

EXTRACTION AND SEPARATION STUDIES OF URANIUM/VI/
WITH TRIS-/2-ETHYL HEXYL/ PHOSPHATE

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A solvent extraction method is proposed for the extraction and separation of uranium from salicylate media using tris-/2-ethyl hexyl/ phosphate dissolved in xylene as an extractant. The optimum conditions were evaluated from a critical study of pH, salicylate concentration, extractant concentration, period of equilibration and diluent. The method permits the separation of uranium from thorium, cerium, titanium, zirconium, hafnium, copper, vanadium and chromium from binary mixtures and is applicable to the analysis of uranium in synthetic samples. The method is precise, accurate, fast and selective.

INTRODUCTION

In view of increasing demand of uranium in nuclear energy programme the investigation was undertaken to evaluate and select a solvent extraction procedure for the quantitative extraction and separation of uranium from salicylate media.

Various organophosphorus compounds such as tributylphosphate /TBP/, trioctylphosphine oxide /TOPO/ and di-2-ethyl hexyl/ phosphoric acid were used as extractants for uranium from media containing different complexing ions, but the possibility of tris-2-ethyl hexyl/ phosphate /TEHP/ as an extractant has not been explored as yet. The proposed method provides extractive separation of uranium by extraction of its salicylate complexes into tris-2-ethyl hexyl/ phosphate dissolved in xylene.

EXPERIMENTAL

Apparatus

A Unicam SP 500 spectrophotometer with 1-cm silica cells and a Control Dynamics digital pH-meter with combined glass electrode were used for measuring absorbance and pH values, respectively.

Chemicals and reagents

The stock solution of uranium(VI) was prepared by dissolving 1.0 g of uranyl nitrate in 250 ml of distilled water containing 2 ml of concentrated nitric acid. This solution was standardized by known method¹ and diluted further as required to give a working solution.

A 4% m/v solution of tris-2-ethyl hexyl/ phosphate /97%, Aldrich/ in xylene was used without purification.

0.1% aqueous solution of 4-2-pyridylazo/ resorcinol /PAR/ was used for uranium determination².

All other chemicals used in this work were of analytical reagent grade.

General extraction procedure

To an aliquot of solution containing 10-180 µg of uranium(VI), add 0.1 g of sodium salicylate to give a

concentration of 0.025M in a total volume of 25 ml; adjust the pH of the solution to 3.0-4.7 with dilute hydrochloric acid or sodium hydroxide and equilibrate the mixture in a separatory funnel for 15 sec with 5 ml of 4% tris-/2-ethyl hexyl/ phosphate in xylene. After phase separation, uranium from the organic phase was stripped with 0.8M of hydrochloric acid and determined spectrophotometrically using PAR /Ref. 2/ as the chromogenic agent.

RESULTS AND DISCUSSION

Extraction conditions

The extraction of uranium(VI) was studied at various pH values /3.0-7.0/, sodium salicylate concentration /0.005-0.125M/ and TEHP concentrations /0.5-5%/. It was found that 4% solution of tris-/2-ethyl hexyl/ phosphate in xylene extracts uranium quantitatively from 0.025M sodium salicylate solution at pH 3.0-4.7.

Effect of solvents

The suitability of several diluents such as xylene, toluene, benzene, nitrobenzene, chloroform, carbon tetrachloride, hexane and cyclohexane using the proposed method was investigated and it was found that the extraction was quantitative with either xylene or toluene as diluent. The extractions were incomplete with other diluents.

Period of extraction

The period of equilibration was varied between 10 and 60 sec. The minimum shaking time was found to be 10 sec. However, prolonged shaking had no adverse effect on the extraction of uranium.

Effect of stripping agents

Different stripping solutions such as mineral acids, sodium hydroxide, ammonium hydroxide and water were tried for the back extraction of uranium from the organic phase. It was found that 0.7-3.0M of hydrochloric acid, 0.1-2.0M of sulphuric acid, 0.5-3.0M of nitric acid, 0.1-2.0M of perchloric acid, 0.5-2.0M of sodium hydroxide and 1.0-3.0M of ammonium hydroxide were suitable for the stripping of uranium quantitatively from the organic phase. Water do not strip uranium from the TEHP phase.

Nature of the extracted species

The lg- \lg plot of distribution ratio vs. lg of salicylate concentration /at fixed pH and extractant concentration/ and TEHP concentration /at fixed pH and salicylate concentration/ yielded a molar ratio of 1:2 with respect to both extractant and salicylate. Hence the extracted species was thought to be a neutral complex of probable composition $UO_2 /H sal/_{2.2} TEHP$ where TEHP is tris-(2-ethyl hexyl)phosphate.

