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THE USE OF TRIALKYL PHOSPHINE OXIDES AS EXTRACTANTS IN THE FLUOROMETRIC DETERMINATION OF URANIUM

J. C. White

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THE USE OF TRIALKYL PHOSPHINE OXIDES AS EXTRACTANTS IN THE FLUOROMETRIC DETERMINATION OF URANIUM

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ABSTRACT

Tri-n-octyl and tri-n-decylphosphine oxides were shown to be excellent extractants for uranium in its fluorimetric determination. These phosphine oxides quantitatively extract uranium from solutions that are as concentrated as 12 molar with respect to such acids as sulfuric, phosphoric and hydrochloric acids. The extraction is also quantitative in the presence of such anions as citrate, oxalate, and tartrate that form strong complexes with the uranyl ion in solution. A simple extraction procedure was developed which is applicable under essentially all conditions. In this procedure, 5 ml of 6 M HNO_3 is added to a 1-ml aliquot of the sample which is then shaken for 5 minutes with 5 ml of 0.1 M phosphine oxide in varsol.

Although the reagents are not commercially available, their synthesis is not particularly difficult. A detailed procedure is presented for the preparation of tri-n-octylphosphine oxide.

THE USE OF TRIALKYL PHOSPHINE OXIDES AS EXTRACTANTS IN THE FLUOROMETRIC DETERMINATION OF URANIUM

J. C. White

Fluorometry is the most widely accepted technique for the determination of microgram quantities of uranium. Since the fluorescence of the uranium compound is subject to quenching, i.e. the reduction of intensity of emitted light by extraneous elements, these interferences must either be removed or their concentration reduced to the point where their effect is insignificant. The latter alternative can be applied successfully in some cases since the fluorometric method is extremely sensitive for uranium, of the order of 10^{-11} g of uranium; however, for maximum application and reliability, the uranium is usually separated from its interferences.

The rather high solubility of uranyl compounds in a variety of organic solvents has made solvent extraction an attractive means for this separation. Among the solvents that have been successfully applied are ethyl ether, dibutyl carbitol, penta-ether (dibutoxytetraethylene glycol), ethyl acetate and tributyl phosphate (TBP).[1] Recently, Blake, Brown, and Coleman[2] of the Raw Materials Section, Chemical Technology Division, Oak Ridge National Laboratory, which has pioneered in the application of organophosphorous and nitrogen compounds as extractants for uranium from raw materials, reported on the applicability of high molecular weight trialkylphosphine oxides for this purpose. On the basis of their comprehensive report, it seemed feasible that the trialkylphosphine oxides might be superior to the organic solvents which have been used for the separation of uranium prior to the fluorometric determination. The purpose of this investigation was to apply tri-n-decylphosphine oxide (TDPO) and tri-n-octyl phosphine oxide (TOPO) in the procedure for the fluorometric determination of microgram quantities of uranium.

EXPERIMENTAL

Tri-n-Decyl Phosphine Oxide (TDPO); tri-n-Octyl Phosphine Oxide (TOPO)

An 0.1 M solution of TDPO in Varsol was prepared by dissolving 17 g of TDPO in 365 ml of commercial grade Varsol. The solution was filtered through a "plug" of glass wool to clarify the solution; then stored in an amber bottle. This solution was used over a period of 6 months without any apparent deterioration in its extraction characteristics for uranium.

Tri-n-decyl phosphine oxide is a white crystalline compound that melts at 46 to 48° C and boils at 245 to 250° C (0.3 to 0.5 mm). The particular batch used in this study contained these impurities: 1.7 per cent phosphinous acid and 1.6 per cent phosphinic acid. These acids apparently have no adverse effect on the extraction of uranium.

Blake et al[2] found that similar extraction coefficients for uranium existed for the n-octyl, n-decyl and n-dodecyl phosphine oxides.

The solution of trioctylphosphine oxide was prepared by dissolving 38.6 g of TOPO in a liter of Varsol to give an 0.1 M solution. This phosphine oxide has a melting point of 51 to 52° C and a boiling point at 205° C (0.15 mm). It is chemically similar to the tridecyl derivative. The impurities in the particular batch used in this work were: 0.2 per cent phosphinous acid, 0.5 per cent phosphinic acid.

The reagents are not commercially available at the present time. A method for the synthesis of trioctylphosphine oxide[2] is given in Appendix 1.

Varsol, a commercial, kerosene-type, aliphatic hydrocarbon mixture which is widely used as a diluent for organic extractants in the fluorometric determination of uranium, was used throughout these tests. Simple aromatic hydrocarbons and non-polar compounds can be used although Blake[2] found that the extraction coefficients for uranium decreased with the higher polar character of the diluent.

