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**SOME FACTORS INFLUENCING THE USE
OF TRIBUTYL PHOSPHATE FOR THE
EXTRACTION OF URANIUM IN ANALYSIS**

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February 27, 1951

K-25 Plant

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2

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SOME FACTORS INFLUENCING THE USE OF TRIBUTYL PHOSPHATE
FOR THE EXTRACTION OF URANIUM IN ANALYSIS

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A B S T R A C T

A study has been made of the analytical application of tributyl phosphate extraction of uranium from aqueous solution. The extraction of uranium from nitric acid solutions by tributyl phosphate was favored by the addition of sodium or ammonium nitrate, by high tributyl phosphate concentration in tributyl phosphate-hexane mixtures, and, in the absence of other nitrates, by increasing the nitric acid concentration. With undiluted tributyl phosphate a distribution coefficient of 110 was obtained from 5 molar nitric acid and 290 from a 2 molar nitric acid solution containing 30 g./100 ml. sodium nitrate.

Iron(III), copper(II), nickel(II), and chromium(III) were extracted in trace amounts. Sulfate, phosphate, fluoride, chloride, and silicate interfere by one or more of the following methods: by decreasing the extraction of uranium; by extracting with the uranium or by increasing the extraction of other impurities; and by the formation of emulsions.

Uranium was extracted from the tributyl phosphate with sodium carbonate solution or with sodium or ammonium sulfate solution.

SOME FACTORS INFLUENCING THE USE OF TRIBUTYL PHOSPHATE
FOR THE EXTRACTION OF URANIUM IN ANALYSIS

TABLE OF CONTENTS

INTRODUCTION.....	6
REAGENTS, APPARATUS, AND PROCEDURE.....	6
Reagents and Solutions.....	6
Apparatus.....	7
Experimental Procedure.....	7
PRESENTATION AND DISCUSSION OF DATA.....	8
Extraction of Uranium.....	8
Effect of Nitric Acid Concentration.....	8
Sodium Nitrate as a Salting Agent.....	8
Ammonium Nitrate as a Salting Agent.....	12
Other Metal Nitrates as Salting Agents.....	13
Comparison of Tributyl Phosphate and Pentaether.....	13
Effect of Uranium Concentration.....	14
Dilution of Tributyl Phosphate.....	14
Extraction of Other Metals.....	17
Interference by Anions.....	18
Washing the Organic Phase.....	20
Re-Extraction of Uranium.....	20
DETERMINATION OF URANIUM.....	22
Organic Phase.....	23
Determination in Re-Extraction Solution.....	23
RECOVERY OF TRIBUTYL PHOSPHATE.....	24
SUMMARY.....	24
BIBLIOGRAPHY.....	26
APPENDIX.....	28

SOME FACTORS INFLUENCING THE USE OF TRIBUTYL PHOSPHATE
FOR THE EXTRACTION OF URANIUM IN ANALYSIS

The purpose of this investigation was to study the applicability of tributyl phosphate to the solvent extraction procedure for the determination of uranium. Work at other installations had suggested that tributyl phosphate might offer one or both of the following advantages: improved specificity with resulting increase in purity of the uranium, and decreased cost due to the possibility of using less salting agent. Tributyl phosphate extraction of uranium has been applied successfully to nitric acid solutions of Hanford and Oak Ridge National Laboratory waste (8) and to solutions obtained from the treatment of monazite sands (3,4). In these applications, a counter-current column is used and the tributyl phosphate is diluted to 20% or less with a second organic liquid. While a diluent is necessary in column operation in order to decrease the density and viscosity of the tributyl phosphate, rapid separation of the phases is not as critical in analytical batchwise extractions and the higher distribution coefficient obtained with 100% tributyl phosphate is advantageous.

Little information has been published on the analytical application of tributyl phosphate extraction of uranium from nitrate solutions. Feldman (7) has used this solvent to remove uranium in order to simplify spectrographic determination of the contaminants and it is used by Robinson (14) and Kelley (10) in connection with the fluorescent determination of uranium.

The present investigation covered the extraction of uranium from nitric acid and nitrate salt solutions, the extraction of iron, copper, nickel, and chromium, the interference by sulfate, phosphate, fluoride, chloride, and silicate, the effect of diluting the tributyl phosphate with hexane, and the efficiency of various aqueous solutions for the re-extraction of uranium. A comparison of the uranium distribution coefficients obtained with tributyl phosphate and pentaether (dibutoxytetraethylene glycol) was made since this latter solvent is currently used for analytical extraction work in the K-25 laboratories.

REAGENTS, APPARATUS, AND PROCEDURE

Reagents and Solutions

Tributyl Phosphate. Commercial grade tributyl phosphate was used directly from the drum in which it was received from the Commercial Solvents Corporation. A brief investigation indicated that the uranium distribution coefficient was unaffected by saturating the tributyl phosphate with water or by previous use for the extraction of uranium.

