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Extraction Chromatographic Separation of Uranium (VI) with Amberlite LA-1 from Malonic Acid

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Uranium(VI) was extracted between pH 2.5 to 6.0 from 0.01 mol dm^{-3} malonic acid on a column of silica gel with Amberlite LA-1 as the extractant. It was stripped from the column with 1—2 mol dm^{-3} of hydrochloric, sulfuric, and nitric acids. Uranium(VI) was separated from alkali, alkaline earths, manganese, iron, cobalt, nickel, zinc, yttrium, lanthanum, cerium in binary mixtures by exploiting the difference in the pH of formation of malonato complexes. Uranium was separated from zirconium, hafnium, thorium, scandium, and titanium by taking its advantage of stability of chloro or sulfato complexes. The method was tested for the standard reference rock samples.

Solvent extraction separations of uranium(VI) from mineral acid media using liquid anion exchanger has been studied, but such studies from the organic acid media are lacking. The separation of uranium by extraction chromatography using sulfate media was carried out with Alamine-336[1)] or Amberlite LA-2.[2)] The studies from nitrate media[3–5)] made use of tridodecylamine or trioctylamine as extractants. However, maximum work has been carried out from chloride media,[6–9)] where Teflon was used as the stationary support with normal trioctylamine as the stationary phase. Such methods permitted the separation of uranium from actinide elements. In continuation of our work[10)] with dicarboxylic acids, such as malonic acid, as the complexing media, extraction chromatographic studies were extended for the separation of uranium (VI) on silica-gel column coated with Amberlite LA-1 as the stationary phase. This paper describes some novel methods for the separation of uranium(VI) from associated elements. The method was tested for the analysis of uranium(VI) from rock samples.

Experimental

Apparatus and Chemicals. The apparatus used was similar to one described earlier.[11)] The stock solution of uranium(VI) was prepared by dissolving 1.055 g of uranyl (VI) nitrate (BDH, England) in 100 cm^3 of demineralized water containing 1% of nitric acid. The solution was standardized gravimetrically.[12)] It was found to contain 4.9 mg cm^{-3} of uranium(VI). A solution containing 98 μg cm^{-3} was prepared by appropriate dilution. Silica gel (100—200 mesh) was made hydrophobic by procedure described earlier.[11)] The column (10×0.7 cm) was packed with silica gel coated with Amberlite LA-1.

General Procedure. An aliquot of solution containing 98 μg of uranium(VI) was mixed with 5 cm^3 of 0.01 mol dm^{-3} malonic acid, and the pH of the solution was adjusted between 2.5—6.0 with 0.01 mol dm^{-3} malonic acid or sodium hydroxide. Then the solution was passed on the column when uranium(VI) was extracted in the stationary phase containing Amberlite LA-1. It was then stripped with various mineral acids and alkalies. Ten fractions each of 5 cm^3 were collected and uranium(VI) from each fraction was determined spectrophotometrically at 530 nm as its complex with 4-(2-pyridylazo)resorcinol (PAR).

Results and Discussion

The study of extraction of uranium(VI) as a function of pH was carried out in the pH range 1.0—8.0. The extraction commenced at pH 1.0 (45.2 %) and it was quantitative in the range 2.5 to 6.0. On further increase of the pH the extraction decreased. The optimum pH for the quantitative extraction of uranium (VI) was therefore 2.5 to 6.0 (Fig. 1).

The extraction of uranium(VI) was carried out by varying the concentration of malonic acid from 1×10^{-4} mol dm^{-3} to 5×10^{-1} mol dm^{-3}. The extraction was quantitative from 1×10^{-3} mol dm^{-3} to 2.5×10^{-1} mol dm^{-3}. At higher concentration of malonic acid there was a decrease in the extraction, probably due to the setting up of a competitive equilibrium between the anionic metal malonato complex and the simple malonate anion for Amberlite LA-1. All the extractions were carried out with 1×10^{-2} mol dm^{-3} malonic acid as it was adequate for complex formation (Fig. 2).