For a detailed report of the physical and chemical properties of the phosphine oxides, reference to the work of Blake et al[2] is recommended.

Effect of Different Variables on the Extraction of Uranium

The effect of variables on the extraction of uranium with tri-n-octyl and tri-n-decyl phosphine oxides prior to its fluorometric determination was studied.

Concentration of nitric acid in extraction medium. In the extraction of hexavalent uranium with an organic solvent, the extraction coefficient is a function of the species in which the uranium ion exists. For example, the extraction coefficients[2] of TDPO and TOPO for uranium are markedly increased when nitrate ions are added to the solution. For this reason, either nitric acid or nitrate ion in some other form is usually added to facilitate the extraction of uranium. Indeed, in the case of most solvent extractions, the addition of nitrate to the extraction medium is imperative for quantitative application. For tributylphosphate, for example, the test aliquot is often evaporated to dryness; then redissolved in nitric acid prior to extraction.

In this investigation the evaporation step was eliminated. A one-ml aliquot of the stock solution (10 μg U/ml) was taken, following which five ml of varying concentrations of nitric acid was added to the test portion.

Two stock solutions were used, 1 M H_2SO_4, and 1 M H_3PO_4. Five ml of 0.1 M TDPO in Varsol was added; then the extraction was carried out by shaking the solution mechanically for 10 minutes. A one-ml aliquot of the organic phase was taken for the fluorometric determination of uranium. Six determinations were made at each acid concentration. The results are shown in Table I.

Table I

Effect of Nitric Acid Concentration on the Extraction of Uranium from 1 M H_2SO_4 Solutions with Tridecylphosphine Oxide

Conditions: 1 ml of 1 M H_2SO_4 solution, 10 μg U/per ml
5 ml of 0.1 M TDPO
5 ml of HNO_3
Shaking time, 10 minutes

Nitric Acid, M	Uranium, μg	Standard Deviation, μg
12	9.2	0.8
9	9.6	0.6
6	9.1	0.5
3	9.0	0.5
1	9.6	0.7

The nitric acid concentration is not critical over the range 1 to 12 M in the extraction, as may be seen from the above data. Direct plate measurements on the stock solution showed 9.4 μg per ml, which is in excellent agreement with the results obtained. Quantitative extraction was achieved at all acid concentrations under the conditions of the test. These results are not unexpected since Blake[2] et al showed that the extraction coefficient of uranium in the presence of sulfate and phosphate increased as the nitrate and hydrogen ion concentrations increased. The pH of the extraction medium should not greatly exceed 1 and the nitrate concentration should not fall much below 1 M or the extraction coefficient will be seriously decreased to the point that quantitative extraction will be imperiled.

pH of extraction medium. In some applications of the fluorometric method to microgram quantities of uranium, it is desirable to have as high a pH as possible; hence, aluminum nitrate nonohydrate, $Al(NO_3)_3 \cdot 9H_2O$, was used as a source of nitrate and hydrogen ions. Aluminum possesses the added advantage in this application in that Al^{+3} ions serve to complex sulfate and phosphate ions and thereby decrease the effect of these anions on the extraction coefficient of uranium. The nitrate concentration was varied from 0.03 to 0.3 M and the pH maintained between 1 and 2.5. Here again, quantitative recovery of 10 µg of uranium was obtained in all cases. The results are summarized in Table II.

Table II

Effect of $Al(NO_3)_3 \cdot 9H_2O$ as a Source of Nitrate Ions in the Extraction of Uranium with Tridecylphosphine Oxide from Sulfuric, Phosphoric, Oxalic, Citric and Tartaric Acid Solutions

Conditions: Uranium - 1 ml (10 µg/ml).
$Al(NO_3)_3 \cdot 9H_2O$ - 5 ml.
TDPO, 0.1 M - 5 ml.
Shaking Time - 10 min.

Acid Solution	Nitrate Concentration 0.3 M	0.1 M	0.03 M	Uranium Found, µg Direct Plate
	Uranium, µg			
Sulfuric, 1 M	10.5	9.5	10.2	9.5
Phosphoric, 1 M	10.7	10.0	10.1	9.5
Oxalic, 0.5 M	10.2	9.9	10.2	9.5
Tartaric, 0.5 M	10.4	10.0	9.9	9.9
Citric, 0.5 M	10.1	9.3	10.2	9.9

Extraction Time

The optimum extraction time was determined by shaking the phases for various periods of time ranging from 15 seconds to 10 minutes. The conditions were the same as used in the previous tests: 1-ml test aliquot, 1 M H_2SO_4, 10 μg uranium, 5 ml 0.1 M TDPO. Five ml of 6 M HNO_3 was arbitrarily chosen as the nitrate concentration. The results are represented in Figure 1.