The physical properties and specifications of commercial grade tributyl phosphate are presented in the appendix. The present price is \$0.565 to \$0.615 per pound depending upon the quantity purchased (13). This compares favorably with the current price of \$1.10 per pound for pentaether.

Preparation of Solutions. Stock uranium solutions were prepared by dissolving weighed amounts of uranium nitrate hexahydrate in water and diluting in volumetric flasks. Aliquots of these stock solutions were used in the preparation of solutions for extraction. The amounts of nitric acid used to prepare solutions of definite nitric acid content was calculated on the assumption that concentrated reagent grade nitric acid is 16 molar. For example, a concentration stated as 1.6 molar acid is 10% by volume of concentrated nitric acid.

Anhydrous salts were used to prepare all other solutions with the exceptions noted in the tables or in the accompanying discussion.

Apparatus

Pear-shaped separatory funnels of appropriate size (60, 125, or 250 ml.) were used except when investigating the change in the volumes of the phases. In the latter case, 50 ml. glass-stoppered graduated cylinders were used.

Colorimetric determinations were made on three different spectrophotometers during the investigation; in chronological order of use, these were a Coleman model 11, a Beckman model DU, and a Beckman model B.

Calibration curves for the General Electric X-Ray photometer were prepared but the instrument was not used for any of the determinations reported in this paper.

Experimental Procedure

Temperature. The only attempt to control temperature in the following experiments was to permit the solutions to come to room temperature, approximately 23°C., before mixing the phases. The uranium distribution coefficient varies inversely with temperature in the range from 10° to 50°C. when 20% tributyl phosphate in hexane is used for the extraction (8) and, therefore, high temperatures should be avoided during the initial extraction. Conversely reextraction is more efficient if a hot aqueous phase is used.

Equilibration. Mixing of the phases was accomplished by shaking the funnels vigorously by hand for one minute. This was considered sufficient since Ferguson and Runion (8), using 20% tributyl phosphate in hexane, found no difference when the equilibration time varied from 10 seconds to 20 hours.

Measurement of Distribution Coefficients. Distribution coefficients were calculated from the results of uranium determinations on aliquots of both phases. Throughout this report the distribution coefficients have been calculated as the ratio of the concentration in the organic to the concentration in aqueous phase. The procedures used for the determination of uranium during this investigation are described below.

The alkali-peroxide colorimetric procedure for the determination of uranium was applied to aqueous phases containing only nitric acid or sodium nitrate with no preliminary treatment other than evaporation to remove large amounts of acid. Polarographic and fluorescent methods were used for low concentrations of uranium. If interfering elements were present, additional portions of tributyl phosphate were used to remove the uranium from the aqueous phase and the uranium was then determined as described below.

Generally, uranium in the organic phase was determined by exhaustively re-extracting into sodium sulfate solution and determining the uranium by the alkali-peroxide procedure. The organic phases were washed by shaking with solutions of ammonium nitrate (70 g./100 ml.) or sodium nitrate (60 g./100 ml.) if interfering metals were present. In a few cases, uranium was determined gravimetrically by ammonia precipitation from ammonium sulfate solution, polarographically in the organic phase without re-extraction, or fluorometrically in an aqueous extract of tributyl phosphate.

Two significant figures are used to express uranium distribution coefficients in the tables below. High coefficients, particularly, lack precision because of the lack of precision in the determination of small concentrations of uranium in the aqueous phase. For example, triplicate extractions of a sodium nitrate solution resulted in uranium distribution coefficients of 1000, 1300, and 1400 and these values were considered to be in agreement because of the limitations imposed by the precision of the colorimetric method at the uranium concentration involved. Metals other than uranium were determined colorimetrically, polarographically, or spectrographically. With the exception of hexavalent chromium, the metals were extracted in trace amounts only and the aqueous phase was considered unchanged.

PRESENTATION AND DISCUSSION OF DATA

Extraction of Uranium

Effect of Nitric Acid Concentration. Distribution coefficients obtained with three concentrations of uranium and several concentrations of nitric acid are shown in table I and graphically in figure 3. The distribution coefficients increased rapidly with increasing nitric acid content in the range investigated, up to 8 molar acid. A coefficient of at least 100 has been considered desirable for analytical purposes and this value was attained with 5 molar nitric acid.

Salting with Sodium Nitrate. Ferguson and Runion (8), using 20% tributyl phosphate - 80% hexane, reported an increase in the value of the uranium distribution from 0.24 to greater than 200 when the sodium nitrate concentration was increased from 0 to 5 molar. Data obtained with undiluted tributyl phosphate at various concentrations of sodium nitrate and nitric acid are presented in table II and in figures 1 and 2.