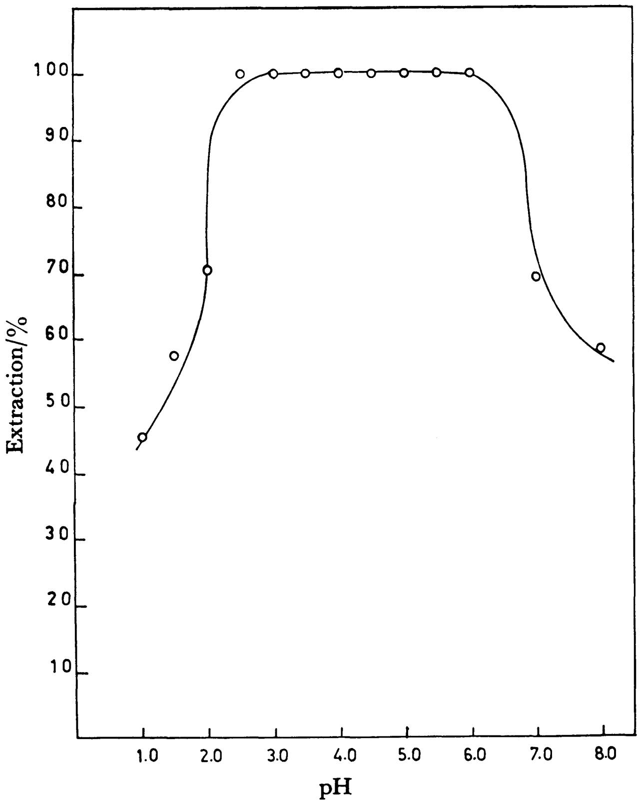

Fig. 1. Effect of pH on extraction of uranium(VI) from malonic acid.

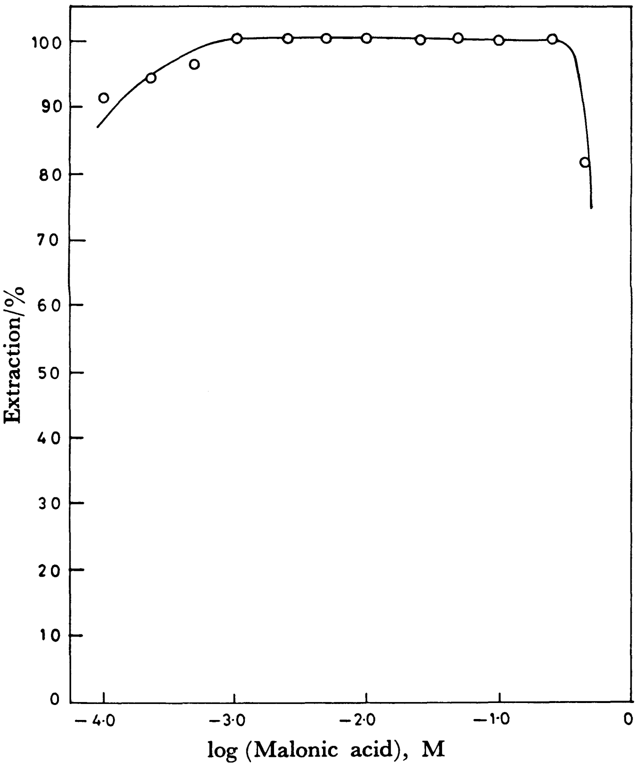

Fig. 2. Effect of malonic acid concentration. (1 M = 1 mol dm^{-3}).

On the basis of batch extraction,[13] the probable mechanism of extraction involves the following transformations:

$$UO_2(NO_3)_2 + 2(\text{malonic acid}) \longrightarrow UO_2(\text{malonate})_2^{2-} + 2HNO_3 + 2H^+ \quad (1)$$

$$[(R_2NH_2)_2(\text{malonate})]_o + [UO_2(\text{malonate})_2]_w^{2-} \longrightarrow [(R_2NH_2)_2 \cdot UO_2(\text{malonate})_2]_o + (\text{malonate})_w^{2-} \quad (2)$$

where subscript o and w refer to organic and aqueous phase respectively.