Under the conditions of the tests, equilibration is rapid and uranium is extracted in a remarkably short time into the TDPO-Varsol phase. The extraction of 10 μg is quantitative in the first minute. Since the extraction time is therefore essentially unimportant, an arbitrary shaking period of 5 minutes was used in subsequent tests as a matter of convenience in performing the other operations of the procedure.

Composition of Test Aliquot

As previously mentioned, the presence of other species that form complexes of varying strengths with uranyl ions seriously affects the extraction coefficient. For example, sulfate, phosphate, fluoride, chloride, etc.[2] ions interfere with the extraction of uranium with tributyl phosphate (TBP) and do not yield quantitative results in media that contain these ions. In these tests 10 μg of uranium in solutions containing various concentrations of these extraneous anions was extracted with a mixture of 0.1 M TDPO, and 5 ml of 6 M HNO_3. The phases were shaken for 5 minutes, after which the amount of uranium in the organic phase was determined fluorometrically. The results are shown in Table III.

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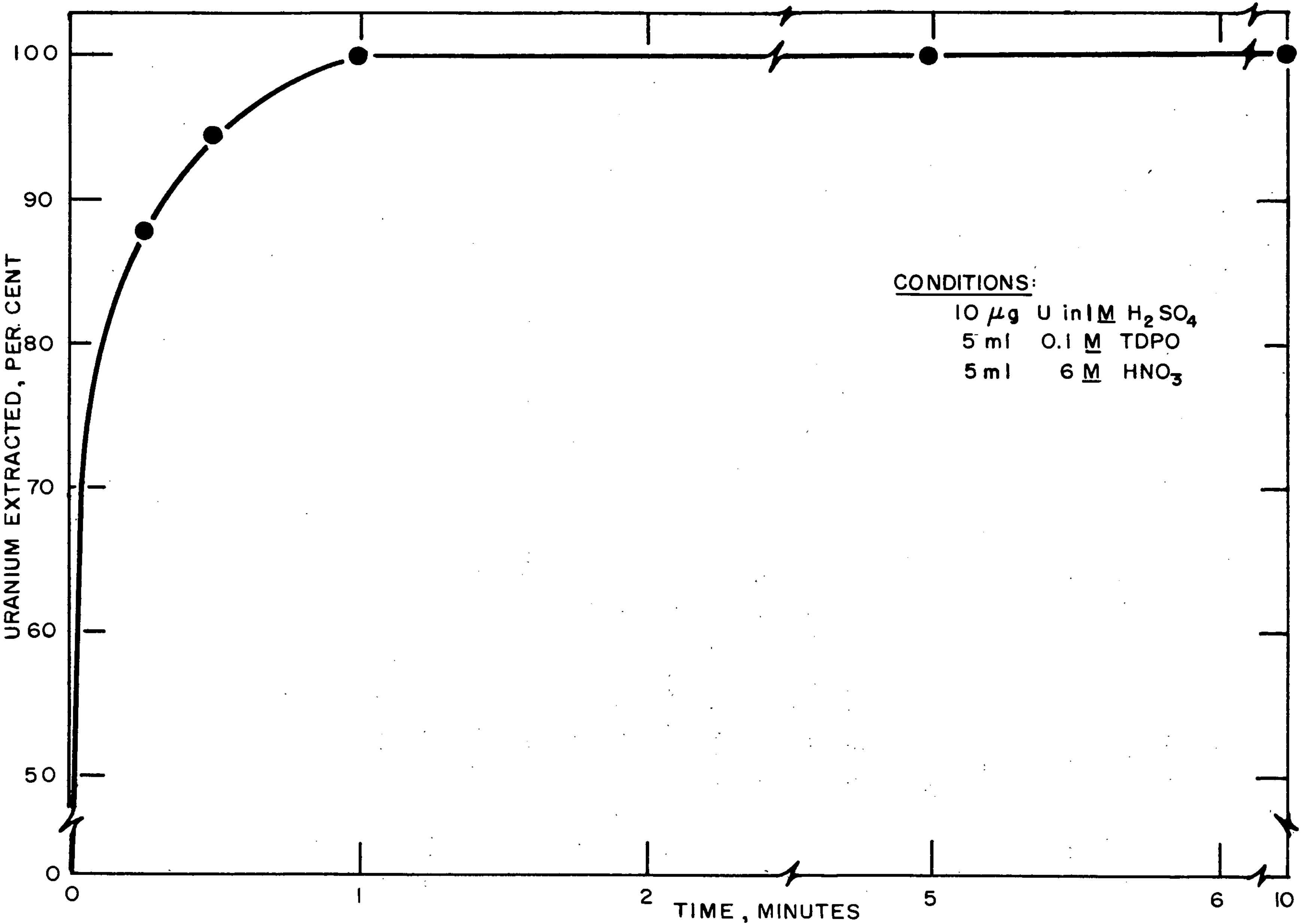