TABLE I
EXTRACTION OF URANIUM FROM NITRIC ACID SOLUTIONS

Nitric Acid Concentration (Molarity)	Distribution Coefficients (organic/aqueous) 5 mg. U/ml.
2	33
5	110
6	120
8	150

Initial volumes: Aqueous, 25 ml.; Organic, 10 ml.

TABLE II
SODIUM NITRATE AS A SALTING AGENT

Sodium Nitrate (g./100 ml.)	Nitric Acid (molarity)	Uranium Distribution Coefficient (organic/aqueous)
0	2	41
10	2	89
20	2	170
30	2	290
40	2	460
30	0	1200
30	0.5	510
30	1	330
30	3	270
30	4	270

Initial uranium concentration in aqueous phase - 5 mg./ml.

Initial volumes: Aqueous, 50ml., Organic, 20 ml.

EFFECT OF NaNO_3 ON TRIBUTYL PHOSPHATE
EXTRACTION OF URANIUM

FIGURE 1

TRIBUTYL PHOSPHATE EXTRACTION OF URANIUM
FROM NaNO_3 SOLUTIONS, EFFECT OF ADDING
NITRIC ACID

FIGURE 2

The effectiveness of sodium nitrate as a salting agent is much greater with tributyl phosphate than with pentaether. For example, a distribution coefficient of 1200 was obtained with tributyl phosphate and a solution containing 30 g./100 ml. sodium nitrate while Kraus (11) reported a value of 39 with pentaether and a solution prepared by dissolving 90 g. sodium nitrate in 100 ml. of water.

The data of table II indicate a decrease from 1200 to 290 when the nitric acid concentration was changed from 0 to 2 molar in a solution containing 30 g./100 ml. sodium nitrate. If sodium nitrate is used as a salting agent, the use of large amounts of nitric acid is both unnecessary and undesirable from the point of view of uranium extraction.

Ammonium Nitrate as a Salting Agent. Experiments with ammonium nitrate, similar to those with sodium nitrate, were carried out and the results are presented in table III. Ammonium nitrate was found to be a satisfactory salting agent since 30 g./100 ml. in 1.0 molar nitric acid resulted in a distribution coefficient of 220. As was the case with sodium nitrate, the uranium distribution coefficient was decreased by the addition of small amounts of nitric acid to the salt solution. This is illustrated by the values of 420 and 220 obtained with the solutions containing 30 g./100 ml. of ammonium nitrate and nitric acid concentrations of 0 and 1 molar, respectively.

TABLE III
AMMONIUM NITRATE AS A SALTING AGENT

Ammonium Nitrate (g./100 ml.)	Nitric Acid (molarity)	Uranium Distribution Coefficient (organic/aqueous)
0*	3.2	52
31*	2.5	170
52*	2.1	340
61*	1.9	450
68*	1.8	460
78*	1.6	730
70	2	370
80	0	900
30	0	420
30	1	220

*To 20 ml. 3.2 M HNO_3 containing 5 mg. U/ml. were added 0.0, 8, 16, 20, 24, and 32 g. NH_4NO_3 , respectively. Resulting volumes were shaken with 10 ml. tributyl phosphate.

For others: Initial uranium concentration - 5 mg./ml.
Volumes: 25 ml. aqueous, 10 ml. organic.

Other Metal Nitrates as Salting Agents. The nitrates of calcium and iron are good salting agents for use with pentaether (11) and, therefore, these nitrates were tried with tributyl phosphate. Aluminum nitrate has also been used with pentaether (1) and so it was included in this experiment. The use of these salts would be limited in analytical work because additional steps must be added to the procedure to remove these metals prior to the uranium determination. The formula of the salt, the concentration used, the amount of nitric acid present, and the distribution coefficients obtained are shown in table IV.

TABLE IV
METAL NITRATES AS SALTING AGENTS
(Comparison of Tributyl Phosphate and Pentaether)

Formula	g./100 ml.	Nitric Acid (molarity)	Uranium Distribution Coefficients (organic/aqueous)	
			Tributyl Phosphate	Pentaether
---	---	2	35	1.8
NH_4NO_3	70	2	370	70
NaNO_3	40	2	460	18
NaNO_3	66	0	1800	140
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	58	2	370	32
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	53	2	430	33
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	60	2	1000	83

5 mg. uranium/ml. in original aqueous phase.

Volumes: 25 ml. aqueous, 10 ml. organic

Data obtained with nitric acid, sodium nitrate, and ammonium nitrate are included in the table to facilitate comparison. The effectiveness of calcium, ferric, and aluminum nitrates as salting agents is indicated by the high distribution coefficients obtained, 370 and higher. These salts are very soluble in water and much greater concentrations could be used if desired.

