattern as does the extraction of uranyl nitrate, except that the variation with nitrate concentration is approximately linear rather than sigmoid. The extraction of thorium is a function of nitric acid concentration, thorium

concentration and total nitrate normality. There is an apparent threshold of nitrate concentration below which thorium will not extract detectably.

Influence of Various Nitrates on the Extraction of Uranium and Thorium by Ether. The most effective salting-out agent for uranium was found to be aluminum nitrate. Salts such as $\text{Al}(\text{NO}_3)_3$, $\text{La}(\text{NO}_3)_3$, $\text{Mg}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, LiNO_3 and nitric acid, which are capable of affecting salting of thorium, as well as uranium, into ether, produce markedly greater uranium extraction if thorium is absent from the solution. Other salts, such as $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ and NH_4NO_3 , which do not give appreciable thorium extraction, show only minor differences in uranium extraction in the presence or absence of thorium. The explanation tentatively advanced is that of salting back from the ether into the aqueous phase.

Analyses of Ore Samples for Protoactinium. Experiments have indicated that the protoactinium contained in the carbonate fractions from the uranium extraction process is to be found in the acid insoluble silicious fraction of these residues.

333 MLC 1905 Determination of Physical Constants for U^{233} .

A. The radiation spectrum of pure U^{233} . M. Studier. In addition to alpha radiation, there seems to be a complex quantized spectrum associated with radioactively pure U^{233} . A similar spectrum for Pu^{239} has previously been analyzed by Ghiorso (OK 1511).

The U^{233} used in the measurements to be reported was purified by repeated ether extraction and precipitation of LaF_3 from U^{233} solution to remove any traces of Th or Pa^{233} (the beta-active parent of U^{233}).

A lead absorption curve was taken using a 16.1 mg sample (3.75×10^6 alpha disintegrations per minute) of U^{233} . The sample, in the form of fused UO₂ evenly spread on the bottom of a glass Nessler tube, was placed in a position relative to an inverted mica-window Geiger tube such that its solid geometry factor was 10%. The Geiger tube was surrounded with paraffin to minimize the effect of scattering of radiation and the paraffin was shielded with lead brick. The accuracy of the determination of the hardest component is poor because of the very low counting rates obtained with heavy lead absorbers. A more accurate determination will be made when more U^{233} becomes available.

An aluminum absorption curve was also obtained. For the determination of the harder components the sample and conditions were the same as those used in determining the lead absorption curve. A 0.7 mg sample (1.6×10^7 alpha disintegrations per minute), mounted on a Pt disk and placed in a position giving 15% geometry factor, was used for the determination of the softer components. The absorption curve obtained with the 16.1 mg was normalized to the curve obtained with the 0.7 mg and this composite curve used to resolve the components of the radiation.

The counting rate of each component relative to the alpha disintegration rate was calculated. Since the counting efficiency of this type of G-M tube for x-rays is not well known, no attempt was made to determine the actual number of x-rays emitted.

In addition to the components listed, the aluminum absorption curve indicated the presence of a very soft component (probably conversion electrons - see below - with perhaps some alpha particles) with a half thickness of 2 - 2.5 mg of aluminum. The 87 KEV component obtained from the aluminum curve is probably the same as the 92 KEV component obtained from the lead curve. The apparent abundances of the two are in good agreement. The identification of the 14 mg and 72 mg components as x-rays rather than beta particles is based upon the very marked difference between aluminum and lead absorptions.

8-72-8

Table 1 below summarizes the data obtained.

Table 1. Quantized Radiation from U²³³

Half Thickness in gms/cm ²	Corresponding Energy in KEV	Alpha Disintegrations per X-ray Count at 100% Geometry (Mica Window Counter)
3.25 gm Pb	430	1.35 x 10 ⁶
0.74 " "	230	4.8 x 10 ⁵
0.213 " "	130	1.9 x 10 ⁵
0.100 " "	92	1.9 x 10 ⁵
3.53 " Al	87	1.7 x 10 ⁵
0.165 " "	19	4.8 x 10 ³
0.072 " "	14	9.6 x 10 ³
0.014 " "	8	8.7 x 10 ²

The presence of negatively charged particles (probably conversion electrons) was demonstrated in the following manner. A sample of U²³³ (1.6 x 10⁷ alpha disintegrations per minute) was mounted on a Pt disk and placed in the plane of the mica window of a Geiger-Muller tube, one centimeter from the closest edge of the window and facing the same direction. Radiation directly into the tube was minimized by mounting the sample on a sheet of lead. The counter tube together with the sample was then brought into the field of a strong permanent magnet. As the sample was brought into the field, the particles (negatively charged, as determined from the polarity of the magnet) were deflected through 180 degrees into the Geiger tube window. As the field strength increased, the counts increased from a background of 230 c/m, passed through a maximum of 2500 c/m, and decreased to background as the sample was brought very near to the magnet. Although no accurate measurement of the energy of these particles was made, they are believed to be quite soft, as they are so strongly deflected by this relatively weak magnetic field, and as the aluminum absorption curve indicates the presence of a very soft component in the total radiation.

If it is assumed that no alpha particles penetrate 1.2 cm of air and the 3.8 mg of mica window, there are approximately 230 alpha particles for every x-ray count at 100% geometry. With an additional 10 mg of aluminum absorber (a total amount of absorber equivalent to approximately 15 mg of aluminum), there are approximately 625 alpha particles for each x-ray count at 100% geometry. These figures agree well enough with the sum of the counts to be expected from the extrapolated figures of Table 1, the differences being in the right direction to be accounted for by the unknown number of conversion electrons that would be counted.

S-72-9

B. New half-life determination for U^{233} . E. Hyde, F. Hagemann, L. I. Katzin.

A new half-life determination has been carried out on U^{233} , in which the specific activity of the sample was determined by a dilution-counting method, and the isotopic ratio of the uranium sample was determined by a revised method in which the isotopic ratio was brought to a value near unity. The U^{233} sample used was the same as that used by Anderson and May for physical measurements. The new half-life and higher purity values obtained affect only the values of the cross-sections for U^{233} .

The uranium was purified by ether extraction followed by a peroxide precipitation. The solution obtained by dissolving the peroxide in nitric acid was evaporated in a weighed platinum crucible and ignited to constant weight at $700^{\circ}C$. After dissolving the 0.273 milligrams of U_3O_8 in nitric acid and quantitatively transferring to a volumetric flask, it was diluted to 25.0 ml. Aliquots of 100 microliters each were removed to separate 10.0 ml flasks and made up to volume. Finally, 100 microliter aliquots from these dilutions were evaporated onto platinum counting discs and counted for from thirty to sixty minutes. The average count on four dilutions, using 2-3 plates per dilution, was 1895 counts per minute, after corrections for background and coincidence had been made. Taking the standard value of 53% geometry for counts made on platinum plates, it is calculated that the specific activity of the sample was 20,400 disintegrations per minute per microgram.

Of the original 25 ml of uranium solution, 4.98 ml were taken and mixed with a solution of natural uranium containing 0.6760 mg of uranium. On the basis of the specific activity estimated in earlier experiments (CC 2165) the U^{233} activity represented a purity of 87.5%, and the mixture should have had an isotopic ratio of U^{233} to U^{238} of 0.99. The mixture of uranium was reduced electrolytically to the uranous state, and HF added to precipitate UF_4 . The precipitate was separated, washed with ether, and air-dried. The sample was then submitted to Dr. Dempster for mass spectrographic analysis.

The mass spectrographic report is that the mixture contains U^{233} and U^{238} in the ratio 1.24 to 1. With the data already given, this enables one to calculate that the original U^{233} was 97% isotopically pure. The specific activity of pure U^{233} by these data is therefore 21,100 disintegrations per minute per microgram, and the half-life value 1.62×10^5 years.

333 MLC 1907 Determination of Decay Chain of U²³³. A. Ghiorso, P. Eisenau,
L. I. Katzin, M. Studier.

The members of the three natural radioactive series, the uranium-radium series, the actinium series and the thorium series, have masses which correspond respectively to the formulae $4n+2$, $4n+3$ and $4n$, where n is an integer. No representative is known in nature of the series whose mass numbers correspond to $4n+1$. Isotopes of this series have been produced in the laboratory in the form of Pa²³³, U²³³, and Np²³⁷. For the sake of simplicity in the following discussion, we will call this series the "neptunium series" after the member which represents the highest atomic number in the series as known at the present time.

Predictions have been made as to the types of radioactivity and order of magnitude of half life of the members of the series immediately following U²³³. On the other hand, there are vacant places in the table of isotopes of the elements above element 80, which correspond to $4n+1$ mass numbers, but which would remain vacant if the predicted modes of decay were found to be correct. It becomes necessary, therefore, in an experimental determination of the path taken by the decay chain, to be particularly careful at the points where divergence between theory and superficial expectations occur. One possibility which must be carefully examined at these points is that of branching into both alpha and beta decay.

The method followed in studying the Np series has consisted of carefully purifying samples of U²³³ of several milligrams weight, setting the material aside for from several days to a number of weeks, and then submitting the material to chemical procedures designed to extract thorium, radium and other expected members of the decay chain. When an appreciable amount of the radium isotopes have been extracted and purified, their decay to the lower members of the series may be followed, and extractions of lead, bismuth and various other members of the series attempted.

The chemical procedure usually followed has been to precipitate either lead or barium sulfate carrier precipitate from the U²³³ solution, to extract radium isotopes. An additional sulfate precipitation or two is made to remove any last traces of these isotopes from the uranium solution before extraction of the Th²²⁹ by means of lanthanum fluoride is attempted. The sulfate precipitates are then put through a series of three to five dissolutions and reprecipitations designed to purify the radium and possible lead isotopes from uranium, lead sulfide is precipitated to remove the lead isotopes present from the radium, and a final sulfate precipitation is made and the precipitate mounted for counting. Similarly, the lanthanum fluoride precipitate containing the thorium isotope is put through a series of dissolutions and reprecipitations to free it from uranium. In addition, argentic-peroxydisulfate oxidation cycles are interposed to eliminate any possible plutonium contamination which might exist. The final lanthanum fluoride precipitate is then mounted on a platinum plate for counting.

The procedures as outlined above are deficient for the following reasons. In the presence of considerable amounts of uranium, lead sulfate may not extract the radium completely. In addition, its chemistry diverges from that of radium at certain points, suggesting the possibility of losses during purification from U²³³.

When barium sulfate is used for the extraction of radium, it seems to adsorb about a third of the thorium present. This is undesirable for two reasons: it introduces the danger of a long-lived contamination in the radium, and it complicates the estimation of the yield of thorium from which the half-life of the thorium must be calculated. Likewise, it is not always possible completely to free the LaF_3 from uranium activity, which then contaminates the thorium and renders inaccurate the measurements on that isotope. Experiments are under way to develop a procedure which will avoid all of these undesirable features.