FIGURE 1. EFFECT OF TIME ON EXTRACTION OF URANIUM WITH TRIDECYLPHOSPHINE OXIDE

Table III

Extraction of Uranium by Tridecylphosphine Oxide in Solutions Containing Different Acids

Conditions: 1-ml test aliquot (10 μg uranium)
5 ml of 6 M HNO_3
Shaking time, 5 minutes

Acid	Concentration, Molarity	Uranium, μg*
Sulfuric	1	9.7
	2	10.6
	6	10.0
	12	10.2
Phosphoric	1	9.7
	2	9.7
	5	10.0
	10	9.1
Hydrochloric	1	9.8
	2	9.6
	5	9.9
	10	10.2
Oxalic	0.5	9.6
Sulfuric 0.5 M	0.25	9.7
Phosphoric 0.5 M	0.25	9.7
Citric	0.5	9.4
Sulfuric 0.5 M	0.25	10.1
Phosphoric 0.5 M	0.25	10.1
Tartaric	0.5	9.6
Sulfuric 0.5 M	0.25	9.7
Phosphoric 0.5 M	0.25	9.8

* Average of duplicate analyses

Within the limits of precision of the fluorometric method, 5 to 10 per cent, the extraction of uranium was quantitative in all cases. Of particular importance is the fact that even in solutions as concentrated as 12 M H_2SO_4 or

10 M H_3PO_4, 10 µg of uranium was quantitatively extracted under the conditions of the test. These results attest to the great applicability of TDPO as an extractant for uranium.

Effect of Concentration of Extractant

Three concentrations, 0.01, 0.05, and 0.1 M TDPO in Varsol were studied. The composition of the test aliquot was varied, but 5 ml of 6 M HNO_3 was added to each aliquot prior to extraction. The results are given in Table IV.

Table IV

Effect of Concentration of Tridecylphosphine Oxide on Extraction of Uranium from Various Acidic Media

Conditions: 1-ml test aliquot (10 µg U/ml)
5 ml of 6 M HNO_3
5 ml of TDPO in Varsol
Shaking time, 10 minutes

TDPO, M	Acid, 1 M		
	HCl	H_3PO_4	H_2SO_4
	Uranium, µg		
0.01	9.6 8.8	7.5 6.5	8.7 8.2
0.05	10.1 9.6	9.7 10.0	10.4 10.2
0.1	10.1 10.1	10.0 10.2	10.5 10.9

The most consistent results were observed when the 0.1 M TDPO solution was used, although essentially the same readings were found for the 0.05 M TDPO solution. The readings were in agreement with that obtained for a direct plate of uranium. Only in the case of 0.01 M TDPO were low readings noted.

Ratio of Volume of Test Aliquot to Extractant

In all of the previous tests, the ratio of the volume of the test aliquot to that of the phosphine oxide solution was held constant at 6:5. This ratio was chosen since, in the majority of cases, a one-ml aliquot of the sample solution is taken for analysis. Five ml of acid was then added to form a total of 6 ml of aqueous solution.

Tests were made to determine how large a ratio could be tolerated. In these tests the volume of organic was maintained at 5 ml; 10 μg of uranium in either H_2SO_4 or H_3PO_4 was taken, and nitric acid was added to the solution. The volume of the aqueous solution was either 15, 25, or 40 ml which yield ratios of 3, 5, and 8 to 1. Nitric acid was added to the aqueous solution so that the solution was either 1 or 3 M with respect to nitric acid. The samples were shaken for 10 minutes instead of the usual 5 minutes in order to afford a margin of safety in attaining equilibrium during extraction. A 1-ml aliquot of the organic phase was taken for fluorometric analysis. The results are shown in Table V.