Comparison of Tributyl Phosphate and Pentaether. Duplicate aliquots of the solutions used in the preceding experiment were extracted with pentaether and the distribution coefficients obtained are also presented in table IV. At the salt concentrations used, tributyl phosphate is the

more efficient solvent but the comparison may not be valid at higher salt concentrations since Kraus' data (11) indicated that the pentaether distribution coefficients increased rapidly with increase in concentration of the calcium and ferric nitrates. The effect of higher concentrations of these nitrate salts on tributyl phosphate distribution coefficients was not investigated since, as mentioned previously, the addition of these metals would normally be kept at a minimum.

A major item in the cost of the pentaether extraction procedure is the large amount of ammonium nitrate required to obtain efficient salting of the uranium into the organic phase. The high distribution coefficients obtained with tributyl phosphate suggest that the amount of salt could be materially reduced when this solvent is used.

Effect of Uranium Concentration on the Distribution Coefficient. Preliminary experiments had indicated that the uranium distribution coefficient was decreased by reducing the concentrations of uranium. Since this effect would be important in the extraction of trace quantities of uranium and in washing the organic layer, distribution coefficients were determined at uranium concentrations of 0.1, 1, and 10 mg./ml. in 2 molar nitric acid and in 2 molar nitric acid containing 40 g./100 ml. sodium nitrate. The data, presented in table V, do not show a decrease in distribution coefficient with decreasing uranium concentration. Lack of precision in the determination of uranium is sufficient to explain the differences obtained.

TABLE V

EFFECT OF URANIUM CONCENTRATION ON THE DISTRIBUTION COEFFICIENT

Initial Uranium Concentration (mg./ml.)	Distribution Coefficients (organic/aqueous)	
	2 molar HNO_3	2 molar HNO_3 + 40g. NaNO_3 /100 ml.
10	33	480
1	35	300*
0.1	45*	560*

*Uranium determined by fluorescence.

Initial volumes: aqueous, 25.; organic, 10 ml.

On the basis of the results obtained with other metal nitrates, it is reasonable to assume that the concentration of uranyl nitrate would influence the distribution coefficient. However, it was concluded from the above data that small concentrations of uranium can be extracted satisfactorily if sufficient nitric acid or nitrate salts are present.

Dilution of Tributyl Phosphate. For use in countercurrent columns, tributyl phosphate is diluted with other organic liquids to reduce viscosity, to alter the specific gravity of the organic phase, to permit easier

re-extraction of the uranium with water, and to reduce the extraction of certain impurities by nearly saturating the organic phase with uranium (8).

Distribution coefficients obtained with 100, 75, 50, and 25% by volume tributyl phosphate in hexane at several concentrations of nitric acid and sodium nitrate are shown in table VI. The nitric acid data are also presented graphically in figure 3.

TABLE VI
DILUTION OF TRIBUTYL PHOSPHATE WITH HEXANE

Sodium Nitrate (g./100 ml.)	Nitric Acid (molarity)	Uranium Distribution Coefficients (organic/aqueous)			
		100% TBP	75% TBP	50% TBP	25% TBP
0	2	33	30	23	12
0	5	110	88	60	27
0	6	120	97	62	26
0	8	150	88	49	18
20	2	180	140	110	45
30	2	270	230	180	67

Initial uranium concentration - 5 mg./ml.

Volumes: aqueous, 25 ml.; organic, 10 ml.

In every case, the efficiency of uranium extraction decreased as the concentration of hexane increased but, at the three lower tributyl phosphate concentrations, there was an optimum nitric acid concentration. This maximum occurred at approximately 5 molar acid with 25% tributyl phosphate, about 6 molar for 50%, and between 6 and 8 molar for 75%.

The effect of hexane is apparently due to dilution; i.e., the decreasing quantity of tributyl phosphate used is believed to be sufficient explanation of the manner in which the distribution coefficients decreased as the hexane content of the solvent was increased.

The separation of phases has been satisfactory even when no diluent was employed but the use of 75% tributyl phosphate - 25% hexane resulted in shorter "disengaging time" and somewhat cleaner separation. The handling characteristics of undiluted tributyl phosphate are very similar to those of pentaether and a diluent is unnecessary in most cases.

Several other organic liquids have been used at other installations for diluting tributyl phosphate. R. L. Moore (12) reported a correlation between symmetry of the diluting molecule and the extraction coefficient:

DILUTION OF TRIBUTYL PHOSPHATE WITH HEXANE

FIGURE 3

symmetrical compounds such as carbon tetrachloride and benzene gave higher coefficients than chloroform and trichloroethylene.

Carbon tetrachloride is non-inflammable and by its use the organic phase can be made heavier than the aqueous. The heavier organic phase is advantageous during the extraction step since repeated extractions can be carried out without removing the aqueous phase to other separatory funnels. Washing the organic phase and re-extraction into a second aqueous phase would be more difficult than when the organic is lighter than the aqueous.

The use of mixtures of tributyl phosphate with dibutyl carbitol results in high distribution coefficients (5) as would be expected from the fact that dibutyl carbitol itself may be used to extract uranium (11).