Another complication in the experiments is introduced by the presence in the U^{233} of minute amounts of U^{232} . Range determinations with mica absorbers have demonstrated the presence of approximately five U^{232} alphas per 10,000 U^{233} alphas. This corresponds to approximately one part in 10^7 of U^{232} in the uranium, as the ratio of the specific activities of the two isotopes is about 5×10^3 . U^{232} decays to radiothorium (1.9 year half life) which then leads through ThX (3.64 days), Tn , ThA , ThB (10.6 hours), ThC (60.5 minutes), and the extremely long range ThC' . Because the ThB and the ThC half-lives are longer than those of NpB and NpC , the lead and bismuth fractions isolated from decaying mixtures of ThX and NpX by procedures taking as much as half an hour between separation and counting should show only ThB and ThC activities. In experiments of this sort, the presence of ThB and ThC has actually been demonstrated. In order to circumvent this complication, it is necessary to set the radium fractions aside for several weeks to allow complete decay of the ThX , before significant experiments on the Np series members following the radium isotopes can be performed. In the discussions to follow, reference will be made only to experiments in which these precautions have been observed.

Th^{229} (RaDp) decays by alpha emission (contrary to some predictions) and the branching to beta emission, if it exists, seems to be quite low. The range of the alpha particles is fairly close to that of U^{233} , but precise measurements are not yet available. When freshly purified Th^{229} is allowed to stand over a period of time, alpha activity grows in at a rate corresponding to a half-life of approximately one month. Some initial perturbations are undoubtedly due to the presence of radio-thorium from decay of U^{232} . The half-life of RaDp is probably of the order of thousands of years, on the basis of yields obtained.

The radium preparations are alpha active, and decay with the expected rate of about one month half-life. For this isotope also, predictions of beta activity have been made. The data available to date do not eliminate the possibility of a branching decay. When a sample of Ra^{226} (NpX) is allowed to stand in an alpha counter for several hours and then removed, the counter shows signs of contamination. This is undoubtedly due to active deposit from neptunium (Np^{231}).

Attempts to determine the half-life of the emanation by following its growth in freshly purified NpX indicate that its half-life must be quite short. It is not possible to state whether the emanation is alpha or beta active. Attempts to isolate polonium or element 85 from solutions of NpX have been unsuccessful, indicating that any isotopes of these elements which are members of the chain are quite short-lived.

Experiments in which lead sulfide, bismuth sulfide or bismuth phosphate have been precipitated from solutions of NpX have shown the same decay period, an alpha activity of approximately 44 minute half-life with a branching decay which has given one component of very long range which probably represents NpC' . It has not yet

S-72-12

been possible to determine the branching ratio. These experiments indicate that NpB, the first lead isotope in the series, must be rather shorter lived than 44 minutes.

When lead sulfide is separated from NpX solutions, which have stood for a number of hours, it is possible to demonstrate the presence of the already known activity of Pb^{209} (3.3 hours). The presence of the activity is to be expected, regardless of branching at any of several places earlier in the decay chain, and its presence is confirmation of the series being handled.

In summary, we may say that the Np series goes from Np^{237} through beta active Pu^{233} to U^{233} , which then goes by successive alpha emissions through Th^{229} and Ra^{225} . The exact path of decay from the emanation of mass number 221 to Pb^{209} is uncertain, but it involves three alpha decays and two beta decays in some combination as yet not definitely determined.

351 MLC 1901 Extraction of U²³³. F. Hagemann, N. Mellman, M. Studier.

Recently uranium was extracted from several pounds of irradiated thorium "carbonate" using a continuous batch type extractor. The apparatus and procedure used will be described in detail in a later report. Mention only is made at this time of difficulties encountered due to the ether used as a solvent.

The extracted uranium was removed from the ether by distilling the ether off over water. A large amount of organic residue, mostly water soluble, remained. Upon salting and again extracting the uranium with ether, it was found that the uranium could not be reextracted from the ether into water. It was necessary to evaporate the ether and destroy the organic residue with HNO_3 - H_2O_2 and aqua regia before the usual extraction procedure could be used. Whether the obnoxious material was present originally as an impurity in the ether or was formed by decomposition during extraction or distillation is not known at present.

Hints of similar behavior were found when low grade ether was used in an early extraction experiment. The phenomenon points up the necessity for careful checking on the ether when extraction is reduced to a routine basis.

S-72-14

351 MLC 1902 Extracting solvents for uranium. E. K. Hyde and M. J. Wolf.

The use of ethyl ether and hexane as extractants for uranium from thorium was discussed in CC 2165. The usefulness of a number of other solvents for the same purpose has been investigated. Since the behavior of protoactinium in the extraction is also of interest, some of the more promising solvents were tested for protoactinium extraction.

Procedure: The procedure was modified somewhat from that described before. In each experiment 5 ml of solution, made up to the desired concentration in $\text{Th}(\text{NO}_3)_4$, HNO_3 , NH_4NO_3 and/or $\text{Al}(\text{NO}_3)_3$ and U^{233} tracer, were shaken with an equal volume of solvent in a glass-stoppered centrifuge cone. After equilibration, two 2 ml samples of the solvent were pipetted off and delivered to clean centrifuge cones. Oxalic acid was added to the first sample to precipitate thorium oxalate. The oxalate (and hence the thorium) was determined by dissolving the washed precipitate in an excess of standard ceric sulfate and back-titrating with ferrous ammonium sulfate.

The solvent in the second sample was removed by steam distillation. After precipitating thorium as ThF_4 from the aqueous residue, the supernatant solution containing uranium was evaporated in a platinum dish and transferred to a plate for radioactive assay. The procedure for protoactinium was similar to that used for U^{233} , except that thorium was not precipitated. A solution 2 N in $\text{Th}(\text{NO}_3)_4$, 1.9 N in NH_4NO_3 , 1.1 N in HNO_3 and containing from 12,000 to 19,000 counts of Pa^{233} per minute per ml was prepared. After equilibration with solvent as described above, a 2 ml aliquot of the solvent was steam distilled, and the aqueous residue was evaporated off directly on a platinum plate for beta counting.

Blank determinations were run in every case.

Values obtained by these procedures are accurate to an estimated $\pm 5\%$ with relative errors somewhat less.

The results tabulated below (Table 2) show the per cent of each element extracted into the solvent from an equal volume of solution which in the case of uranium and thorium had the standard composition 2 N $\text{Th}(\text{NO}_3)_4$, 1 N HNO_3 and 3 N NH_4NO_3 , and in the case of protoactinium had the composition mentioned above (2 N $\text{Th}(\text{NO}_3)_4$, 1.1 N HNO_3 , 1.9 N NH_4NO_3).

A-72-15

Table 2

Extraction of Uranium, Thorium and Protactinium
from Standard Nitrate Solutions

Type	Solvent	% U Extracted	% Th Extracted	% Pa Extracted
"Cellosolve" Derivatives	Benzyl cellosolve	65	21	--
	Diethyl cellosolve	50	24	--
	2-ethyl butyl ether of ethylene glycol	59	7	--
	Dibutyl carbitol	59	2.7	0.15
Ketones	methyl ethyl ketone - 15% toluene	47	22	--
	methyl n-propyl ketone	53	11	--
	methyl iso-butyl ketone (hexone)	57	2	20
	methyl n-amyl ketone	47	0.9	2.9
	Di-isopropyl ketone	56	0.3	63
	cyclohexanone	--	11	--
	methyl cyclohexone	--	large	--
Esters	ethyl acetate	49	1.8	0.26
	amyl acetate	31	0.3	31
	2-ethyl butyl acetate	8.7	0.02	--
	methyl amyl carbinol	34	4.7	--
	nitro methane	--	large	--
	Diethyl ether	35	negl.	0.19

S-72-16

Detailed studies have been made on the distribution of uranium and thorium between the solvent and a solution of varying thorium nitrate, ammonium nitrate and nitric acid concentration for the solvents ethyl acetate, methyl n-amyl ketone, di-isopropyl ketone and dibutyl carbitol (See Figures 1 - 3). The data for the dibutyl carbitol were obtained by N. Hellman.

The conclusions to be drawn from these data are the following:

(1) The cellosolve derivatives in general are good solvents for uranium but are unsatisfactory because of their affinity for thorium. In addition certain undesirable physical characteristics argue against their use. Dibutyl carbitol is fairly promising because of its high uranium extraction and very low protactinium extraction. Its principal defect is that it removes thorium in quantities larger than might be desirable.

(2) The ketones as a class show some promise. The uranium-thorium separation effected by hexone, methyl n-amyl ketone, and di-isopropyl ketone is quite good. Unfortunately the 30% extraction of Pa by hexone and the 2.9% extraction by methyl n-amyl ketone render them of little use for an initial "decontamination" separation of U^{235} from both Pa^{233} and thorium. Di-isopropyl ketone is an even better Pa solvent but here the Pa extraction is so high and the thorium extraction so low that the possibility of the initial separation of uranium together with protactinium from thorium, followed either by a cooling period during which the Pa could decay to uranium or by an extraction with a second solvent in which Pa is insoluble, presents itself. The alicyclic ketones are useless because of high thorium extraction.

(3) Ethyl acetate combines high uranium extraction with low Pa extraction. It, like dibutyl carbitol, removes somewhat more thorium than is desirable. In addition it is susceptible to acid hydrolysis. However, ethyl acetate and dibutyl carbitol appear to be the best substitutes for ether in the process now used to isolate U^{235} .

(4) The extraction of uranium and thorium into any given solvent is a function of total nitrate concentration and of the nature of the salting agent. Aluminum increases the uranium extraction somewhat but offsets this advantage with a very marked increase in thorium extraction. This differs from the behavior of aluminum in ether (see Hellman's report) where uranium extraction is greatly increased at only a small sacrifice in decontamination from thorium. The di-isopropyl ketone curves indicate that thorium and ammonium nitrate may be interchanged with but little effect on uranium extraction.

The small insert graph on the methyl n-amyl ketone graph shows that with this solvent uranium extraction is unaffected by acid concentration as long as a small amount (enough to keep the uranium in the uranyl state) is present. The thorium removal is markedly increased with increasing acid. Hence in extraction operations, the acid concentration should be kept low.

S-72-17

351 MLC 1912 Factors Affecting the Extraction of Uranium and Thorium by Organic Solvents, Especially Ether.

A. Extraction of HNO_3 and Thorium by ether from thorium nitrate and ammonium nitrate solutions. M. J. Wolf and N. N. Hellman. The extraction of nitric acid and of thorium from aqueous solutions by diethyl ether was studied as a function of total nitrate, thorium, and nitric acid concentration. The total nitrate concentration was adjusted by the use of either NH_4NO_3 or $\text{Th}(\text{NO}_3)_4$.

Solutions containing the desired concentration of nitrate, thorium, and nitric acid were shaken vigorously for ten minutes in glass-stoppered centrifuge tubes with an equal volume of diethyl ether. A 2 to 4 ml aliquot of the ether was drawn off and evaporated over distilled water, and the latter was then analyzed for acid and thorium. The analyses of acid and thorium were done on separate samples. Thorium was determined by precipitating the thorium with oxalic acid, dissolving the precipitate in an excess of standard ceric sulfate and back titrating with standard ferrous iron solution. Where the $\text{Th}(\text{NO}_3)_4$ concentration was less than 1 N in the aqueous phase, practically no thorium was extracted by the ether, and the acid was therefore determined by titration of the water over which the ether had been evaporated.

