

## SOLVENT EXTRACTION SEPARATION OF URANIUM WITH ADOGEN-464

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A selective and quantitative extraction method for uranium(VI) in presence of aqueous 20% lithium nitrate solution (pH 3) using 0.1M Adogen-464 (a quaternary ammonium salt) in chloroform medium, has been described. Uranium was subsequently determined by spectrophotometric method. The effects of different parameters on the extraction behaviour are reported. The method was applied in the trace determination of uranium in few ores.

### Introduction

High molecular weight amines have long been used extensively as extractants of different metal ions,<sup>1</sup> according to a process whose mechanism involves formation of anionic metal complexes which are incorporated into the amine matrix through the ion exchange process. Reports on such extraction process of uranium by tri-octyl-amine (n and iso), Aliquat-336, Amberlite LA-1, etc., are found in the literature,<sup>2-5</sup> but no such studies were taken up with Adogen-464, a methyl trialkyl (C<sub>8</sub>-C<sub>10</sub>) ammonium chloride. The present communication reports the extraction of uranium as an anionic  $\text{UO}_2(\text{NO}_3)_3^-$  complex from aqueous lithium nitrate solution with Adogen-464 in chloroform. The effects of several variables, such as pH, amine concentration and nature of the diluents, concentration and nature of the aqueous nitrate solution, and the presence of several foreign ions, etc. have been investigated in detail. Separation of uranium from a few synthetic mixtures and also from several ores containing trace amounts of the metal is reported.

### Experimental

#### *Reagents*

Adogen-464 (Aldrich Chemical Co.) was used without further purification. A stock solution of uranium was prepared by dissolving  $\sim 1.6$  g  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in demineralized water up to a volume of 250 ml. The solution was standardized by EDTA<sup>6</sup> titration and a 50  $\mu\text{g}/\text{ml}$  U(VI) solution was prepared by appropriate dilution.

### Apparatus

A Sambros Model 335 digital pH meter and a Shimadzu model 160A uv-vis spectrophotometer were used.

### General extraction procedure

The aqueous phase (10 ml), containing 50  $\mu\text{g}$  U(VI) in a solution of 20% lithium nitrate at pH 3 was equilibrated in a separatory funnel with 10 ml 0.1M Adogen-464 (nitrate form) in chloroform for five minutes, and kept aside for another five minutes. After the separation of two layers, the metal ion was stripped back from the organic phase with 10 ml 4M  $\text{HNO}_3$  and was estimated by a spectrophotometric method<sup>7</sup> using the oxine reagent. The metal content was computed from a calibration curve.

### Results and discussion

Variation of pH of the aqueous phase within the range from 1 to 7 shows (Fig. 1) that the extraction is maximum between pH 2.5 to 3.5. At higher pH, hydrolysis may affect the extraction efficiency.

Different organic solvents were tested as diluents for Adogen-464 and their relative efficiency with respect to the percentage of extraction are chloroform > carbon tetrachloride > chlorobenzene > nitrobenzene > xylene > toluene > benzene > diethyl ether > butan-1-ol > iso-amyl alcohol.

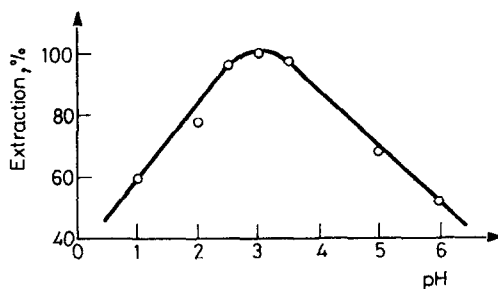


Fig. 1. Dependence of extraction efficiency on pH

Variation of amine concentration within the range of 0.025M to 0.4M shows that the extraction is quantitative at 0.1M Adogen-464 in chloroform solvent.

Similarly the study on the effect of the  $\text{LiNO}_3$  concentration shows (Table 1) that the extraction efficiency increases with the  $\text{LiNO}_3$  concentration up to a maximum

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value at 20%  $\text{LiNO}_3$  in the aqueous phase and then slowly decreases, perhaps due to a competitive extraction process of the nitrate ions. Exactly similar trends are found in presence of both  $\text{NaNO}_3$  and  $\text{KNO}_3$ ; the maximum extraction condition appear, however, at higher percentage of salt.

Indeed, the effect of increasing aqueous nitrate concentration is such that the metal ion can be stripped from the organic phase by 4M  $\text{HNO}_3$ . Some other reagents

Table 1  
Effect of nitrate concentration

Nitrate ion, %	With $\text{LiNO}_3$ extraction, %	With $\text{NaNO}_3$ extraction, %	With $\text{KNO}_3$ extraction, %
2	32.4	20.5	—
5	40.6	39.8	12.6
10	59.7	52.5	20.2
15	78.7	67.2	37.5
20	99.6	78.2	50.1
25	68.2	99.2	62.4
30	50.1	69.8	99.4
40	38.2	52.4	70.2

which were tested as stripping agents are  $\text{Na}_2\text{CO}_3$ , (0.5–4M),  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HBr}$  (0.2–6M). The alkalis were unsuitable, as they not only accelerated the hydrolysis of uranium, but also promoted emulsion formation, water reduces the molarity from 6M to lower and in that higher pH precipitation occurs. Thus for practical purposes 4M  $\text{HNO}_3$  appeared the most suitable stripping agent.