The uranium(VI) was stripped after its extraction from the stationary phase with hydrochloric, sulfuric, and nitric acids and aqueous ammonia. The stripping was quantitative with 1.0 to 2.0 mol dm^{-3} for all acids, or with 0.5 to 1.0 mol dm^{-3} of aqueous ammonia. Since uranium(VI) formed anionic sulfato complex at lower concentration of sulfuric acid, hence could not strip uranium (*i.e.* <0.25 mol dm^{-3}). At high concentration of hydrochloric acid (>6.0 mol dm^{-3}), uranium(VI) formed negatively charged chloro complex, which in turn was reextracted in the extractant. These facts formed the basis for its separation from several metal ions (Fig. 3).

Separation of Uranium(VI) from Binary Mixtures. Uranium(VI) was separated from several elements in binary mixtures by utilizing the differences in their capacity to form anionic complexes. Thus, since alkali, alkaline earths, iron(II), yttrium, zinc, cadmium, lead, nickel, cobalt, aluminium, manganesee(II), lanthanum, and cerium(III) could not form anionic malonato complexes they were not extracted and hence were separated from uranium(VI). Uranium(VI) was then subsequently stripped from the column with 2 mol dm^{-3} nitric acid. Further, since uranium formed anionic sulfato complex at lower concentration of sulfuric acid, it was possible to separate it from scandium, titanium(IV), vanadium(V), iron(III), bismuth(III) as they could not form such complexes and were stripped out with 0.1 mol dm^{-3} sulfuric acid. Uranium which was retained in the form of anionic sulfato complex in the liquid anion exchanger and was subsequently stripped with 2 mol dm^{-3} nitric acid. Uranium(VI) also formed negatively charged chloro complex at 6 mol dm^{-3} hydrochloric acid but zirconium, hafnium, and thorium could not form such chloro complex and hence were stripped out first with 6 mol dm^{-3} hydrochloric acid and then uranium(VI) was stripped with 2 mol dm^{-3} nitric acid.

Separation of Uranium(VI) from Multicomponent Mixtures. The differences in acidity at which various metals formed mineral acid complexes or inability of few to form malonato complexes was exploited to develop new separations. A mixture of lead, bismuth, and uranium (VI) were passed on the column at pH 5.0, when malonato complexes of bismuth and uranium(VI) were extracted, while lead passed through the column as the uncomplexed species. Then bismuth was stripped with 0.1 mol dm^{-3} sulfuric acid and finally uranium (VI) was stripped with 2.0 mol dm^{-3} nitric acid.

The separation of yttrium, scandium and uranium (VI) was carried out by passing the mixture through the column, when yttrium passed through as it could not form extractable malonato complex, while scandium was stripped with 0.1 mol dm^{-3} sulfuric acid fol-

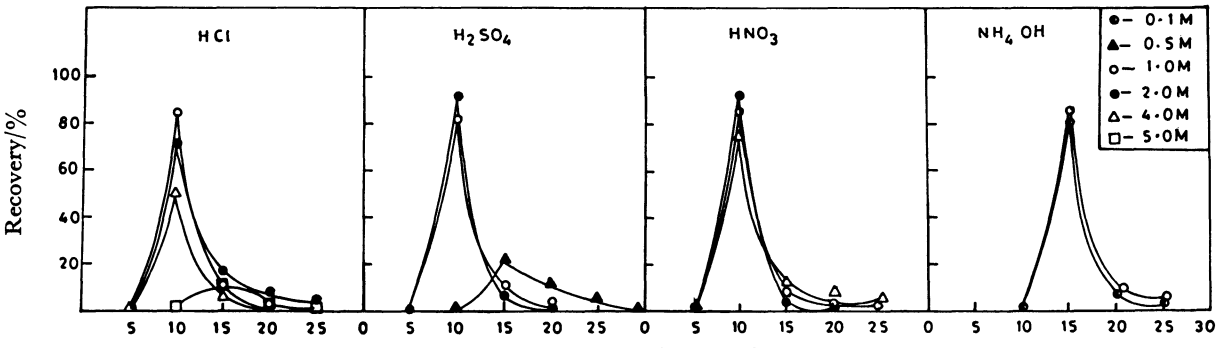

Fig. 3. Elution behavior of uranium(VI) in malonate media with various eluants.

lowed by stripping of uranium(VI) with 2 mol dm^{-3} nitric acid.