Where appreciable amounts of thorium were extracted by the ether, this procedure was not applicable since all of the thorium present reacted with alkali below the indicator end-point. Such solutions were, therefore, titrated potentiometrically using a Beckman pH meter with a glass electrode and a calomel half-cell. A preliminary titration of a known solution containing known acid and thorium nitrate concentrations was made against standard alkali. The break occurred in the curve at about pH 2.5 where thorium begins to interfere. Acceptance of this point as the acid end-point introduces an error of only -2.6% which can readily be corrected for.

The results on the extraction of nitric acid are summarized in Table 3 and Figure 4. Up to 65% of the nitric acid in the aqueous layer is extracted by ether as the total nitrate concentration reaches 12 N. Varying the acid concentration between the limits 0.5 N and 2 N has no marked influence on the percentage of acid extracted by the ether; the absolute amount of acid extracted in this range being proportional to its original concentration in the aqueous phase. Thorium nitrate salts out more nitric acid into the ether than does the stoichiometrically equivalent amount of ammonium nitrate. In extractions of U^{233} by ether using NH_4NO_3 as a salting agent the total nitrate concentration is generally 8-10 N. Under these conditions it can be assumed that the extraction of nitric acid is roughly about as complete as the uranium extraction. Hence, unless adequate provision is made, the nitric acid thus extracted may seriously interfere in the extraction of uranium from ether into a second aqueous phase.

The extraction of thorium into ether was found to vary with nitric acid concentration, thorium concentration and total nitrate normality (Fig. 1 and Table 4). It is interesting to note that there is apparently a minimum total nitrate concentration which must be exceeded before the thorium begins to extract detectably into ether and that beyond this point the extraction occurs at an exponentially increasing rate. The effect of increasing either acid or thorium concentration above the minimum is to increase continually the percentage extraction of thorium. Nitric acid is the more marked in its effect.

Table 3

Extraction of HNO_3 by Ether from Aqueous Solutions of Varying Acid, Ammonium Nitrate and Thorium Concentrations

Solution Composition	Total Nitrate Concentration of Aqueous Phase	% HNO_3 Extracted by equal volume of ether
0.5 N HNO_3 , 1.0 N $\text{Th}(\text{NO}_3)_4$ Varying NH_4NO_3	2.5	14
	4.5	26
	6.5	36
	8.5	50
	10.5	62
1.0 N HNO_3 , 1.0 N $\text{Th}(\text{NO}_3)_4$ Varying NH_4NO_3	3	18
	5	31
	7	42
	9	56
	11	63
2.0 N HNO_3 , 1.0 N $\text{Th}(\text{NO}_3)_4$ Varying NH_4NO_3	4	27
	6	36
	8	46
	10	57
	12	64
1.0 N HNO_3 , 0.0 N NH_4NO_3 Varying $\text{Th}(\text{NO}_3)_4$	2	11
	5	41
	8	78
	10	77

8-72-19

Table 4

Extraction of Thorium by Ether as Influenced by Thorium,
Nitric Acid, and Total Nitrate Concentration

Initial Concentrations in Aqueous Phase, Normality			% Thorium Extracted by Equal Volume of Ether
Total Nitrate [†]	Nitric Acid	Thorium Nitrate	
10	1	9	30
9	0	1	0.00
9	0	2	0.11
9	0	3	0.25
9	0.5	1	0.00
9	0.5	2	0.32
9	0.5	3	0.30
9*	0.5	3	0.20
9	1.0	1	0.25
9	1.0	2	0.52
9	1.0	3	0.77
9	2.0	1	1.15
9	2.0	2	2.45
9	2.0	3	3.40
8	1.0	7	6.40
6	0.0	1	0.00
6	0.0	2	0.00
6	0.0	3	0.00
6	1.0	1	0.00
6	1.0	2	0.00
6	1.0	3	0.00
6	2.0	1	0.00
6	2.0	2	0.49
6	2.0	3	1.03
3	0.	1	0.00
3	0	2	0.00
3	0	3	0.00
3	0.5	1	0.00
3	0.5	2	0.00
3	1.0	1	0.00
3	1.0	2	0.00
3	2.0	1	0.00

[†]The difference between the total nitrate concentration and the sum of the nitric acid and $\text{Th}(\text{NO}_3)_4$ concentrations was made up with NH_4NO_3 .

*50 cc batch stirred with electric stirrer 10 min. All other data on 5 cc quantities shaken by hand.

S-72-20

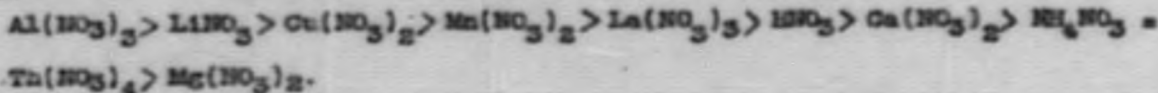
B. Influence of various nitrates on the extraction of uranium and thorium by ether. H. H. Bellman. An investigation of the influence of various nitrates on the extraction of uranium and thorium into ether was made in order to determine the most suitable agent to accomplish the salting of traces of uranium into ether to achieve its separation from accompanying thorium. The influence of HNO_3 , NH_4NO_3 , LiNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, $\text{Al}(\text{NO}_3)_3$, and $\text{Th}(\text{NO}_3)_4$ were determined (Table 5 and accompanying plates).

The procedure employed consisted of shaking 5 ml of ether with 5 ml of aqueous phase of appropriate composition with respect to salting agent, thorium, and U^{233} tracer. This was done in a glass stoppered 15 ml centrifuge cone. After 10 minutes shaking the tubes were centrifuged to effect a clear separation of the layers. A 2 ml aliquot was then taken from the ether layer, the ether evaporated over water, and the resulting aqueous solution analyzed for thorium and uranium. The thorium analyses were performed by the precipitation of the oxalate by oxalic acid in 1 N HCl and the subsequent oxidimetric determination of the oxalate by titration with Ce^{+4} . Uranium analyses were made by counting the extracted U^{233} . Five to eight thousand counts per minute of tracer were used in each experiment. It was found that variation in the amount of tracer from 100 to 100,000 c/m in 5 ml volume did not change the percentage extraction. In those studies where thorium was present (except those testing $\text{Th}(\text{NO}_3)_4$ as a salting agent) its concentration was held at 1 N. Nitric acid was present in 0.5 N concentration in all experiments.

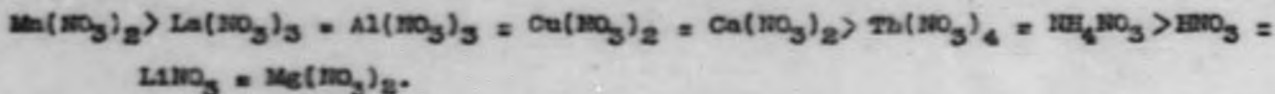
All the salts tested except $\text{Mg}(\text{NO}_3)_2$ were able to induce uranium extractions of better than 60%. The most effective salting agent was $\text{Al}(\text{NO}_3)_3$. It was found that HNO_3 , LiNO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, and $\text{Al}(\text{NO}_3)_3$, which are capable of effecting appreciable salting of thorium as well as uranium into ether, would produce markedly greater uranium extraction if thorium were absent. The divergence of the percentages of uranium extraction in the presence or absence of thorium becomes most marked at the total nitrate concentration at which the thorium begins to salt detectably into the ether. This suggests "counter salting" of the uranium from ether by other salts or acid which may also have been salted into the ether. This "counter salting" concept may be used to explain the decrease in uranium extraction encountered with thorium, aluminum and copper nitrates at high nitrate concentrations.

Thorium extraction apparently is not detectable until the nitrate concentration is 3-5 N, the exact normality depending on the salt. Ammonium, calcium, and magnesium nitrates effect practically no extraction of thorium, less than 1% being extracted by the ether at the nitrate concentration optimum for the extraction of uranium. Nitric acid, $\text{Al}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ are marked in producing thorium extraction--as much as 54% extraction occurring with $\text{Cu}(\text{NO}_3)_2$ at 11 N total nitrate.

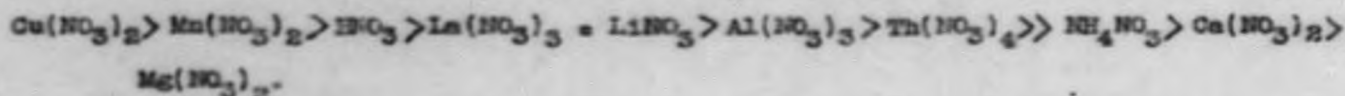
In the absence of thorium the extraction effects of these salts on uranium, judged by the maximum extraction they induced within the concentration range studied, are as follows:



In the presence of thorium the salts, rated on the maximum uranium extraction they are capable of effecting within the limits of concentration studied, are as follows:



The relative effect of these salts in producing thorium extraction is as follows:

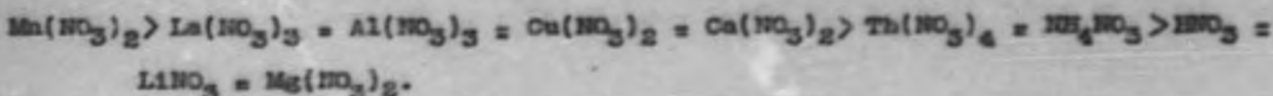


Though the percentage extraction effected by these various salts will change in different solvents, it is expected that the relative salting abilities will remain the same.

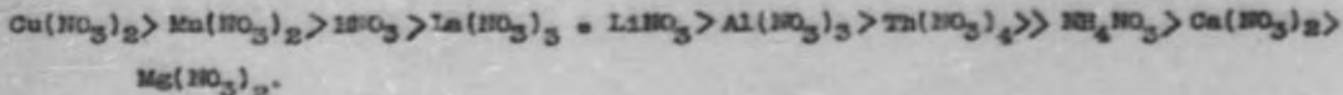
As judged by these data $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 would be very suitable for extraction purposes, where it is intended to free the uranium from thorium. Aluminum nitrate might be used also, since it achieves maximum uranium extraction at total nitrate normalities so low that thorium extraction has not become marked. However, this possibility may exist only for ether, since in other solvents the effects on uranium extraction relative to thorium extraction may not be the same and hence thorium extraction may occur at the salt concentrations necessary to achieve maximum uranium extraction.

1-72-22

In the presence of thorium the salts, rated on the maximum uranium extraction they are capable of effecting within the limits of concentration studied, are as follows:



The relative effect of these salts in producing thorium extraction is as follows:



Though the percentage extraction effected by these various salts will change in different solvents, it is expected that the relative salting abilities will remain the same.

As judged by these data $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 would be very suitable for extraction purposes, where it is intended to free the uranium from thorium. Aluminum nitrate might be used also, since it achieves maximum uranium extraction at total nitrate normalities so low that thorium extraction has not become marked. However, this possibility may exist only for ether, since in other solvents the effects on uranium extraction relative to thorium extraction may not be the same and hence thorium extraction may occur at the salt concentrations necessary to achieve maximum uranium extraction.