Extraction of Other Metals

Metals frequently encountered in K-25 samples are iron, copper, nickel, and chromium. Solutions of these metals were prepared from the following salts: ferric nitrate nonahydrate, cupric nitrate trihydrate, nickelous nitrate hexahydrate and chromic nitrate nonahydrate. The concentration of the metal and nitric acid present in these solutions and the distribution coefficients obtained when the solutions were shaken with tributyl phosphate are shown in table VII. Only trace amounts of these metals were extracted under these conditions although all of the solid nitrate salts used are appreciably soluble in tributyl phosphate.

TABLE VII

EXTRACTION OF IRON, COPPER, NICKEL, AND CHROMIUM

Metal Concentration (g./100 ml.)	Nitric Acid (molarity)	Distribution Coefficients (organic/aqueous)			
		Iron	Copper	Nickel	Chromium
		($\times 10^{-4}$)*	($\times 10^{-4}$)*	($\times 10^{-4}$)*	($\times 10^{-4}$)*
1	1.6	2	---	---	---
2	1.6	6	---	---	---
2	3.2	3	---	---	---
2	6.4	30	---	---	---
5	1.6	8	11	0.5	1
5	3.2	---	4	0.65	1.4
5	4.8	---	---	---	1.3
10	1.6	170	---	---	---
10	3.2	---	4	0.6	0.24

*Each value should be multiplied by 10^{-4} , i.e., 2 in table corresponds to a distribution coefficient of 0.0002.

To determine the effect of sodium nitrate on the extraction of iron(III), copper(II), nickel(II), and chromium(III), a 2 M nitric acid solution containing 30 g./100 ml. sodium nitrate and 1 g./100 ml. of each of the four metals was shaken with tributyl phosphate. Direct spectrographic analysis of the organic layer indicated trace amounts of iron and copper but nickel and chromium were undetected. Colorimetric and polarographic analyses of a nitric acid solution used to re-extract the metals from the organic phase indicated that the iron and copper distribution coefficients were 0.01 and 0.007, respectively.

The tributyl phosphate was attacked when nitric acid solutions containing chromium(VI) were extracted. The aqueous solution contained 5 g./100 ml. chromium added as ammonium dichromate and was 3.2 molar in nitric acid. Both aqueous and organic phases were darkened so badly that the interface could not be observed accurately.

Other elements which have been reported as extracting into tributyl phosphate from nitric acid and nitrate solutions are thorium (3), plutonium (8), cerium (15), and zirconium (8).

Interference by Anions

The three principal ways in which anions interfere in solvent extraction are: decreasing extraction of uranium into the organic phase, extracting with the uranium or increasing the extraction of other impurities, and causing the formation of emulsions. For example, uranium distribution coefficients are decreased by the presence of phosphate, making quantitative recovery of the uranium difficult. Furthermore, phosphate extracts to some extent and it may accompany the uranium and be weighed with it in gravimetric determinations. The presence of chloride results in an increase of the extraction of several metals, notably iron.

The data of table VIII show the effect of several anions on the extraction of uranium. Five milliliter volumes of solutions of the anions and 10 ml. nitric acid were added to 50 ml. of the solution described in the table and the extraction was carried out with a 10 ml. volume of tributyl phosphate. Some of the experiments were repeated after adding ferric nitrate to minimize the interference by the anions. Control extractions, in which water was added instead of the anion solutions, were run at the same time as the extractions made without the addition of ferric nitrate. The experiment was designed to emphasize the effect of the anions and, therefore, nitric acid was the only salting agent added and relatively small volumes of tributyl phosphate were used.

Phosphate, sulfate, and fluoride reduced the extraction of uranium. The difference between test and control experiments was not significant for either chloride or silicate. Iron was fairly effective in reducing the interference by sulfate, phosphate, and fluoride. One additional experiment, not included in table VIII, indicated that aluminum nitrate was also effective in preventing the interference by fluoride.

The effect of chloride was also tested by extracting uranium from a solution containing 90% by volume concentrated hydrochloric acid. The only nitrate present was that added as uranyl nitrate. The distribution

TABLE VIII
EFFECT OF ANIONS ON URANIUM DISTRIBUTION

Anion	Grams Anion Added to 50 ml.	Compound Used	Percent of Total Uranium Extracted		
			Ion Present	Fe Added*	Control
Phosphate	5	H_3PO_4	50	80	90
Sulfate	5	H_2SO_4	83	89	90
Chloride	1.9	HCl	94	---	92
Silicate	0.18	$Na_2SiO_3 \cdot 9H_2O$	95	---	98
Fluoride	1	$KF \cdot 2H_2O$	82	92	94

*10 g. $Fe(NO_3)_3 \cdot 9H_2O$ added to 65 ml. of aqueous solution.