The separation of chromium(III), vanadium(V), and uranium(VI) was achieved by washing out chromium (III) with water followed by stripping of vanadium(V) with 0.1 mol dm^{-3} sulfuric acid and uranium(VI) finally with 2 mol dm^{-3} nitric acid.

The separation of uranium(VI) from aluminium, iron(III) or titanium(IV) was effected by passing the mixture through the column. Aluminium was washed with water as it did not form extractable malonato complex. Iron(III) or titanium(IV) was stripped with 0.1 mol dm^{-3} sulfuric acid and finally uranium (VI) was stripped from the column with 2 mol dm^{-3} nitric acid.

The separation of cerium(III), zirconium(IV) or hafnium(IV) was effected by washing cerium(III) with water, zirconium(IV) or hafnium(IV) was stripped latter with 6 mol dm^{-3} hydrochloric acid and finally uranium with 2 mol dm^{-3} nitric acid.

An interesting separation of uranium from lanthanum, thorium, and zirconium was achieved by passing the mixture through the column. When lanthanum was washed with water, thorium was stripped with 0.25 mol dm^{-3} sulfuric acid when zirconium and uranium (VI) were retained on the column as their sulfato complexes. Zirconium was stripped with 6 mol dm^{-3} hydrochloric acid when uranium(VI) was retained on the column as its chloro complex which was finally stripped with 2 mol dm^{-3} nitric acid (Table 1)(Fig. 4).

In all the separation it was interesting to note that uranium could be separated from other elements in the presence of various mineral acids. At 0.1 mol dm^{-3} sulfuric acid uranium(VI) forms anionic sulfato[14] complex, and thus it was possible to separate it from scandium, titanium, vanadium, iron(III), and bismuth. Similarly uranium(VI) forms chloro complex[15] with 6 mol dm^{-3} hydrochloric acid and gets reextracted where other elements like zirconium, hafnium, and thorium could be stripped with 6 mol dm^{-3} hydrochloric acid. Since uranium(VI) did not form nitrato complex at lower concentration of nitric acid, it was possible to strip uranium(VI) with 2 mol dm^{-3} nitric acid in all such cases.

TABLE 1. SEPARATION OF URANIUM(VI) FROM MULTICOMPONENT MIXTURES

	Mixtures	Taken μg	Found μg	Recovery %	Eluant
1)	Pb	100	100	100.0	Water
	Bi(III)	100	98.6	98.6	0.1 M† H_2SO_4
	U(VI)	98	97	98.9	2.0 M HNO_3
2)	Y	100	100	100.0	Water
	Sc	100	100	100.0	0.1 M H_2SO_4
	U(VI)	98	98.2	100.2	2.0 M HNO_3
3)	Cr(III)	100	100	100.0	Water
	V(V)	100	99.3	99.3	0.1 M H_2SO_4
	U(VI)	98	98.2	100.2	2.0 M HNO_3
4)	Al	100	100	100.0	Water
	Fe(III)/Ti(IV)	96.5	95.4	98.8	0.1 M H_2SO_4
	U(VI)	98	97.2	99.1	2.0 M HNO_3
5)	Ce(III)	100	100	100.0	Water
	Zr(IV)/Hf(IV)	50	49	98.0	6 M HCl
	U(VI)	98	97.5	99.4	2.0 M HNO_3
6)	La	100	100	100.0	Water
	Th	100	101	101.0	0.25 M H_2SO_4
	Zr(IV)	50	49	98.0	6.0 M HCl
	U(VI)	98	96.3	98.2	2.0 M HNO_2

† 1 M = 1 mol dm^{-3}.