Uranium(VI) could be extracted quantitatively in the concentration range of 0.2–200  $\mu\text{g}$  in 10 ml in a single extraction with 0.1M Adogen-464 in chloroform. The effect of several diverse ions were studied using the general extraction procedure. The tolerance limit was set as the amount of foreign ion required to effect  $\pm 2\%$  error in the recovery of uranium (the ion concentration is indicated in parentheses).  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{La}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ce}^{3+}$  (10 000 ppm each);  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Gd}^{3+}$  (5000 ppm each);  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  (2500 ppm each);  $\text{Th}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Hf}^{4+}$ ,  $\text{SCN}^-$  (1500 ppm each). The separation of uranium (50 ppm) was possible from more than one foreign ion in the following mixtures, within an error  $\leq \pm 2\%$ .

1.  $\text{U}^{6+}$  (50 ppm) +  $\text{Th}^{4+}$  (250 ppm) +  $\text{Zr}^{4+}$  (200 ppm) +  $\text{Hf}^{4+}$  (250 ppm)
2.  $\text{U}^{6+}$  (50 ppm) +  $\text{Al}^{3+}$  (300 ppm) +  $\text{Zn}^{2+}$  (250 ppm) +  $\text{Cr}^{3+}$  (200 ppm)
3.  $\text{U}^{6+}$  (50 ppm) +  $\text{Ce}^{3+}$  (500 ppm) +  $\text{Dy}^{3+}$  (2500 ppm) +  $\text{Tb}^{3+}$  (2500 ppm).

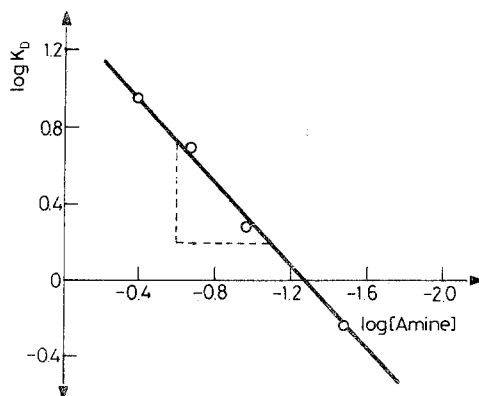


Fig. 2. Variation of  $K_D$  with Amine concentration

*Nature of the extracted species*

The distribution coefficient ( $K_D$ ) of uranium(VI) defined by

$$K_D = \frac{\text{conc. of U(VI) in org. phase}}{\text{conc. of U(VI) in aq. phase}}$$

was determined as a function of the amine concentration. The plot of  $\log K_D$  against  $\log [\text{Amine}]$  (Fig. 2) yields straight line with a slope of 1.00. The overall extraction reaction then may be considered analogous to that reported earlier,<sup>11</sup> i.e.,

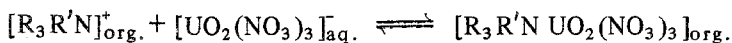


Table 2  
Extraction of uranium from ore samples

Sample	Ore taken, g	Amount present, $\mu\text{g}$	Amount found, $\mu\text{g}$ (proposed method)*
1. Uraninite I	0.5	2.80	2.70
2. Uraninite II	0.5	3.06	3.00
3. Monazite	1.0	0.10	0.089

\*Average of three determinations.

Table 3  
Percent recovery

Sample	Amount added, $\mu\text{g}$	Amount found,* $\mu\text{g}$	Recovery, %
1	0	2.7	—
	10	12.9	101.5
	20	22.3	98.3
	30	33.2	99.1
2	0	3.0	—
	10	13.6	102.0
	20	23.9	103.1
	30	33.2	100.1
3	0	0.08	—
	10	10.09	99.9
	20	20.1	100.0
	30	30.2	100.3
	40	40.29	100.4

\* Average of three determinations.

### Application

Two different samples of uraninite ores were dissolved by the usual method<sup>9</sup> based on treatment with dilute  $\text{HNO}_3$  followed by concentrated  $\text{H}_2\text{SO}_4$  acid. Manazite sample was also attacked by  $\text{HNO}_3$ , and by  $\text{HClO}_4$  treatment according to a more convenient process.<sup>10</sup> Known aliquots of each of the solutions were subjected to extraction by Adogen-464 followed by spectrophotometric measurement. The results are given in Table 2. The validity of the result was checked by evaluating the recovery of known amounts of uranium added into these solutions prior to extraction (Table 3).

The overall method is simple, rapid and largely free from interference.

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