Table V

Effect of Large Ratio of Volume of Aqueous to Organic Phases on Extraction of Uranium with TDPO

Conditions: Uranium, 10 μg
TDPO, 0.1 M, 5 ml
Shaking time, 10 minutes

Aqueous/Organic Ratio	H_2SO_4 Molarity	H_3PO_4 Molarity	3 M HNO_3 Uranium, μg	1 M HNO_3 Uranium, μg
3	0.067	-	9.7	9.6
5	0.04	-	10.2	9.4
8	0.025	-	9.7	9.7
3	-	0.067	9.9	10.3
5	-	0.04	10.5	10.2
8	-	0.025	10.3	10.2

The results indicate that the extraction of uranium is quantitative under all those conditions which were tested. This experiment shows the great sensitivity of this extractant under rather adverse conditions. In the case of the ratio of 8 to 1, the concentration of uranium in the aqueous phase prior to extraction was 0.25 µg per ml; nevertheless, the extraction after 10 minutes was quantitative. This points out the potential use of TDPO or TOPO in the recovery of uranium from salvage material, and from the standpoint of the analyst, it offers an extremely rapid method for the separation of uranium in low concentrations where sampling problems dictate the use of rather large aliquots.

Extraneous Ions

In all previous tests, no foreign cations other than alkali metals or aluminum were present in the extraction media. Experiments were conducted to ascertain the degree of interference of a number of ions that are known to quench the fluorescence of uranium. In these tests 10 µg of uranium in 1 M H_2SO_4 was mixed with the solution of the interfering ion. Five ml of either 1 or 6 M HNO_3 and 5 ml of 0.1 M TDPO were added; then the solution was shaken for 10 minutes. A one-ml aliquot of the extract was then taken for fluorometric analysis. The results are given in Table VI.

Table VI

Effect of Other Cations on the Fluorometric Determination of Uranium after Extraction of Uranium with Tridecylphosphine Oxide

10 µg Uranium

Cation	mg/ml	1 M HNO_3	6 M HNO_3	1 M $Al(NO_3)_3 9H_2O$
		Uranium, µg		
V^{+5}	50	5.5	9.8	5.8
	25	8.2	10.1	4.8
As^{+5}	37	10.5	10.3	10.5
W^{+6}	184	3.7	3.7	3.8
	92	3.7	3.8	3.8
	10		5.1	
Fe^{+3}	10	8.0	9.0	-
	5	9.8	10.2	-
Ni^{+2}	10	9.8	9.8	-
Cu^{+2}	10	9.9	9.7	-
Pb^{+2}	10	10.1	10.3	-
Sn^{+2}	10	9.1	9.5	-
Zn^{+2}	10	10.1	10.2	-
ZrO^{+2}	10	9.1	3.0	-
Mo^{+6}	10	9.4	9.5	-
Co^{+3}	10	9.9	9.9	-
Cr^{+3}	10	9.7	9.7	-
Cr^{+6}	10	1.1	0.5	-

Manganese, as $KMnO_4$, was evidently reduced during the extraction step since MnO_2 precipitated out in the form of a suspension in the organic phase. Spectrographic analysis of the organic phase, freed of MnO_2, revealed that no manganese had been extracted. The determination of uranium in the organic phase could not be accomplished.

The range of tungstate concentration under consideration was quite large. Tungstate was extracted and it was found that it quenched the uranium fluorescence as evidenced by the low, but reproducible results. These data are somewhat suspect since the phosphors were highly discolored.

The ion which displays the greatest degree of interference is hexavalent chromium. Ten mg of dichromate quenched approximately 90 per cent of the uranium fluorescence. This interference is easily eliminated, however, by reducing the dichromate to trivalent chromium, in which case no quenching occurs. It is of interest to note that when a direct plate was made on a solution of 10 μg of U and 10 mg of Cr^{+6}, quenching was 100 per cent complete, as no emitted light was measured.

The results of the tests with zirconium in 6 $\underline{M}$ HNO_3 reveal that severe quenching occurred. The quenching was practically eliminated when extraction was made from a less concentrated nitrate media, 1 $\underline{M}$ HNO_3. Ferric iron evidently causes some quenching at the 10 mg level; however, 5 mg of ferric iron seemingly does not interfere.

In general, the magnitude of the interference of the cations that were tested is not a function of the nitrate concentration of the extraction media. A notable exception, however, is pentavalent vanadium where quantitative results were obtained only when the nitrate concentration was increased significantly. This can be explained on the assumption that the extraction coefficient for uranium is increased by the excess nitrate ion more than is the coefficient for vanadium. A semi-quantitative, spectrographic test indicated that approximately the same concentration of vanadium was present in the extracts at both acid concentrations. Furthermore, about twice as much vanadium was found in the 50-mg test as in the 25-mg test, which indicates a fixed distribution coefficient that is not markedly affected by increasing nitrate concentration.

The aluminum nitrate tests were not made in all cases. The results roughly parallel those from 1 M HNO_3 tests.