1-72-22

Table 5

Extraction of Uranium and Thorium by Ether
as Influenced by Various Salting Agents

Salting Agent	Total Nitrate Normality	Thorium Normality	% Uranium Extracted	% Thorium Extracted
HNO ₃	7	1	47	
	7	1	36	21
	5	1	40	3.3
	3	1	10	0.1
	7	0	62	
	5	0	52	
	3	0	23	
LiNO ₃	7.5	1	53	
	7	1	66	19
	5	1	31	
	5.5	1	25	2
	2	1	22	0
	7.5	0	81	
	5.5	0	74	
	3.5	0	36	
2	0	10		
NH ₄ NO ₃	12	1	59	1.2
	9	1	57	0.8
	7	1	47	0.5
	5	1	30	0.1
	3	1	8	0.0
	10	0	59	
	5.5	0	25	
Ca(NO ₃) ₂	7.5	1	59	0.0
	5.5	1	25	0.0
	3.5	1	11	0.0
	7.5	0	63	
	5.5	0	32	
	3.5	0	13	
Mn(NO ₃) ₂	8.5	1	73	43
	6.5	1	70	
	7.0	1	66	
	6.0	1		5.5
	3.5	1	21	0.0
	7.3	0	87	
	5.0	0	74	
	2.5	0	18	
Mg(NO ₃) ₂	9.5	1	44	0.0
	6.5	1	19	0.0
	3.5	1	9	0.0
	9.5	0	38	
	6.5	0	19	
	3.5	0	3	

1-72-23

Table 5 (contd)

Extraction Agent	Extraction Normality	Thorium Normality	% Uranium Extracted	% Thorium Extracted
Cu(NO ₃) ₂	11.0	1	59	52
	8.0	1	62	15
	5.0	1	50	0.5
	3.0		12	0.0
	10.5	0	67	
	7.5	0	91	
	5.0	0	69	
	2.5	0	12	
La(NO ₃) ₃	6.5	1	39	2.1
	4.5	1	18	0.2
	4.5	1	18	
	2.5	1	5	0.0
	5.0	0	93	
	2.5	0	61	
Al(NO ₃) ₃	7.5	1	57	17.6
	5.5	1	63	2.8
	2.5	1	13	0.0
	6.0	0	96	
	4.0	0	54	
	2.0	0	19	
Th(NO ₃) ₄	11.0	—	52	11.4
	9.0	—	58	8.0
	5.0	—	32	0.14
	3.0	—	8	0.0

8-72-24

353 MLC 1909 Analysis of ore samples for protoactinium. Q. Val. Winkle and J. Sedlet.

It was reported in CC 2165 that certain carbonate residues obtained in the uranium extraction from pitchblende contained up to 1.2 parts per million of protoactinium. This value was obtained by measuring the amount of alpha activity carried by MnO_2 from an HNO_3 solution to which thorium nitrate had been added. The thorium diluted out the ionium which otherwise would be partially carried by the MnO_2 . It had been assumed that the two principal alpha activities present were protoactinium and ionium, and that the alpha activity carried on MnO_2 represented the protoactinium fraction. Apparent confirmation was obtained through range measurements on the alpha particles emitted from the MnO_2 .

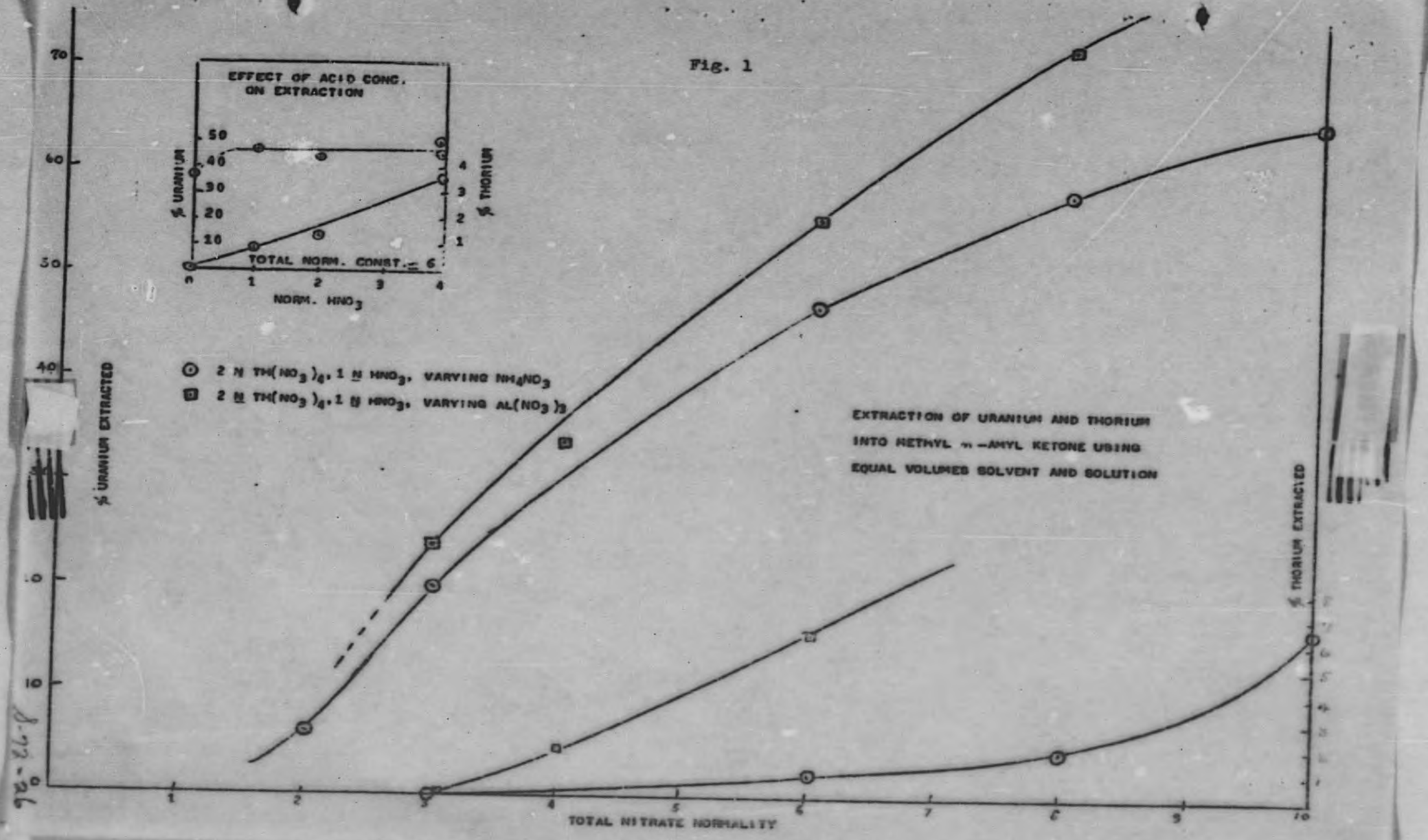
More recently experiments have been performed in which such alpha-bearing MnO_2 was reprecipitated in the presence of HF. Under these conditions, it was found that the original alpha activity was carried almost completely on the MnO_2 , while beta-active Pa^{233} which had been added to the solution remained almost completely in the supernatant solution. Further detailed experiments indicated that the alpha activity which had been carried from the original solution was polonium and not protoactinium. Range measurements were again made which showed the alpha range to be that of polonium, 3.87 cm, rather than protoactinium, 3.67 cm.

A new series of experiments was undertaken in which use was made of zirconium phosphate carrier which was shown by tests to carry protoactinium quantitatively while carrying about 10% of polonium activity and perhaps 1% of radium activity. These experiments showed that although the solution obtained by treating the carbonate fractions with HNO_3 contained no significant amounts of protoactinium, the silica residue from the same fractions contained alpha activity which carried on zirconium phosphate and which could be distinguished from ionium by carrying on MnO_2 in the presence of gross amounts of thorium. This activity was likewise distinguishable chemically from polonium and radium (not carried on MnO_2 or $PbSO_4$ from HF solution). The amount of this alpha activity is such that it represents approximately 0.3 parts per million of protoactinium in the original carbonate material. Detailed study of the alpha range and other identifying characteristics of this activity are under way.

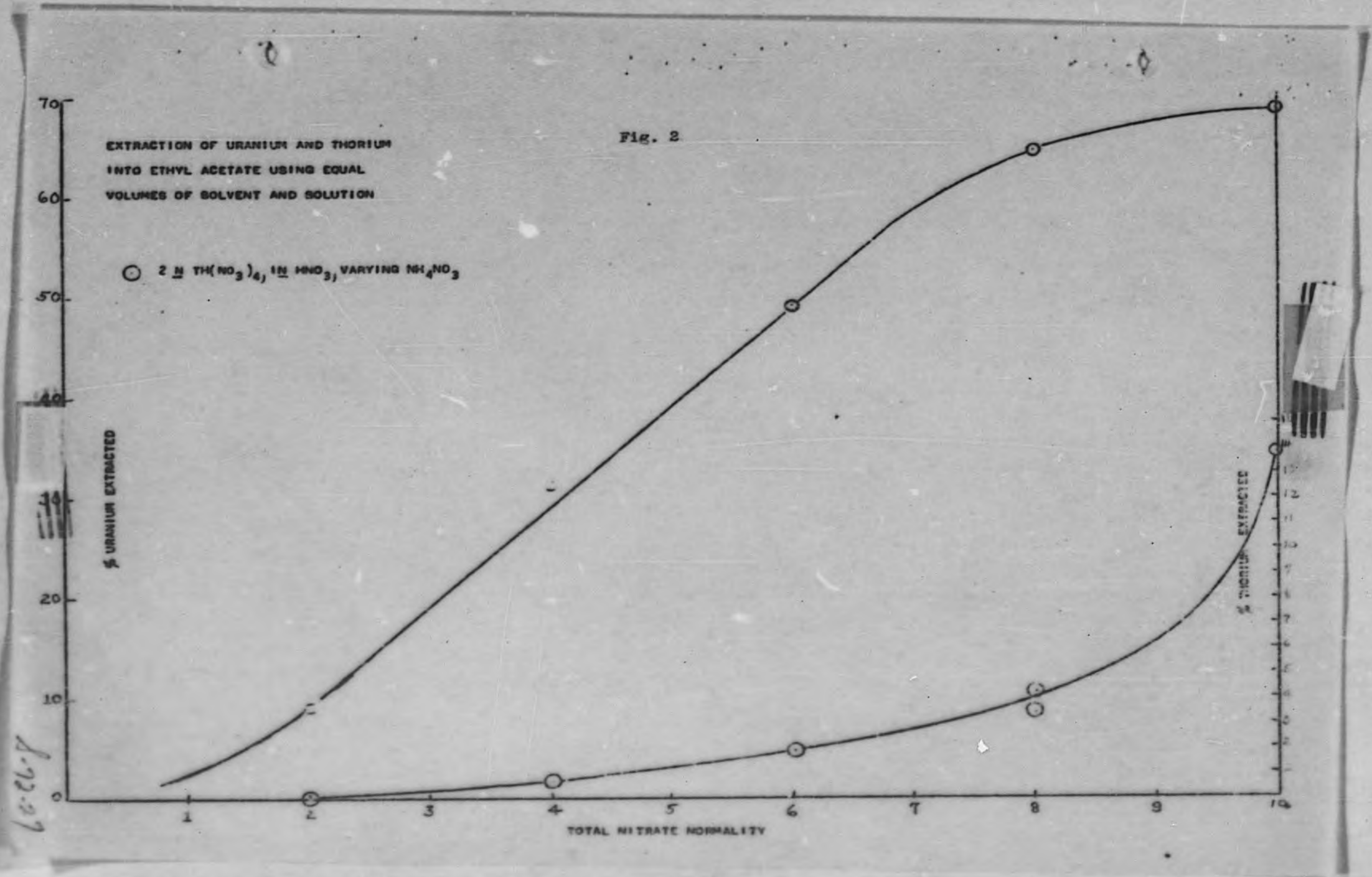
In addition to these carbonate residues, two other fractions obtained from the pitchblende treatment were tested for protoactinium. One of these is the aqueous residue obtained when the uranium is extracted by ether for purification purposes (the "Mallinckrodt" residue). The other fraction is the undissolved mixture of sulfates and other insoluble compounds left behind when the uranium is first extracted from the pitchblende. It is this fraction which contains the radium originally present in the ore. The "Mallinckrodt" residue showed essentially no protoactinium present in its acid soluble portion (silica not tested), while the sulfate fraction contained not more than perhaps 0.4 parts per million of protoactinium.