Separation of Uranium(VI) from Rock Sample. About 0.5 g of the sample was heated with a mixture of hydrofluoric and nitric acid in a platinum crucible. It was then diluted to 100 cm^3 with 0.1 mol dm^{-3} nitric acid. To an aliquot of the solution 5 cm^3 of 0.01 mol dm^{-3} malonic acid was added and the pH was adjusted to 5.0. It was then passed through the

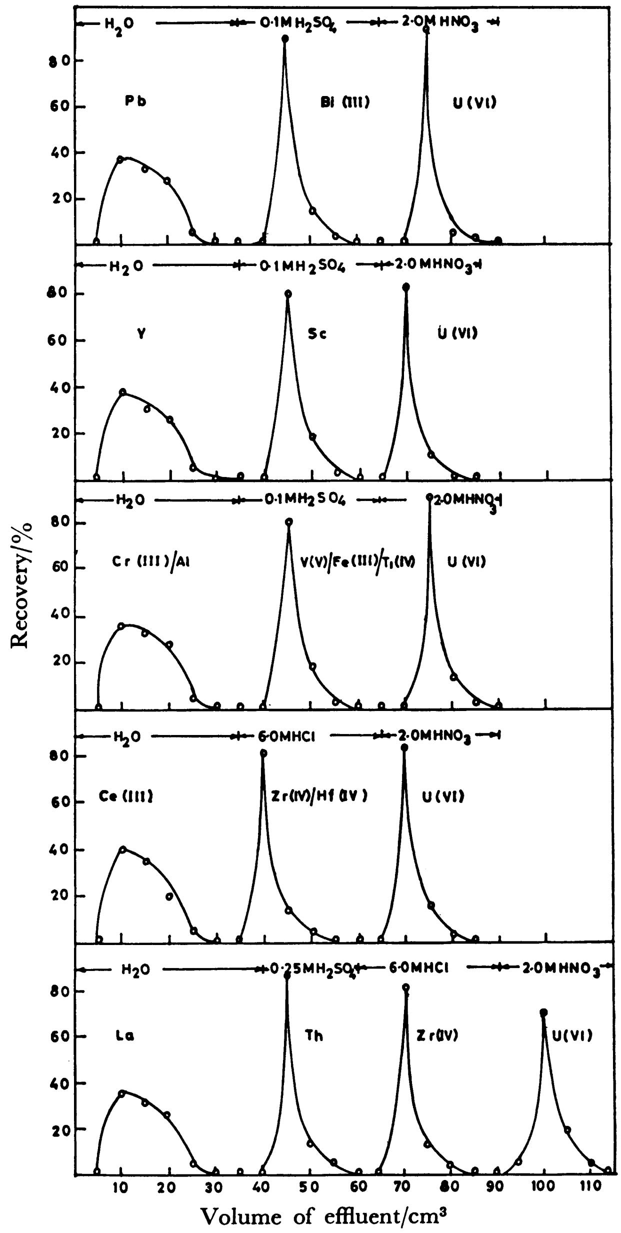

Fig. 4. Separation of uranium(VI) from multicomponent mixtures.

column when elements such as sodium, potassium, calcium, magnesium, manganese, pass through the column. The elements zirconium, thorium, and iron were coextracted with uranium. Thorium and iron (III) were stripped with 0.25 mol dm^{-3} sulfuric acid, while zirconium was stripped with 6 mol dm^{-3} hydrochloric acid under this circumstances uranium(VI) remained on the column either as sulfato complex or chloro complex. Finally uranium was stripped with 2 mol dm^{-3} nitric acid and was determined as usual. The results showed amount of uranium as a mixed oxide as 0.029% against 0.03% in the first sample and 0.079% against 0.08% in the second sample.

The separation of uranium(VI) from lead, bismuth, thorium, zirconium, and hafnium is of significance in the analysis of fission products. Also separation from aluminium, cadmium, iron, titanium, scandium, and cerium is of great importance. The proposed method is simple and rapid.

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