

Solvent Extraction of Uranium(VI) from Thorium (IV), Zirconium(IV), or Titanium(IV)

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A method has been described for the separation of uranium(vi) from titanium(iv), zirconium(iv), or thorium(iv), using sodium diethyldithiocarbamate as a complexing agent and *n*-butanol for solvent extraction. Uranium has been determined spectrophotometrically; 2.35 to 9.4 mg. of uranium can be separated from 2.39 to 9.52 mg. of titanium, 4.58 to 18.24 mg. of zirconium, or 70 to 280 mg. of thorium at pH 2.0. The pH range in which the separation can be carried out successfully is found to be 1.5 to 3.0. The presence of the following ions interfere: Cu(II), Fe(II), Fe(III), Co(II), Ni(II), Bi(III), Cr(VI), Mo(VI), W(VI), Te(IV), Se(IV), Ag(I), Pb(II), Hg(II), Zn(II), Cd(II), Mn(II), In(III), Tl(I), As(III), Sn(IV), Os(VIII), Nb(V), and V(V).

In an earlier publication¹, the separation of titanium from zirconium and thorium by solvent extraction of the cupferrates with *n*-butanol has been described. Several methods for the solvent extraction of uranium(vi), using different complexing agents, have been applied². Zingaro³ observed that uranyl ion formed a complex with diethyldithiocarbamate which is soluble in polar organic solvents like alcohols, ethers, and ketones and also in chloroform⁴. It is well known that uranyl salts have some solubility in *n*-butanol. In this case the uranyl diethyldithiocarbamate complex passes into the organic layer and not the uranyl ion alone, since the complexing agent is present in large excess. Further, the complex being appreciably stable and the stability constant of the complex being of the order of 10^{10} , it is not likely that free UO_2^{2+} ion exists in appreciable amounts. The present communication reports the results of the separation of uranium from titanium, zirconium, or thorium by the solvent extraction method, using sodium diethyldithiocarbamate as a complexing agent and *n*-butanol for extraction.

EXPERIMENTAL

Solutions of uranyl sulphate and zirconium oxychloride were prepared by direct weighing and dissolving (B.D.H. AnalaR) samples in double distilled, CO_2 -free water.

Stock solutions of titanium chloride and thorium chloride were prepared and standardised gravimetrically as titanium oxinate and thorium oxide respectively. Solutions of varying concentrations were obtained by suitable dilutions.

n-Butanol used was also of B.D.H. AnalaR grade. A 0.5% solution of sodium diethyldithiocarbamate was obtained by dissolving a B.D.H. reagent sample in *n*-butanol.

1. Munshi and Dey, *Anal. Chim. Acta*, 1962, 27, 89.
2. Morrison and Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley, New York, 1957, pp. 180, 241-245.
3. *J. Amer. Chem. Soc.*, 1956, 78, 3568.
4. Lacoste et al., *Anal. Chem.*, 1951, 23, 871.

A Unicam SP 500 spectrophotometer was employed for the photometric determination of uranium, using 1 cm glass cells. For pH measurements, a Leeds and Northrup pH-meter was used along with glass-calomel electrodes.

General Procedure.—A 0.5% solution of sodium diethyldithiocarbamate was added to the mixtures of different metallic salt solutions taken in different separating funnels (pH 2.0). After shaking well, the metal contents of the aqueous layers and organic layers were treated separately. Uranium was determined in the organic layer spectrophotometrically by comparing the absorbances against standard calibration curves of uranyl sulphate complex with sodium diethyldithiocarbamate at 385m μ . The metals in the aqueous layer were estimated gravimetrically.

Separation of Uranium and Titanium.—Several mixtures containing 5, 10, 15, 20 ml of 0.002M uranyl sulphate and 5, 10, 15, 20 ml of 0.01M titanous chloride were prepared. Uranium in the organic layer was determined as described above. Titanium in the aqueous layer was estimated gravimetrically as oxinate⁵. The results are recorded in Table I.

TABLE I

Uranium (mg.).			Titanium (mg.).		
Taken.	Found.	Diff.	Taken.	Found.	Diff.
2.35	2.30	-0.05	2.39	2.40	+0.01
4.70	4.65	-0.05	4.79	4.80	+0.01
7.05	6.95	-0.10	7.17	7.20	+0.03
9.40	9.30	-0.10	9.52	9.55	+0.03

Separation of Uranium and Zirconium.—Several mixtures containing 5, 10, 15, 20 ml of 0.002M uranyl sulphate and 5, 10, 15, 20 ml of 0.01M zirconium oxychloride were prepared and taken in separating funnels. Uranium was estimated in the organic layer spectrophotometrically and zirconium in the aqueous layer was precipitated as mandelate⁶ and ignited to the oxide. Some of the results are shown in Table II.

TABLE II

Uranium (mg.).			Zirconium (mg.).		
Taken.	Found.	Diff.	Taken.	Found.	Diff.
2.35	2.32	-0.03	4.50	4.50	-0.00
4.70	4.65	-0.05	9.12	9.10	-0.02
7.05	7.00	-0.05	13.68	13.70	+0.02
9.40	9.32	-0.08	18.24	18.25	+0.01

Separation of Uranium and Thorium.—Several mixtures containing 5, 10, 15, 20 ml of 0.002M uranyl sulphate and 5, 10, 15, 20 ml of 0.061M thorium chloride solutions were taken in separating funnels and uranium was extracted in the organic layer which was

5. Vogel, "Quantitative Inorganic Analysis", Longmans Green and Co., London, 1951, pp. 374, 493.

6. Vinogradov and Ryabchikov, "Detection and Analysis of Rare Elements", Israel Program for Scientific Translations, Jerusalem, 1962, pp. 330.

estimated spectrophotometrically. Thorium was precipitated in the aqueous layer as oxalate and determined as oxide. The results are recorded in Table III

TABLE III

Uranium (mg.)			Thorium (mg.)		
Taken.	Found.	Diff.	Taken.	Found.	Diff.
2.35	2.34	-0.01	70	69.5	-0.50
4.70	4.70	±0.00	140	139.5	-0.50
7.05	7.05	±0.00	210	209.5	-0.50
9.40	9.45	+0.05	280	279.0	-1.00

Effect of pH.—Separations were performed at different pH values and it was observed that for successful separations, the suitable pH was between 1.5 and 3.0-

Effect of Foreign Ions.—The presence of several cations was found to interfere in these separations. The ions which have been found to interfere are: Cu(II), Fe(II), Fe(III), Co(II), Ni(II), Bi(III), Cr(VI), Mo(VI), W(VI), Te(IV), Se(IV), Ag(I), As(III), Zn(II), Cd(II), Hg(II), Pb(II), Sn(IV), Mn(II), V(V), In(III), Tl(I), Os(VIII), Nb(V).

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