S-72-25

Fig. 1

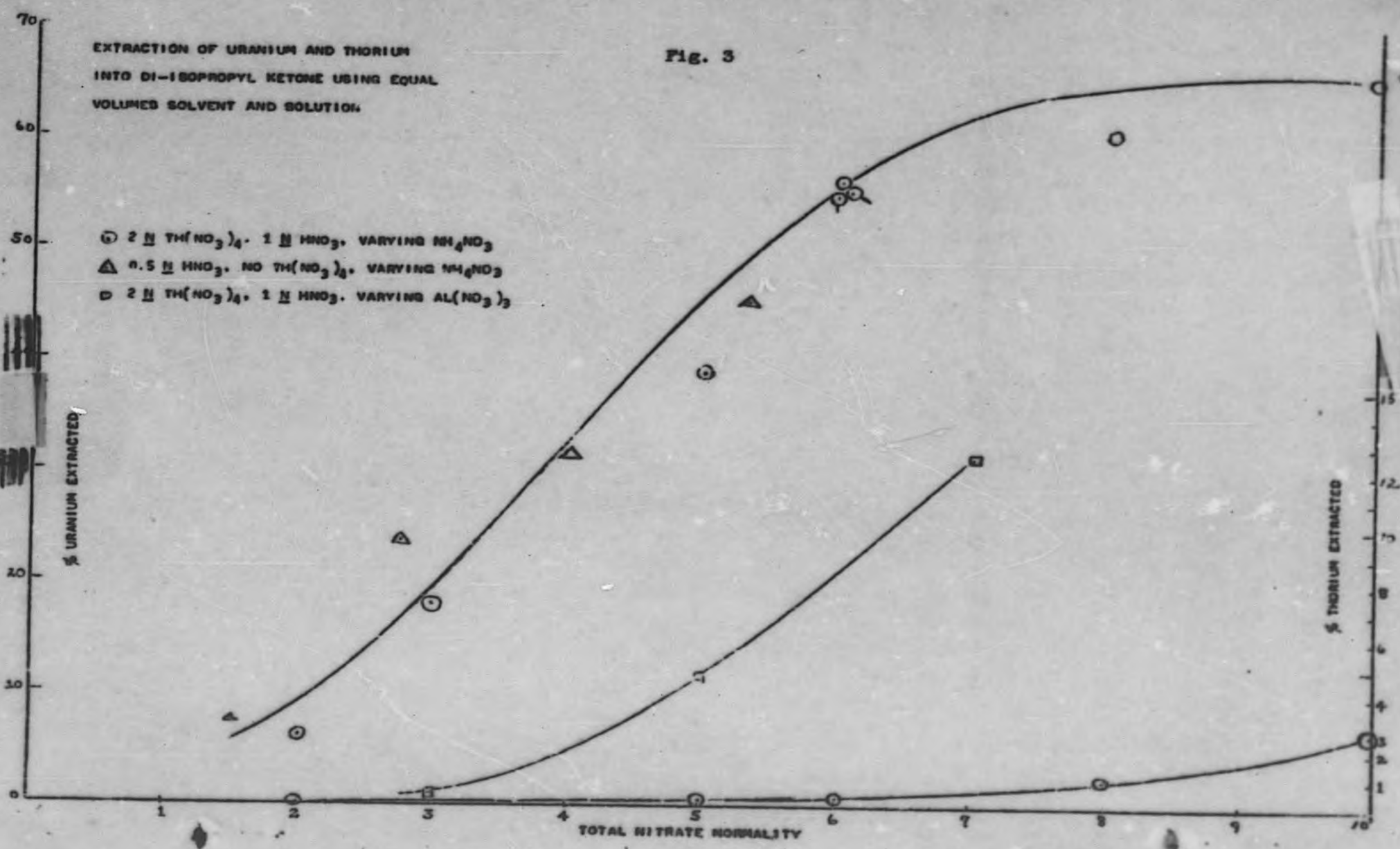


8-72-26



EXTRACTION OF URANIUM AND THORIUM
 INTO DI-ISOPROPYL KETONE USING EQUAL
 VOLUMES SOLVENT AND SOLUTION.

Fig. 3



S-72-28

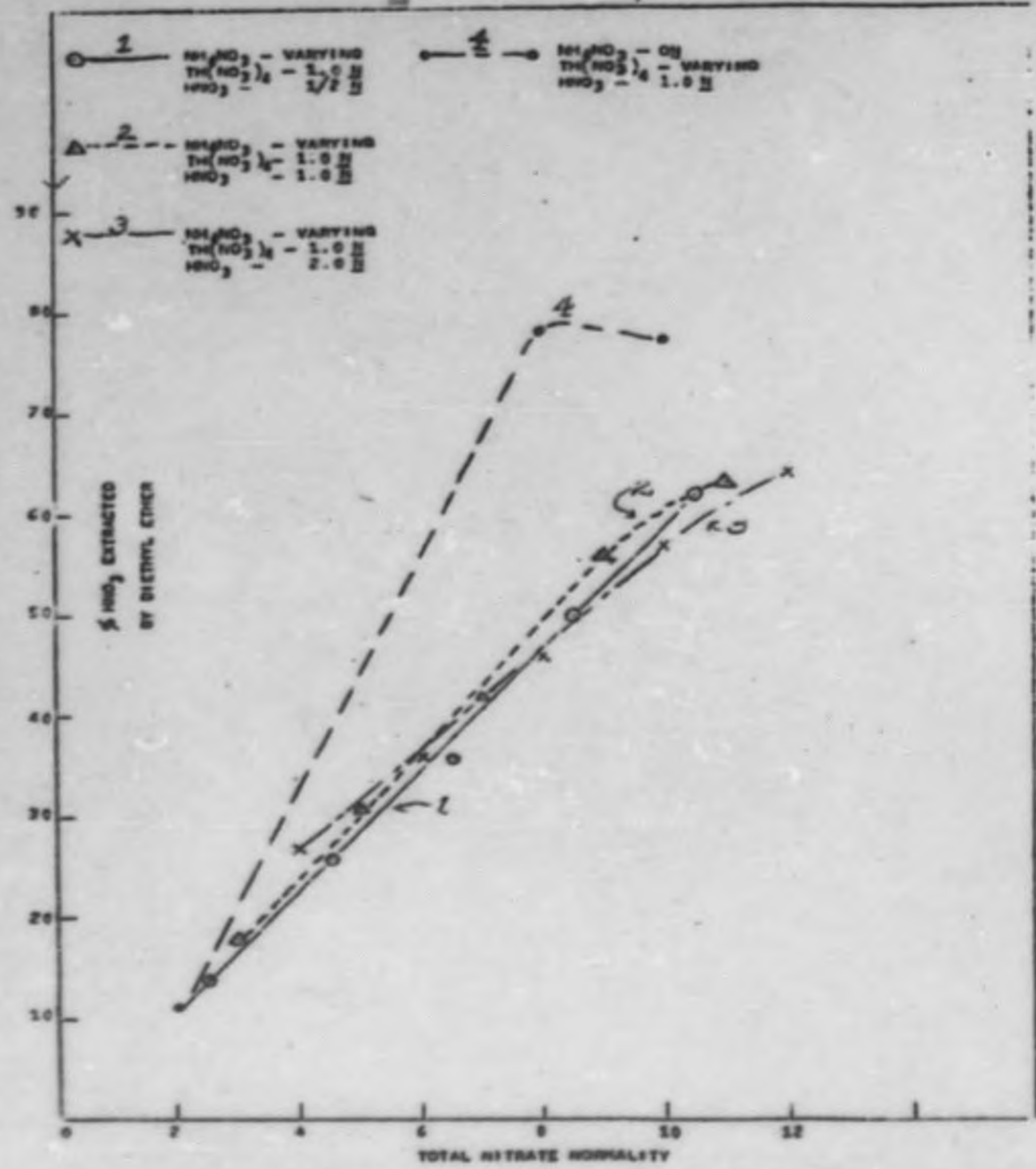


FIG. 4 THE EXTRACTION OF NITRIC ACID AS INFLUENCED BY AMMONIUM NITRATE, THORIUM NITRATE AND NITRIC ACID CONCENTRATION.