The organic phases from these tests were subjected to spectrographic analysis in order to provide a general idea of the extractibility of the interfering ions. These ions were extracted strongly: Mo^{+6}, Cr^{+6}, V^{+5}, ZrO^{+2} (from 6 M HNO_3 only), and Sn^{+2}; less strongly, Cr^{+3}; and Fe^{+3} weakly. These ions were not extracted: Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+4}, and Zn^{+2}.

The interference of thorium was studied more extensively. The results are shown in Table VII.

Table VII

Effect of Thorium on the Fluorometric Determination of Uranium after Extraction of Uranium with Tridecylphosphine Oxide

Conditions: 5 ml 6 M HNO_3
5 ml 0.1 M TDPO
Uranium taken, 1 ml (10 µg U/ml)
Shaking time, 5 minutes

Thorium mg	Uranium, µg	
	1 M H_2SO_4	1 M H_3PO_4
0.0	9.3	9.3
0.023	9.1	9.2
0.23	9.6	9.2
0.46	7.8	7.8
1.4	6.5	6.5
2.3	2.0	3.8
11	0.02	0.06
23	0.02	0.04

As much as 230 micrograms of thorium can be present in the extraction of 10 µg of uranium with TDPO without seriously quenching the fluorescence of the uranium flux. When 460 µg of thorium was present, an error of about 20 per cent was observed. The quenching effect increased essentially linearly with the amount of thorium present up to about 11 mg of thorium, in which case quenching was nearly 100 per cent.

For comparative purposes the thorium tests were repeated with tributylphosphate as the extractant. In the presence of 230 mg of thorium, quenching was approximately 50 per cent complete, or nearly twice as much as that found with TDPO.

Extraction of Uranium from Hydrochloric and Sulfuric Acids[2]

In the previous work the effect of the composition of the test aliquot was essentially nullified by the addition of excess nitrate ions in the form of nitric acid. Brief studies were made to determine how quantitative the extraction of uranium is in the absence of nitrate ions. In this work 1 ml of the test solution containing 10 µg of uranium was diluted with 5 ml of the acid being tested. The uranium was extracted with 5 ml of 0.1 M TOPO for 5 minutes; then a 1-ml aliquot of the extract was taken for the fluorometric analysis. The results are shown in Table VIII.

Table VIII

Extraction of Uranium with Trioctylphosphine Oxide from Hydrochloric and Sulfuric Acids
No Additional Nitrate Added

Conditions: 1 ml test aliquot - 10 µg U
5 ml of acid
5 ml of 0.1 M TOPO
Extract 5 minutes

Hydrochloric Acid, HCl Molarity	Uranium, Micrograms Average of Duplicates
1	9.7
2	9.9
5	9.6
10	9.8
12	7.3
Sulfuric Acid, H_2SO_4 Molarity	
1	4.2
2	4.7
3	10.0
5	7.5
10	0.03
12	0.01
15	0.01
18	0.01

Quantitative results were obtained in hydrochloric acid media with the exception of 12 M HCl, in which case the results were approximately 25 per cent low. These data show that additional nitrate is not necessary for quantitative extraction of uranium from hydrochloric acid systems. This is an advantage whenever nitrate is not desired in the extraction medium.

The effect of sulfuric acid on the extraction is notable in that a definite optimum concentration for quantitative extraction is observed. The extraction curve goes through a maximum and then sharply declines. Although quantitative extraction is indicated in 3 M H_2SO_4, the precision of tests at this concentration was very poor. At concentrations above 10 M H_2SO_4, essentially no uranium was extracted. Here again, the versatility of the phosphine oxides for the extraction of uranium is demonstrated in that by the addition of nitrate ions, the extraction of uranium from these concentrated sulfuric acid solutions is rendered quantitative.

Blake et al had showed that extraction of uranium was excellent from HCl solutions and also from 4 M chloride solutions at pH 1.6. A different behavior was noted in sulfate media in that extraction of uranium increased with increasing concentrations of sulfuric acid to about 3 or 4 M; but when the pH was held constant, an increase in the sulfate concentration resulted in a decrease in extraction of uranium.

These results show that the extraction is quantitative in sulfuric acid in concentrations as high as 3 M, which confirms Blake's findings, but the results also show that at higher concentrations, of the order of 10 M, the extraction virtually falls off to a negligible fraction. Such a severe decrease in the extraction coefficient in concentrated HCl media was not observed.