Five ml. anion solution and 10 ml. HNO_3 added to 50 ml. aqueous solution which contained 2 g. nickel, 1 g. copper, 0.8 g. iron per 100 ml. and 1 mg. uranium/ml. Ten ml. tributyl phosphate was used to extract approximately 65 ml. of aqueous solution.

coefficient obtained was 68 which indicates that uranium could be extracted from chloride solutions although probably less efficiently than with nitrate.

The extent of contamination due to the presence of the anions is indicated in table IX. Extractions were carried out on nitric acid solutions similar to those described in table VIII, the organic layers were washed twice with 5 ml. volumes of a solution containing 50 g./100 ml. sodium nitrate, the uranium was re-extracted with saturated ammonium sulfate solution, precipitated with ammonia, and ignited. The oxides obtained were analyzed spectrographically.

Under the conditions of the experiment, contamination was minor in the presence of sulfate, chloride, and phosphate. The separatory funnel used with fluoride was etched and the high silica content of the oxide was expected. The phases separated poorly and the interface was dirty in the extraction of the solution containing silicate. The high phosphate and iron content of the oxide prepared from the silicate solution is believed due to the poor separation but the low silicon content is unexplained.

The presence of silicate sometimes resulted in the formation of emulsions. Emulsification occurred when "carbon leach" solutions, which contain 25 to 50% by volume of nitric acid and high concentrations of silicate, were extracted with tributyl phosphate in the presence of moderate concentrations of sodium nitrate; no difficulty was experienced when high concentrations of sodium nitrate were used or when no nitrate salts were present.

TABLE IX
CONTAMINATION DUE TO ANIONS

Anion	g. Anion/100 ml.	Parts Per Million of Impurities in U_3O_8				
		Silicon	Phosphorous	Iron	Copper	Nickel
---	---	300	200	60	60	5
Phosphate	5	300	500	100	40	10
Sulfate	5	300	200	100	40	10
Chloride	2	300	200	100	30	2
Fluoride	2	1000	400	80	100	10
Silicate	0.1	200	5000	1000	60	40

Figures are spectrographic results on oxides prepared following extraction of 4 molar nitric acid solutions containing 5 mg. uranium per ml. and 1 g. nickel, 0.5 g. copper, and 0.4 g. iron per 100 ml. and the anions indicated.

Tributyl phosphate is not very soluble in water (see appendix) but solutions used for re-extracting the uranium are saturated with the solvent and, therefore, some phosphate is always introduced in the extraction procedure.

Washing the Organic Phase

In solvent extraction procedures such as the "nitrate wash" procedure (9), the organic phase is shaken with small volumes of solutions of salting agents in order to remove other elements which are extracted with the uranium or which remain in droplets of the original aqueous phase on the walls of the separatory funnel. A wash solution should extract as little uranium and as much of the contaminants from the organic as possible. In addition, it should not introduce any interferences itself.

The solutions used for washing in the work reported in this paper were concentrated solutions of sodium or ammonium nitrate. An undesirable characteristic of ammonium nitrate solution is the difficulty of observing the interface; this is apparently due to similarity of the indices of refraction of the ammonium nitrate solution and the tributyl phosphate.

Nitric acid was not added to the wash solutions if the original aqueous phase contained excess acid. If the original aqueous phase contained high concentrations of nitric acid, subsequent re-extraction of the uranium was simplified by adding sodium or ammonium hydroxide to the wash solution in order to neutralize much of the acid extracted by the tributyl phosphate.

Re-Extraction of Uranium

Solutions used for re-extracting uranium from tributyl phosphate are listed in table X with the distribution coefficients obtained on a single extraction. Sodium carbonate solution was the most effective, followed by saturated ammonium sulfate, 25 g./100 ml. urea, and 20 g./100 ml. sodium

sulfate solutions in that order. Water or neutral hydrogen peroxide solutions were ineffective with tributyl phosphate which contained nitric acid.

The relative volumes of the phases are important in evaluating the data in table X. For example, the solution containing 10 g./100 ml. sodium carbonate was very effective in re-extracting the uranium but this result is dependent upon the presence of sufficient sodium carbonate to neutralize all of the nitric acid in the organic phase. Furthermore, the manner in which the distribution coefficient changes on repeated re-extractions, discussed below, will be affected by the volumes used.

TABLE X

SOLUTIONS FOR RE-EXTRACTING URANIUM FROM TRIBUTYL PHOSPHATE

Aqueous Phase		Distribution Coefficients (organic/aqueous)	
Salt	Concentration	Organic No. 1	Organic No. 2
Na_2CO_3	10 g/100 ml.	0.05	---
$(\text{NH}_4)_2\text{SO}_4$	Saturated	0.1	---
Urea	25 g/100 ml.	0.56	---
Na_2SO_4	20 g/100 ml.	2.9	0.04
Water	---	18	1.6
H_2O_2	3%	24	---
H_2SO_4	1% (V/V)	---	0.24

Organic No. 1 prepared by contacting with uranium solution 3.2 molar in nitric acid.