1-72-29

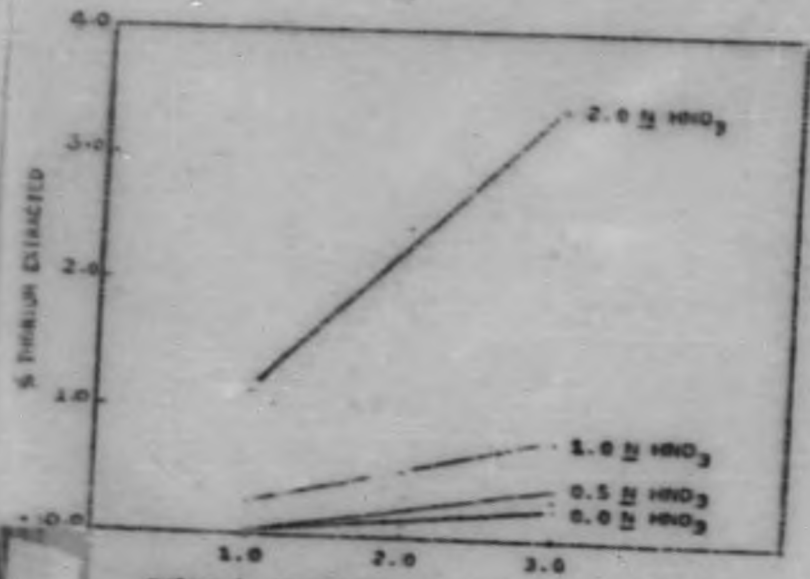
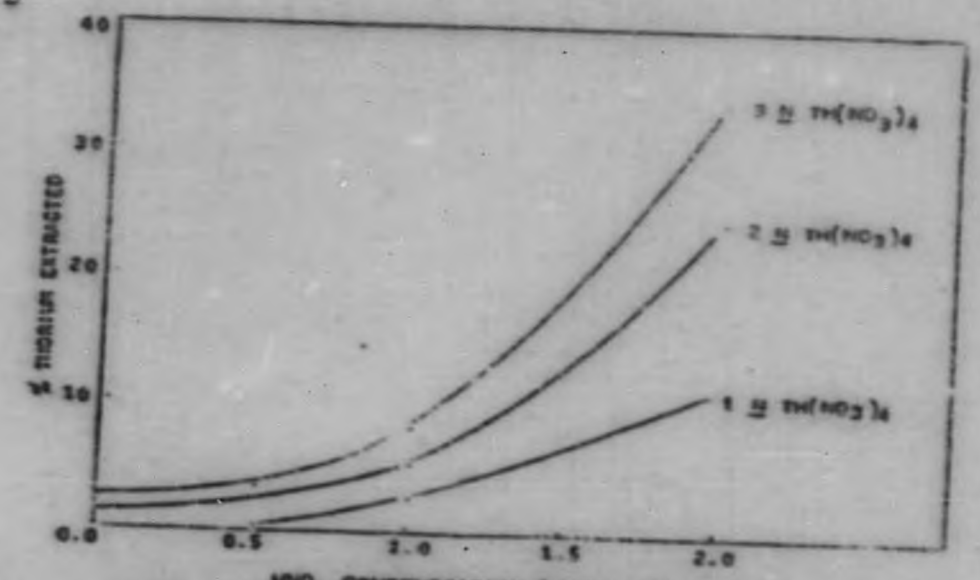
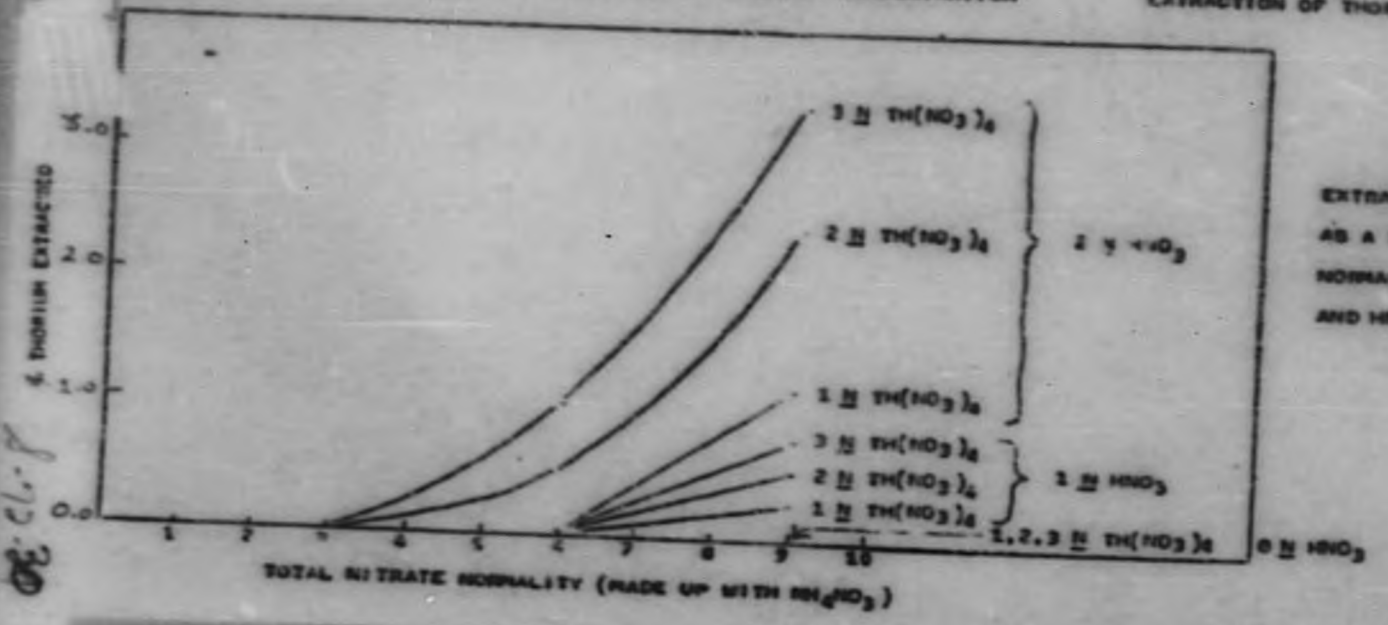


FIG. 5
 $\text{Th}(\text{NO}_3)_4$ CONCENTRATION (TOTAL $\text{NO}_3 = 9 \text{ N}$)
 EXTRACTION OF THORIUM AS A FUNCTION OF THORIUM CONCENTRATION



HNO_3 CONCENTRATION (TOTAL $\text{NO}_3 = 9 \text{ N}$)
 EXTRACTION OF THORIUM AS A FUNCTION OF ACID CONCENTRATION



EXTRACTION OF THORIUM INTO ETHER
 AS A FUNCTION OF TOTAL NITRATE
 NORMALITY, $\text{Th}(\text{NO}_3)_4$ CONCENTRATION,
 AND HNO_3 CONCENTRATION

Handwritten note: 1.2.3 N $\text{Th}(\text{NO}_3)_4$

Figs. 6 - 15

- = Uranium extraction from solutions containing 0.5 N nitric acid and varying normality salting agent to make up the aqueous phase to the indicated total nitrate concentration.
- ⊖ = Uranium extraction from solutions containing 0.5 N nitric acid, 1 N thorium nitrate, and varying normality salting agent to make up the aqueous phase to the indicated total nitrate concentration.
- = Thorium extraction from solutions containing 0.5 N nitric acid, 1 N thorium nitrate and varying normality salting agent to make up the aqueous phase to the indicated total nitrate concentration.