In view of the satisfactory results for the extraction of uranium in hydrochloric acid systems, further tests were conducted to determine the effect of extraneous ions in the solution on the extraction. Thorium, ferric iron, hexavalent chromium, and zirconium were selected for these tests. Ten micrograms of uranium in 5 ml of either 1 or 6 M HCl in the presence of various concentrations of the above elements was extracted with 5 ml of 0.1 M TOPO for 5 minutes, 0.5 ml of the organic extract was taken for fluorometric analysis. The results are shown in Table IX.

Table IX

Effect of Extraneous Ions on the Fluorometric Determination of Uranium after Extraction of Uranium with Trioctylphosphine Oxide from Hydrochloric Acid Solutions

Element, mg	1 M HCl	6 M HCl
	Uranium, μg	
Thorium, Th^{+4}		
0.023	10.2	9.4
0.23	6.8	6.8
0.46	6.7	6.7
1.15	6.9	6.1
2.3	6.0	6.2
Iron, Fe^{+3}		
0.5	6.8	6.6
1	5.2	6.6
5	5.7	6.2
10	5.2	6.2
Chromium, Cr^{+6}		
0.5	3.4	3.4
1	2.8	2.8
5	2.1	2.0
10	1.5	1.5
Zirconium, ZrO^{+2}		
0.5	9.3	8.5
1	8.5	8.2
5	7.8	7.6
10	7.2	4.5

Each of the four elements that were tested interfered in the determination of uranium. The interference was undoubtedly due to a quenching of the uranium phosphor by the element in question since these ions are extracted by TOPO, particularly in hydrochloric acid systems. The phosphors were also discolored which indicated the presence of foreign ions.

CONCLUSION

Tridecylphosphine oxide (TDPO) or its trioctyl homolog (TOPO) in Varsol solution has been shown to be an eminently satisfactory extractant for uranium in its fluorometric determination. A single, simple extraction procedure has been devised that is essentially independent of the nature of the sample solution in which the uranium is contained. This is possible because of the extremely high affinity of TDPO for the uranyl ion. The procedure is applicable to the extraction of uranium from solutions that are as concentrated as 12 molar with respect to such acids as sulfuric, phosphoric, and hydrochloric. In addition, the extraction is quantitative in the presence of such anions as citrate, oxalate, and tartrate that form strong complexes with the uranyl ion in solution. The addition of nitric acid to these solutions enhances the extraction coefficient of uranium to such an extent that extraction is complete. Quantitative results for uranium were also found when hydrochloric acid systems were used.

On the basis of this wide applicability to a variety of solutions, the phosphine oxides are far superior to other extractants from this standpoint alone. The extraction procedure is not subject to stringent conditions. The acidity of the extraction media should preferably be no less than 0.1 $\underline{M}$ (pH 1) although less acid systems can be tolerated. The addition of the 5 ml of 6 M HNO_3 ensures a sufficient acidity and nitrate concentration under virtually all conditions. Equilibration is extremely rapid. Five minutes is ample time for the quantitative extraction of uranium. This is an important consideration in routine analysis where large numbers of samples are involved.

With respect to interference by quenching of the uranium phosphor due to the presence of extraneous ions, significant amounts of these ions apparently can be tolerated. Ten mg of hexavalent chromium present in the extraction media interferes seriously but the trivalent oxidation state does not interfere. Ten mg of ferric iron quenches to a small extent.

The most important disadvantage of the phosphine oxides is their degree of availability. At present no commercial source is known, but it is believed that this situation will be rectified as more uses are made of these reagents.

Application of the phosphine oxides to the extraction of uranium in milligram amounts is obvious. In addition, direct measurement of the absorbance of the uranium in the organic phase is feasible. These possibilities and others are now under investigation.

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APPENDIX I

PREPARATION OF TRIOCTYLPHOSPHINE OXIDE

Reagents

1. Benzene, reagent grade.
2. Ethyl alcohol, 95 per cent.
3. Ethyl ether, anhydrous, reagent grade.
4. Ethyl ether, dried. Anhydrous ethyl ether was allowed to stand for 16 hours over sodium wire.
5. Hydrochloric acid, reagent grade.
6. Iodine, crystals, reagent grade.
7. Magnesium, turnings (for Grignard reaction).
8. 1-Bromooctane.
9. Petroleum ether.
10. Phosphorus oxychloride, $POCl_3$, reagent grade.
11. Sodium carbonate.
12. Standard sodium thiosulfate solution, 0.102 N.