Organic No. 2 prepared by contacting with uranium solution containing 30 g/100 ml. sodium nitrate with no excess nitric acid.

Initial uranium concentration in tributyl phosphate: approximately 10 mg./ml.

Volumes: 20 ml. tributyl phosphate, 5 ml. aqueous.

The gradual decrease of distribution coefficient with successive re-extractions and the effect of nitric acid extracted from the original aqueous phase is shown in table XI.

TABLE XI

CHANGE OF DISTRIBUTION COEFFICIENT ON REPEATED RE-EXTRACTION

Re-Extraction Number	Uranium Distribution Coefficient (organic/aqueous)			
	20 g./100 ml. Na_2SO_4	1% (V/V) H_2SO_4	Water	
	*			
1	6.5	0.04	0.24	1.6
2	2.4	(0.016)	.13	0.8
3	1.1	(0.05)	0.08	0.6
4	0.47	---	(.04)	0.4
5	0.21	---	---	0.3
6	0.11	---	---	0.2
7	(0.05)	---	---	---

Figures in parentheses are considered unreliable because of low concentration of uranium present.

*Organic contained nitric acid.

Initial concentration of uranium in tributyl phosphate: 10 mg./ml.

When no nitric acid was present in the original aqueous phase, the sodium sulfate solution was very effective for the removal of uranium from the tributyl phosphate, but when the original aqueous phase was 2 molar in nitric acid the first re-extraction removed very little uranium and a distribution coefficient less than 1 was obtained only after three re-extractions.

The choice of solution for re-extraction depends upon the method to be used for determining the uranium as well as upon the efficiency of re-extraction. Thus, sodium carbonate was found to be very efficient for the re-extraction but the carbonate would have to be destroyed before the uranium could be determined gravimetrically and large quantities of sodium would contaminate the precipitate: carbonate is also undesirable because of effervescence and pressure generated in the separatory funnel. On the other hand, water would be desirable from the point of view of the uranium determination but complete re-extraction would be tedious and time consuming. Ammonium sulfate solution is a satisfactory choice if the uranium is to be determined gravimetrically.

DETERMINATION OF URANIUM

The methods used and investigated during the course of this work and two fluorescent methods known to be in use at other laboratories are mentioned below. The procedures are merely applications of existing procedures to tributyl phosphate extraction and, therefore, are not described in detail.

Determination in Organic Phase

Volumes of the phases are altered during extraction as is shown by the data in table XII. For this reason, the entire organic phase must be used or its volume measured if the uranium is to be determined directly in the organic phase.

TABLE XII

VOLUME CHANGES DURING ONE EXTRACTION

<u>Nitric Acid</u> <u>(molarity)</u>	<u>Volumes after Mixing (ml.)</u>	
	<u>Aqueous</u>	<u>Organic</u>
0	23	27
1.6	23	28
3.2	22.5	28.5
6.4	22	28.5

(Initial volume of each phase = 25 ml.)

X-Ray Photometer. With the small fixed volume absorption cells, the sensitivity of the determination of uranium in tributyl phosphate is 14 scale divisions per mg. of uranium per ml. which is the same as for the determination in aqueous solution (2). The volume of the organic phase must be known accurately and a minimum of 30 ml. is required with the present absorption cells. The method does not appear to be sensitive to the presence of the nitric acid extracted with the uranium.

Polarograph. A procedure developed by E. D. Marshall of this laboratory for the determination of uranium in tributyl phosphate consisted of adding supporting electrolyte to the tributyl phosphate in the ratio of 5 to 2 and determining the uranium by a standard addition technique. The supporting electrolyte was 0.1 N ammonium chloride and 0.01% gelatin in 80% ethyl alcohol. In making the standard additions the uranium was added in a very small volume or as a solution in 80% ethanol.

Fluorescent. Robinson (14) and Kelley (10) report procedures for the fluorescent determination of uranium in tributyl phosphate. The procedure used by Robinson involves burning an aliquot of the solvent in a gold dish, ignition of the residue, and fusion with a carbonate-fluoride flux. In the procedure described by Kelley, microliter aliquots are added directly to the flux.

Determination in Re-Extraction Solution

The three methods which have been employed to determine uranium in the aqueous solution obtained by re-extracting from tributyl phosphate are gravimetric, colorimetric, and volumetric.

Ammonium sulfate solutions were satisfactory for the re-extraction when the determination of uranium was completed by ammonia precipitation and ignition to uranous-uranic oxide. Favorable distribution coefficients were obtained and non-volatile materials were not introduced.