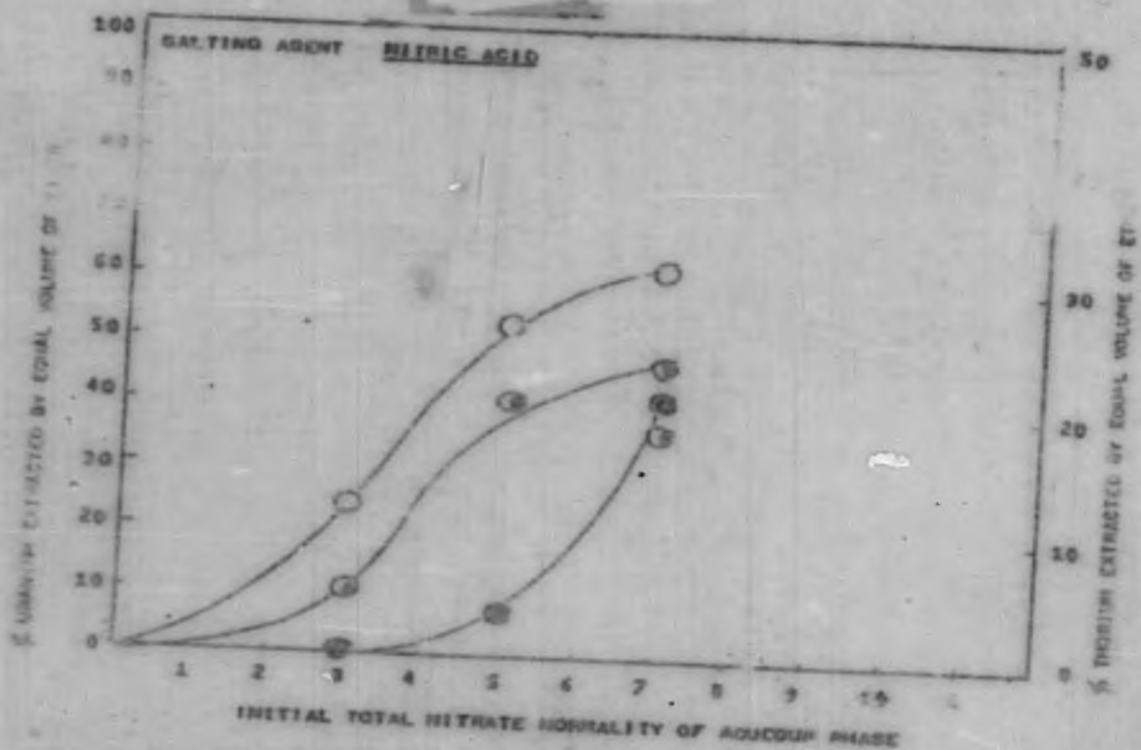


Fig. 6

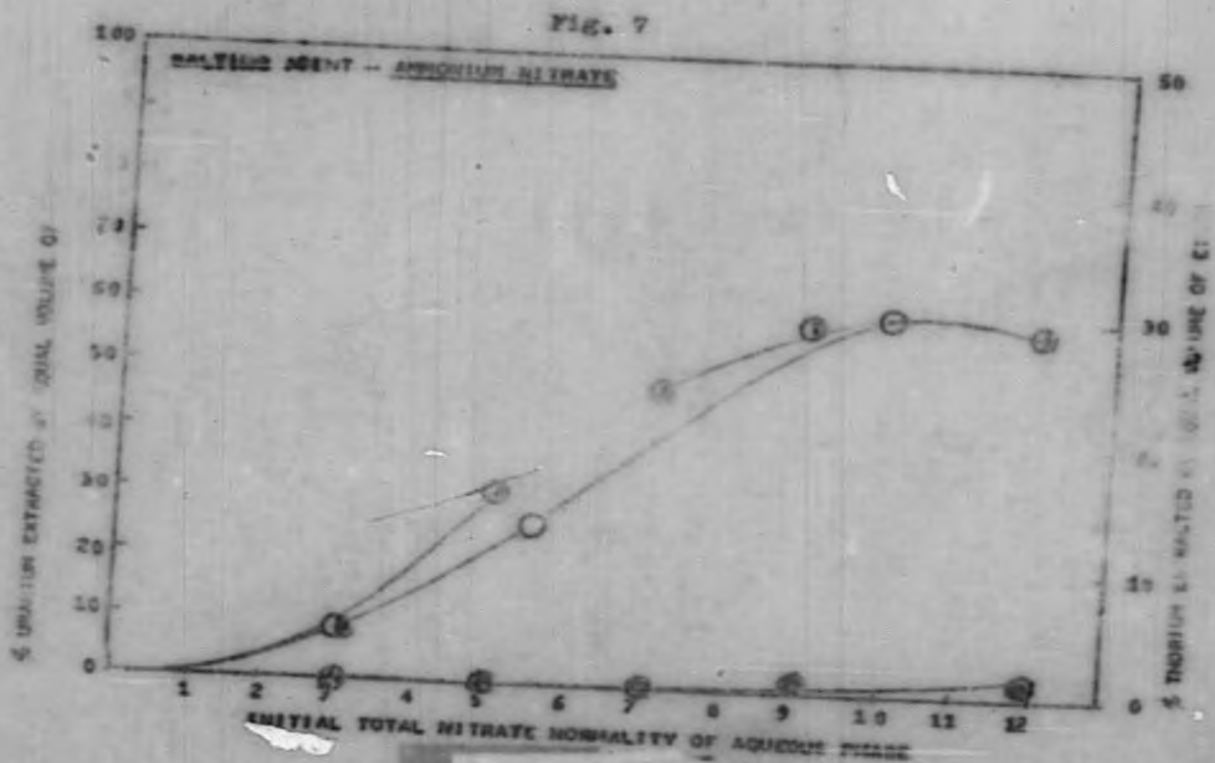


Fig. 7

S-72-32

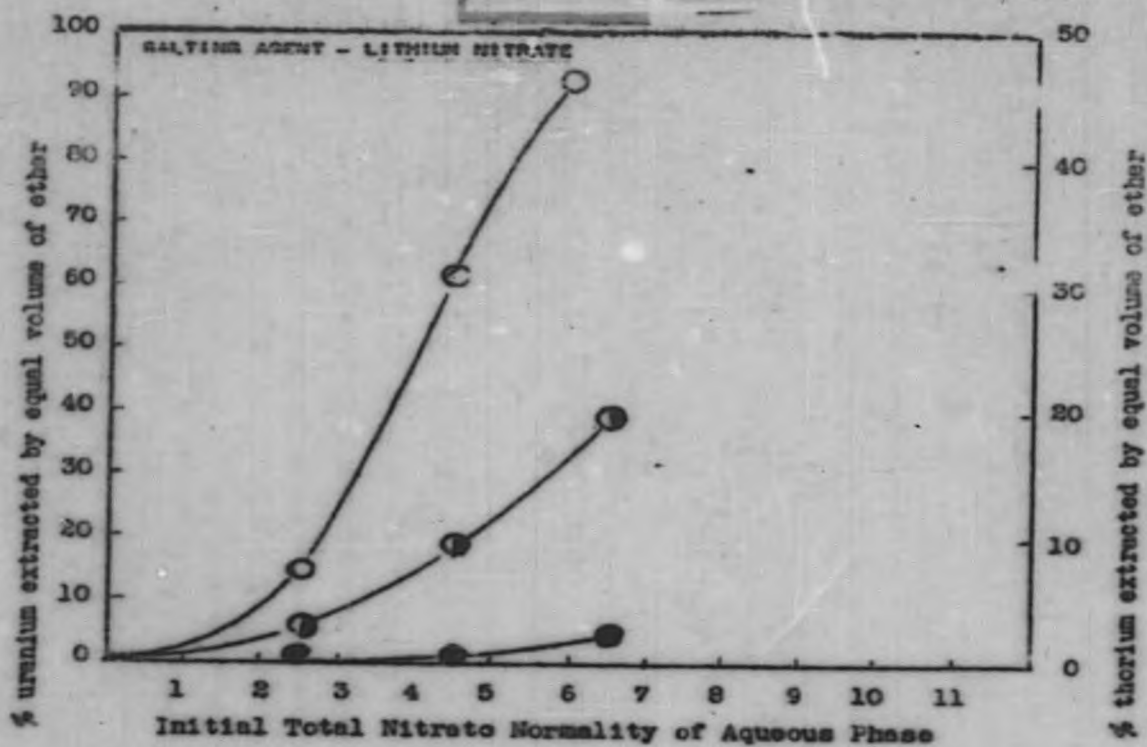
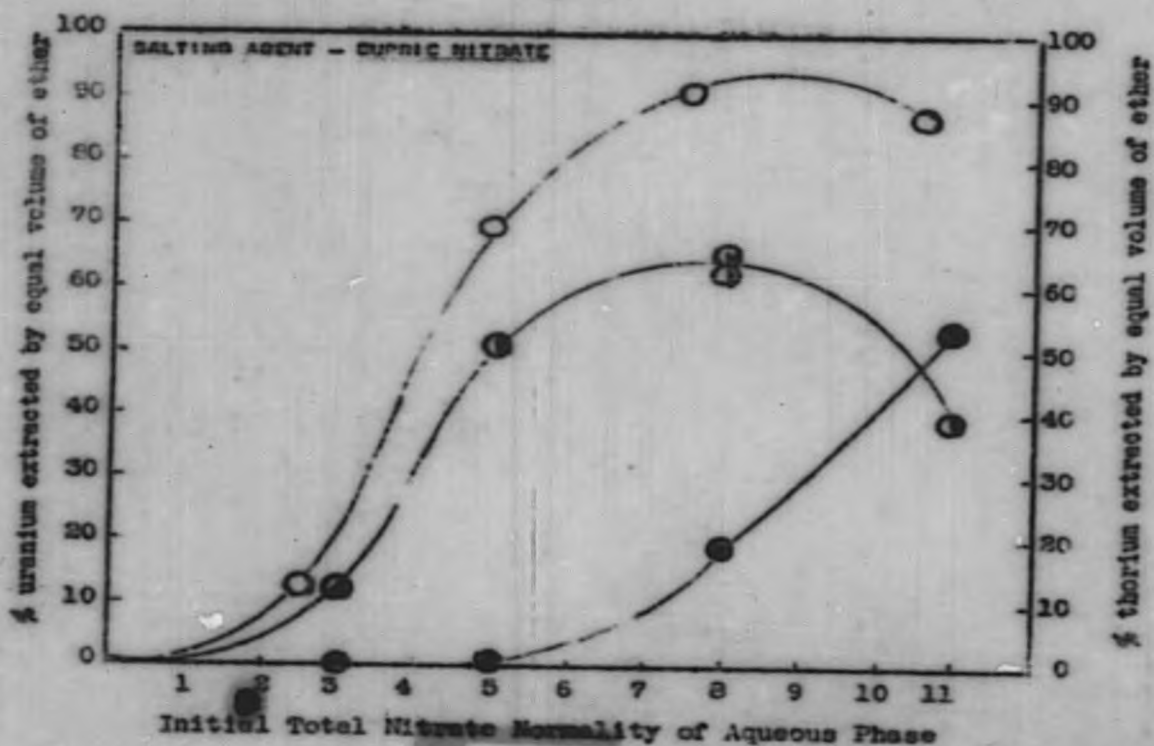


Fig. 8

Fig. 9



L-72-33

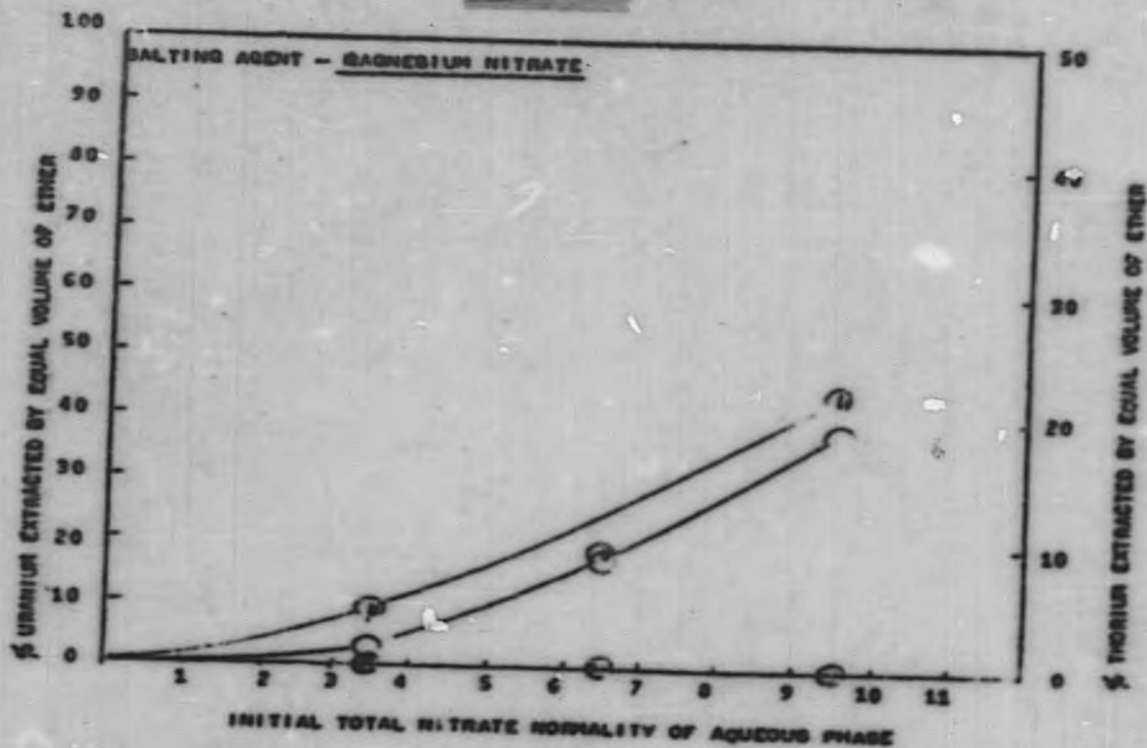
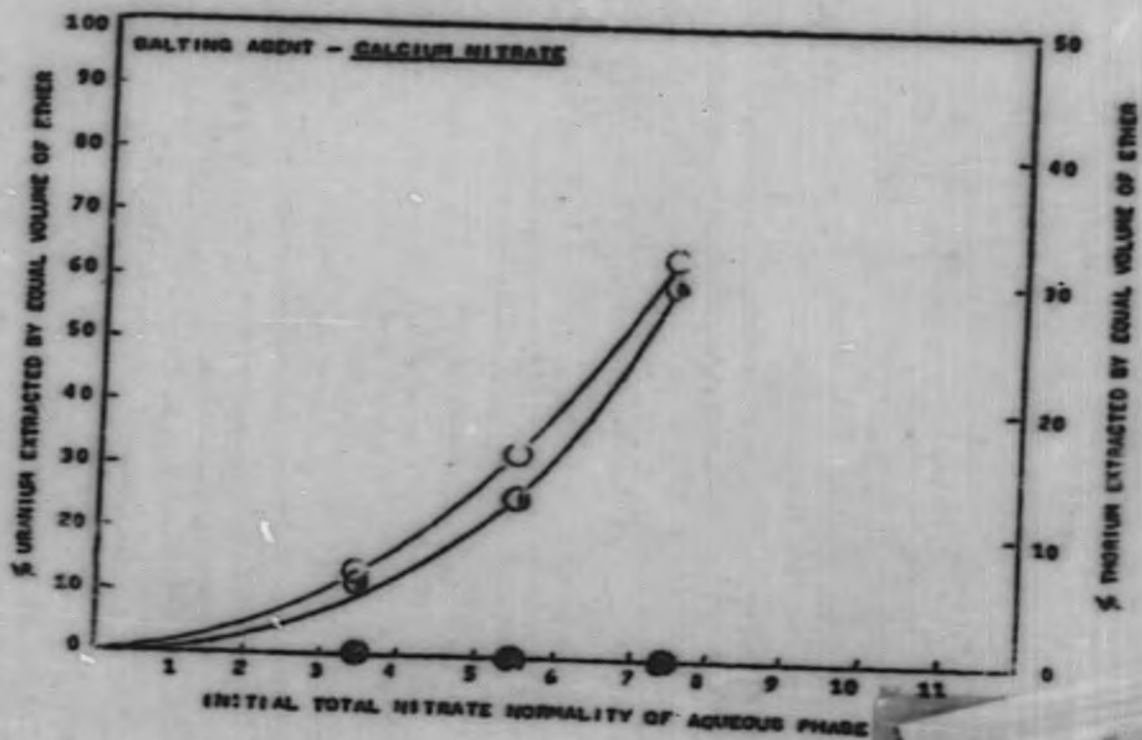


