Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Solvent Extraction of Uranium(VI) by *N*-*m*-Tolyl-*o*-methoxybenzohydroxamic Acid

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To cite this Article Agrawal, Y. K.(1975) 'The Solvent Extraction of Uranium(VI) by *N*-*m*-Tolyl-*o*-methoxybenzohydroxamic Acid', Separation Science and Technology, 10: 2, 167 — 173
To link to this Article: DOI: 10.1080/00372367508058999
URL: http://dx.doi.org/10.1080/00372367508058999

SEPARATION SCIENCE, 10(2), pp. 167–173, 1975

NOTE

The Solvent Extraction of Uranium(VI) by *N*-*m*-Tolyl-*o*-methoxybenzohydroxamic Acid

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Abstract

A simple and rapid spectrophotometric determination of uranium(VI) is described. The uranium(VI) *N*-*m*-tolyl-*o*-methoxybenzohydroxamic acid complex is extracted with chloroform at pH 5.3 to 5.5 from aqueous solution. Maximum absorption of orange-red extract occurs at 510 nm. The colored complex obeys Beer's law over the range 0.3 to 20 ppm of uranium. The effect of acidity, reagent concentration, and diverse ions on the visible absorption of extracted complex has been studied.

INTRODUCTION

N-Phenylbenzohydroxamic acid (PBHA) has been used as a reagent for the extraction and spectrophotometric determination of uranium(VI) with chloroform (*1*) at pH 4.0. Generally Ti^{4+}, Zr^{4+}, V^{5+}, and Mo^{6+} interfere with the determination of uranium(VI) (*2–5*). It has been found that the uranium *N*-*m*-tolyl-*o*-methoxybenzohydroxamate complex can be extracted into chloroform from aqueous solution at pH 5.3 with greater selectivity and sensitivity than PBHA which is used for macrodetermination of uranium. With this consideration a new extraction spectrophotometric method has been developed for the microdetermination of uranium.

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EXPERIMENTAL

Apparatus

A Hilger and Watts ratio recording spectrophotometer with two optically matched 10 mm Corex cells was employed for all absorption measurements. The measurements at constant wave-length were performed on a Beckman DU quartz spectrophotometer. A Beckman pH meter was used for pH measurements.

Reagent and Solutions

N-m-Tolyl-*o*-methoxybenzohydroxamic acid was synthesized by the procedure of Priyadarshini and Tandon (*6*). It was recrystallized before use and its final purity was ascertained by mp, elemental analysis, UV, and IR spectra. A 0.1% w/v solution in ethanol-free chloroform was used for the extraction studies. Ethyl alcohol was removed from the commercial chloroform by washing it five times with about half its volume of water. The chloroform was distilled after drying over fused calcium chloride.

Standard uranium solution was prepared by dissolving 1.0 g uranyl nitrate (E. Merck) in 1 liter of double-distilled water. Its uranium content was determined volumetrically (*7*) and found to be 470 ppm.

Procedure

Place a sample containing 10 to 250 ppm of uranium in a 100-ml separatory funnel and add sufficient double-distilled water to make the volume 50 ml. Adjust the pH to 5.3 to 5.5 by dropwise addition of dilute hydrochloric acid and ammonium hydroxide. Add 10.0 ml of chloroform solution containing *N-m*-T-*o*-MBHA and shake for 5 min. Transfer the organic phase to an Erlenmeyer flask containing 1 g of anhydrous sodium sulphate (A.R., BDH) as drying agent. Transfer the orange-red organic phase to a 25-ml volumetric flask and repeat the extraction with an additional 3.0 ml of reagent solution to ensure complete extraction. Wash the sodium sulfate twice with two more 3-ml portions of chloroform, collect the washing, and make the volume of organic phase up to mark with chloroform. Measure the absorbance values at 510 nm against the reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra

The uranium *N*-*m*-T-*o*-MBHA complex gives an orange-red color with a maximum absorption at 510 nm. The absorption spectrum of the complex is shown in Fig. 1. The reagent has no absorption at this wavelength. The extracted uranium complex in chloroform obeys Beer's law at 510 nm in the concentration range 0.3 to 20 ppm (Fig. 2). The analytical data for the extraction of uranium(VI) are given in Table 1.