It causes the extraction of uranium by solvating the salicylate salt.

Effect of foreign ions

Uranium(VI) was extracted and separated in the presence of a large number of different ions. The tolerance limit was set at the amount of foreign ion required to cause a $\pm 1\%$ error in the recovery of uranium by the proposed method. Results showed that 3000 μg each of chromium(VI), barium(II), magnesium(II), arsenic(III), calcium(II), nitrate, phosphate, thiosulphate, chloride, tartrate and EDTA; 2400 μg each of cyanide, sulphate, citrate, iodide, thiocyanate and nitrite; 1500 μg each of tungsten(VI), silver(I) and mercury(II);

1200 μg each of titanium/IV/, hafnium/IV/, gold/III/ and fluoride; 900 μg each of bismuth/III/, tellurium/IV/, zirconium/IV/ and aluminium/III/; 600 μg of osmium/VIII/; 300 μg each of lead/II/, iron/III/, copper/II/, cadmium/II/ and nickel/II/ and 180 μg each of thorium/IV/, cobalt/II/, palladium/II/, cerium/IV/ and manganese/II/ do not interfere in uranium /60 μg / extraction and subsequent photometric determination with PAR.

Binary separation of uranium/VI/ from thorium/IV/ and cerium/IV/

Both thorium/IV/ and cerium/IV/ showed coextraction with uranium/VI/ when extracted with 4% tris-/2-ethyl hexyl/ phosphate from 0.025M sodium salicylate solution. However, separation of uranium from thorium and cerium from binary mixtures was feasible by selective stripping of uranium with 1M ammonium hydroxide. Thorium and cerium from the organic phase were then stripped with 2M hydrochloric acid and 1M hydrochloric acid, respectively. Stripped thorium and cerium in aqueous solution were determined spectrophotometrically using thoron³ and arsenazoIII /Ref. 4/, respectively. The recovery of the metal ions were found to be $\geq 99\%$. The results of the separation are shown in Table 1.

Separation from other binary mixtures

The extraction of uranium by the recommended procedure facilitates its separation from titanium/IV/, zirconium/IV/, hafnium/IV/, copper/II/, vanadium/V/ and chromium/VI/ as these metal ions cannot be transferred into the TEHP phase and remain completely in the aqueous phase. The aqueous solution was evaporated to dryness, treated with perchloric

TABLE 1

Separation of uranium /VI/ from binary mixtures

Synthetic mixture, mass μg^{-1}	Amount found [*] , μg	Recovery, %
U/60/ - Th/80/	U, 60 ; Th, 79.5	U, 100.0; Th, 99.4
U/60/ - Ce/120/	U, 59.5; Ce, 120	U, 99.2; Ce, 100.0
U/60/ - Ti/200/	U, 60 ; Ti, 199	U, 100.0; Ti, 99.5
U/60/ - Zr/80/	U, 60 ; Zr, 80	U, 100.0; Zr, 100.0
U/60/ - Hf/50/	U, 60 ; Hf, 50	U, 100.0; Hf, 100.0
U/60/ - Cu/10/	U, 59.6; Cu, 10	U, 99.3 ; Cu, 100.0
U/60/ - V/75/	U, 60 ; V, 74.8	U, 100.0; V, 99.8
U/60/ - Cr/20/	U, 60 ; Cr, 20	U, 100.0; Cr, 100.0

^{*}Average of six determinations.

acid to decompose salicylate and finally taken up in water. Titanium, zirconium, hafnium, copper, vanadium and chromium were determined spectrophotometrically with hydrogen peroxide³, alizarin red³, xylenol orange³, 1-/2-pyridylazo/-naphthol², phosphotungstovanadic acid¹ and diphenylcarbazide³, respectively. Finally uranium was recovered from the organic phase and determined as described in the general extraction procedure. The recoveries of uranium and that of the added ions were $\geq 99\%$. The results of the separation are given in Table 1.

Application in the analysis of calcined animal bone and powdered milk

Uranium was added to the calcined animal bone and powdered milk which were known to be free from uranium. The samples were brought into solution with aqua regia and after filtration an aliquot of the solution was taken for

TABLE 2

Analysis of synthetic samples of uranium /VI/

Sample	Certified value, % ^x	Amount found, % ⁺	Standard deviation	Coefficient of variation, %
Calcined animal bone	0.410	0.408	0.010	2.37
Powdered milk	0.210	0.209	0.003	1.57

^xUranium added.⁺Average of six determinations.

the extraction of uranium as per the recommended procedure. The results of analyses by the proposed method are given in Table 2.

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