When the uranium was to be determined by the alkali-peroxide colorimetric procedure, sodium sulfate solution was used to re-extract the uranium. This choice avoided the buffering action of high concentrations of ammonium ion and the change in absorption of the solution due to carbonate.

Nitrate ion must be removed prior to the determination of uranium by ceric sulfate titration. This is usually accomplished by fuming with sulfuric acid and the presence of sodium or ammonium sulfate is undesirable because of spattering and probable loss of uranium. For this reason, water and dilute sulfuric acid were used for the re-extraction when the uranium was to be determined by ceric sulfate titration even though the distribution coefficients were low.

RECOVERY OF TRIBUTYL PHOSPHATE

The recovery of tributyl phosphate for re-use may be accomplished by shaking with ammonium or sodium sulfate solution to remove most of the uranium and then with sodium carbonate to remove traces of uranium and sulfate. The solvent may then be shaken with dilute nitric acid and filtered. For many purposes, this recovery procedure is sufficient. However, the solvent has a yellow color which may be removed by filtering through activated charcoal. "Darco" 20 x 40 grade charcoal has been found suitable for this purpose.

The above procedure may not be satisfactory for certain special cases such the extraction of micro quantities of uranium. Further purification may be accomplished by vacuum distillation, since the boiling point of tributyl phosphate is 177-178°C. at a pressure of 27 mm. of mercury. A 20 inch fractionating column was used when this was tried experimentally, and the tributyl phosphate distilled very slowly even at a pot temperature of 180°C. and a pressure of 2 mm. of mercury; the temperature at the top of the column was 85°C.

SUMMARY

Tributyl phosphate was found to be a powerful extracting solvent for the separation of uranium from solution if the proper salting agents are present. In the absence of nitrate salts, a nitric acid content of 5 molar was required to obtain a distribution coefficient of 100. Very high distribution coefficients were obtained by addition of sodium, ammonium, or other nitrate salts. Increasing the nitric acid concentration from 0 to about 2 molar resulted in a marked decrease in the distribution coefficients when 30 g./100 ml. of sodium nitrate or ammonium nitrate was present.

The viscosity and density of tributyl phosphate are such that a diluent was unnecessary. For specific applications hexane or other diluents could be added if desired but the distribution coefficient would be decreased.

Iron(III), copper(II), nickel(II), and chromium(III) were extracted in trace amounts only from nitric acid solutions. Solutions containing high concentrations of chromium(VI) and nitric acid attacked the tributyl phosphate and appreciable quantities of chromium entered the organic phase.

Sulfate, phosphate, and fluoride decreased the uranium distribution coefficients, but this effect was reduced by the addition of ferric nitrate. Fluoride attacked the glassware and resulted in high silica contamination.

In addition to decreasing the extraction of uranium, orthophosphate extracted slightly. Silicate interfered primarily by causing the formation of emulsions. The presence of chloride resulted in increased extraction of metallic impurities.

Sodium carbonate and sodium or ammonium sulfate solutions were effective for re-extracting the uranium from the organic phase. By increasing the number of re-extraction steps, the uranium could be recovered with water when the original aqueous phase contained little excess nitric acid.

The most important disadvantage of tributyl phosphate extraction is the difficulty of removing the uranium from the tributyl phosphate. A second disadvantage is the fact that solutions for re-extraction are saturated with tributyl phosphate resulting in slight phosphate contamination of the uranium.

In a simple case, the extraction procedure might consist of the following steps:

1. Adjust acidity to 0.5 to 1 M nitric acid and add 3 to 4 grams of sodium nitrate per 10 ml. of sample.
2. Extract with 2 portions of tributyl phosphate (total volume of tributyl phosphate equal to the original volume of sample).
3. Wash combined tributyl phosphate layers with 2-5 ml. volumes of 60 g./100 ml. sodium nitrate solution.
4. Re-extract with 20 g./100 ml. sodium sulfate solution and determine uranium colorimetrically.

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APPENDIX

PROPERTIES AND SPECIFICATIONS OF TRIBUTYL PHOSPHATE

(from advertisement of the Commercial Solvents Corporation (6))

Properties of Commerical Grade Material

Boiling Point (27 mm. Hg).....177 - 178°C.
 Melting Point.....below -80°C.
 Flash Point (Cleveland open cup).....294°F.
 Viscosity (25°C.).....3.41 centipoise
 Viscosity (85°C.).....38.6 Saybolt seconds
 Dielectric Constant (30°C.).....7.97
 Weight/U.S. Gal. (68°F.).....8.13 lbs.
 Solubility in water (25°C.).....0.6%
 Solubility of water in tributyl phosphate (25°C.).....ca. 7%

Specifications

Specific gravity (20°/20°C.).....0.973 - 0.983
 Acidity (as phosphoric).....0.05% by weight max.
 Water - no turbidity when one volume is mixed
 with 19 volumes 60° Be gasoline at 20°C.
 Color.....water - white