Preparation

Synthesis. $C_8H_{17}Br + Mg \longrightarrow C_8H_{17}MgBr$

$$3C_8H_{17}MgBr + POCl_3 \longrightarrow (C_8H_{17})_3PO + 3MgBrCl.$$

Into a 3-neck flask of 5-liter capacity were added ~2 liters of dried ethyl ether, 73 g of Mg, and ~0.2 g of iodine. A double condenser, stirrer, and dropping funnel were connected to the flask. Five hundred and seventy-nine (579) grams of 1-bromooctane was placed in the dropping funnel and introduced very slowly to the magnesium-ether mixture until the reaction commenced and then added dropwise, with stirring. After all the 1-bromooctane was added, the mixture was refluxed (by heating with steam) for one hour. The flask was then placed in a cold water bath while the $POCl_3$ was introduced dropwise with stirring. When all the $POCl_3$ had been transferred into the flask, the white curdy mixture was hydrolyzed by slowly adding 1.5 liters of ice water to the flask. If convenient, the mixture was stirred overnight, otherwise the extraction procedure described below was started at once.

Extraction. The reaction mixture was transferred to a 5-liter separatory funnel with ~1 liter of ether. One liter of 10% Na_2CO_3 solution was then added to neutralize phosphonic acid and the mixture was agitated for 5 minutes. The lower aqueous layer was withdrawn (~200 ml of ethyl alcohol was added to break emulsions) and discarded. The ether phase was then extracted twice with 1-liter volumes of water to remove the sodium salts of the contaminant phosphonic acid. The ether phase was acidified by extraction with 1 liter of 5 per cent HCl followed by extraction with 1 liter of water.

The extraction cycle was repeated until no evidence of insoluble phosphonic acid was observed when the second water wash was acidified with HCl.

$$2(C_8H_{17})_2P(O)OH + Na_2CO_3 \longrightarrow Na_2\left[O(O)P(C_8H_{17})_2\right]_2.$$

Aeration. The ether phase was transferred to a 2-liter beaker and the ether evaporated on a steam bath. Moist air was bubbled through the molten phosphine oxide, by means of a multi-perforated glass tube, for 16 to 64 hours to convert the remaining impurities into phosphonic acid. The phosphine oxide was cooled to $\sim 35^\circ$ C and diluted with 2 liters of ether. The mixture was stirred until homogeneous and then extracted again to remove the newly formed phosphonic acid. After all acid was removed, the ether phase was again evaporated and the phosphine oxide permitted to crystallize.

Distillation. The phosphine oxide was melted on the steam bath ($\sim 50^\circ$ C) and transferred to a 1-liter florence flask. The flask was connected to the vacuum distillation apparatus and heated by means of an electric mantle. The still pot temperature was followed by means of a thermocouple.

The pressure of the distillation system was maintained at ~ 60 mm Hg until all H_2O had been removed. The pressure was then lowered to ~ 200 μ Hg while the temperature was raised slowly. A small amount of liquid and gaseous distillate was removed at 200 μ Hg between 30° C and 180° C. At the latter temperature the phosphine oxide began to distill and solidify, so that the receiver had to be changed. The distillation was continued at 200 μ Hg until the still head temperature was 204° C. Approximately 95 per cent of the distillate came over in the $201\text{-}202^\circ$ C range. The receiver was transferred to a steam bath and the phosphine oxide melted. The melt was transferred to a porcelain tray and allowed to solidify. The crystalline white product was pulverized with a hammer.

Determination of Acidic Impurities.

a. Total acidity. $R_2 - P - OH + NaOH \longrightarrow R_2PONa + H_2O$.

One gram of phosphine oxide was dissolved in 10.0 ml of 50 per cent alcohol and titrated with 0.0102 N NaOH. Ten ml of 50 per cent alcohol was titrated with 0.0102 N HaOH as a blank for the phenolphthalein end point.

b. Dialkylphosphinous acids. $R_2POH + I_2 \longrightarrow R_2PI + HI$.

Two grams of phosphine oxide was dissolved in 20 ml of benzene in a 100-ml erlenmeyer flask. Ten ml of 0.1 N I_2 in 2 per cent KI and 2 ml of pyridine were then added. The mixture was shaken for 4 hours by means of a mechanical shaker and then titrated with standard sodium thiosulfate solution until the iodine color disappeared. Ten ml of the same I_2 solution was titrated with thiosulfate. The difference in the titrations of I_2 in the blank and sample was equivalent to the acid present.

6. Recrystallization. When the total acidity and combined acidity were reduced to below one per cent by repeated aeration and extractions, the product was recrystallized from petroleum ether at dry ice-ethyl alcohol temperatures until the melting point range was less than 1° centigrade.

Batch	Melting Point, °C	Yield Per Cent
1) 2)	51 to 51.5	42
3	50.8 to 51.5	46

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