Fig. 10

Fig. 11



S-72-34

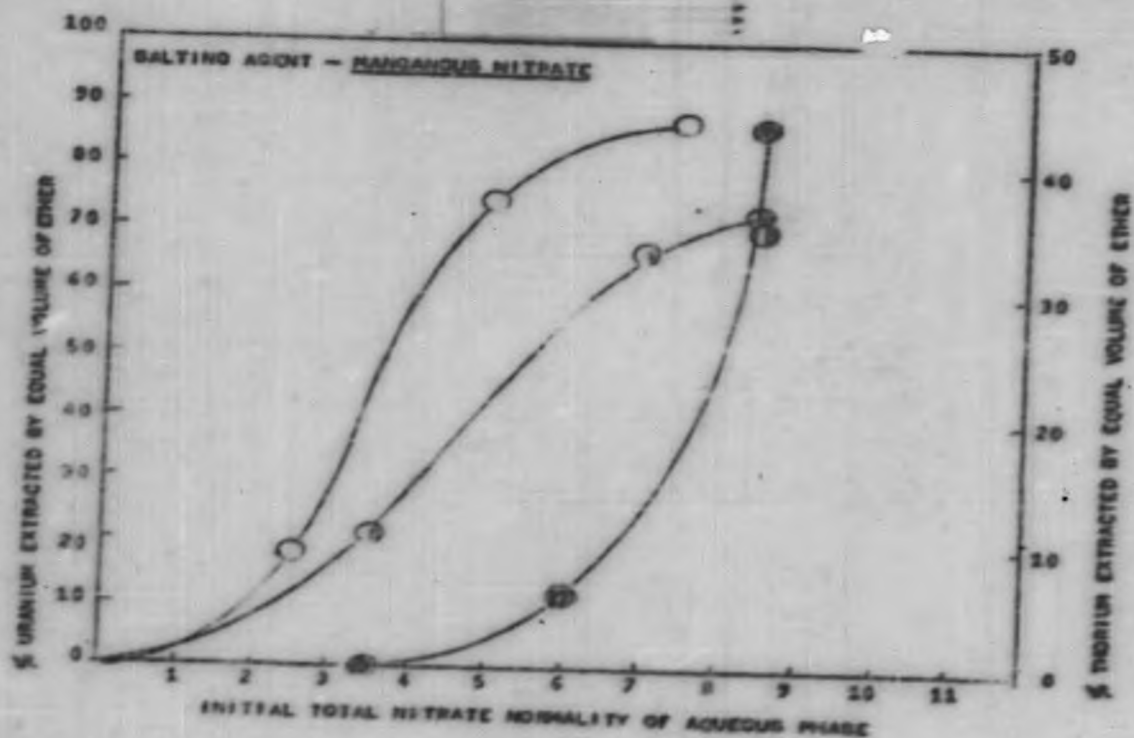
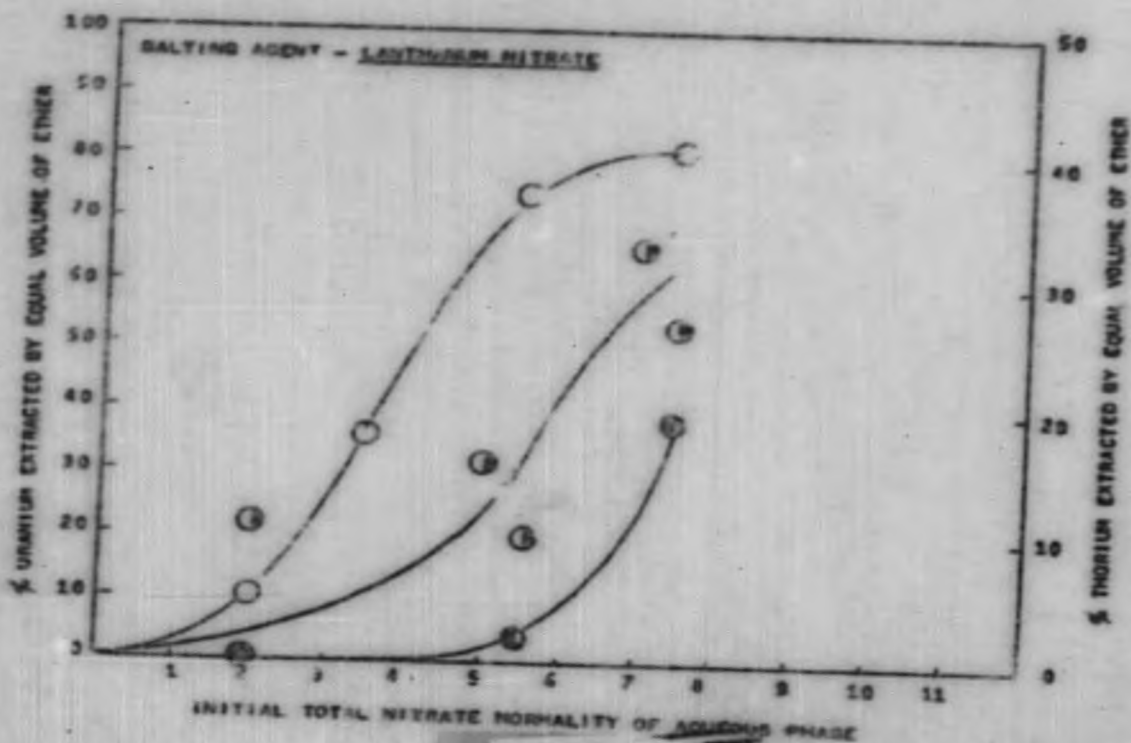


Fig. 12

Fig. 13



S-72-35

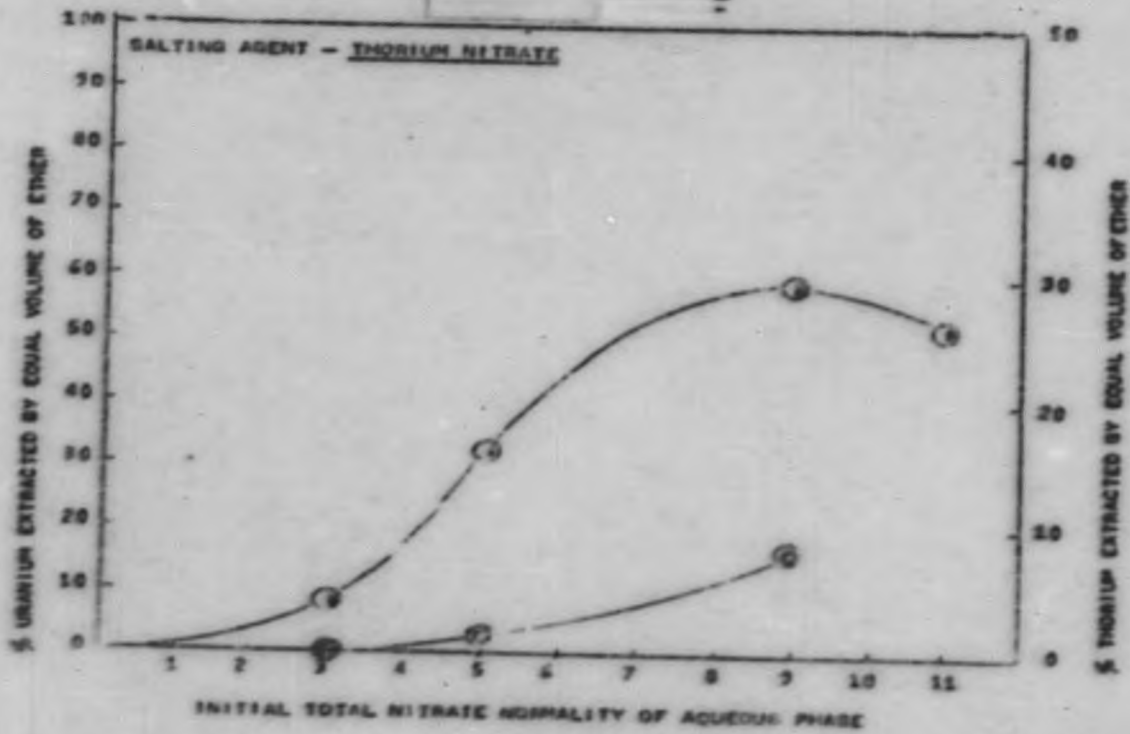
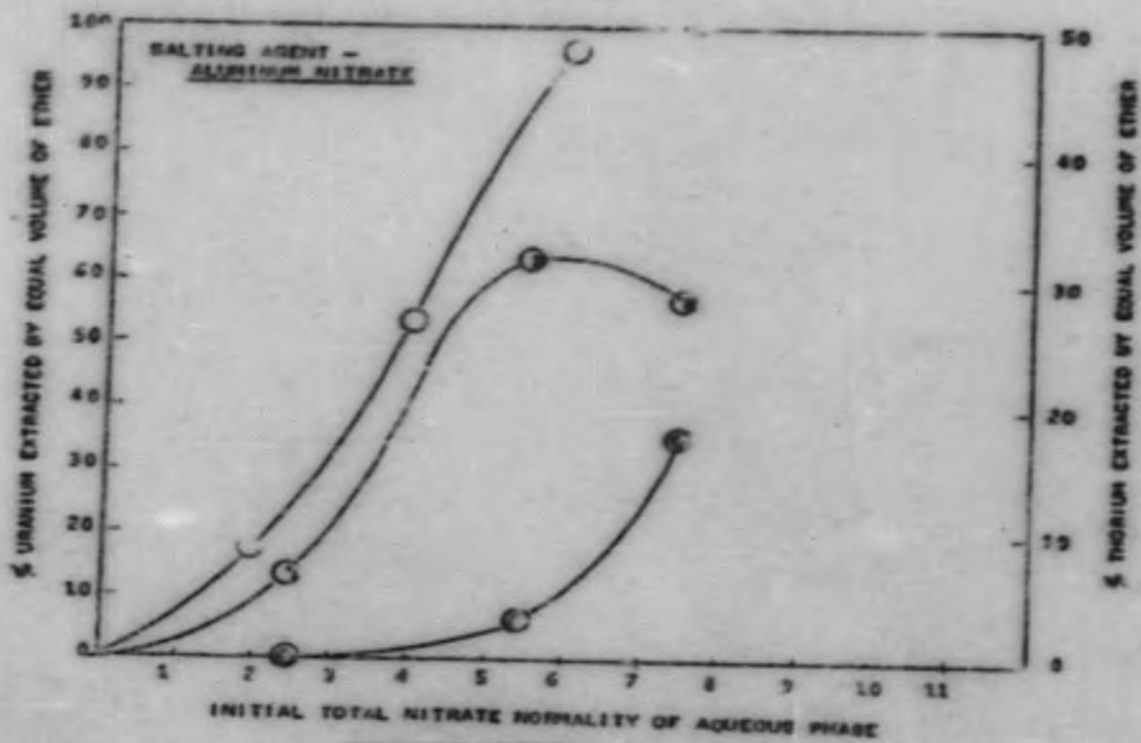


Fig. 14

Fig. 15



S-72-36