Effect of Acidity

The absorbance of the uranium complex in the organic phase is a maximum at pH 5.3 to 5.5 (Fig. 3). The results given in Table 2 show that the extraction begins at pH 3.0 and is quantitative at around 5.3. Extrac-

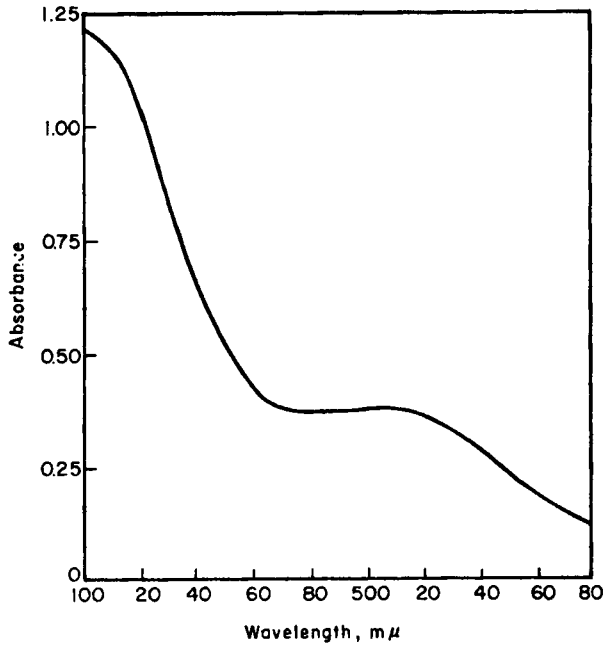

FIG. 1. Absorption spectra of uranium–*N*-*m*-tolyl-*o*-methoxybenzohydroxamic acid complex vs reagent blank.

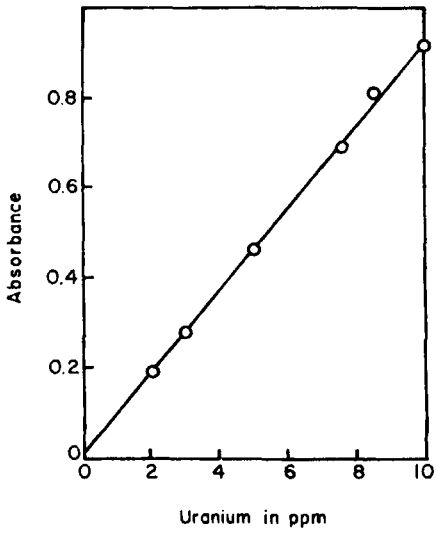

FIGURE 2.

TABLE 1
Analytical Data for the Extraction of Uranium(VI)

Uranium taken (ppm)	Uranium found (ppm)	Error (%)	Standard deviation[a]
2.0	1.99	−0.01	±0.02
3.0	2.99	−0.01	±0.03
5.0	5.01	+0.01	±0.02
7.5	7.50	0.00	±0.01
8.0	8.02	+0.02	±0.01
10.0	10.00	0.00	±0.01
20.0	20.01	+0.01	±0.03
50.0	50.00	0.00	±0.01
75.0	74.99	−0.01	±0.01
100.0	100.02	−0.02	±0.02
200.0	200.00	0.00	±0.01
250.0	250.01	+0.01	±0.01

[a]Analysis of 5 samples.

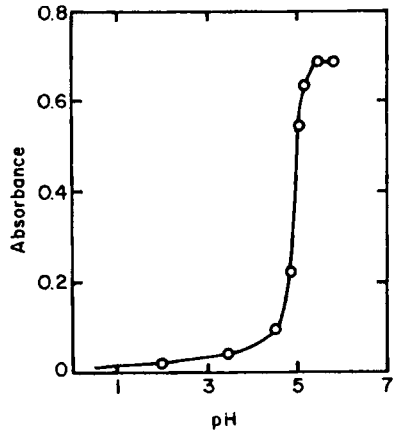

FIG. 3. Effect of pH.

TABLE 2
Extraction of Uranium(VI) *N*-*m*-Tolyl-*o*-methoxybenzohydroxamic Acid Complex as a Function of pH

pH	Extraction (% *E*)	Distribution ratio
2.0	5	0.02
3.0	7	0.09
4.0	10	0.16
4.5	10	0.20
4.8	30	0.69
5.0	50	8.00
5.1	65	20.00
5.3	100	[a]
5.5	100	[a]
5.6	Precipitated	—

[a] Too high to measure.

tion at a higher pH, 5.5, was not possible because the uranyl ions were precipitated. The colored chelate was formed instantaneously and was stable for 24 hr.

Percentage extraction of uranium was computed from

$$\%E = \frac{100\,D}{D + \dfrac{U_{aq}}{U_{org}}}$$

assuming that the volume of the both phases was $U_{org} = U_{aq}$. The distribu-

tion coefficient, D, was determined from

$$D = \frac{\text{Concentration of U in organic phase}}{\text{Total U taken} - \text{U extracted in organic phase}}$$

Effect of Reagent Concentration

Uranium(VI) was extracted at pH 5.3 to 5.5 with varying volumes and concentrations of the reagent. The results indicate that a single extraction with 10 ml of 0.1 *M* *N*-*m*-T-*o*-MBHA was adequate for quantitative extraction while extraction was incomplete with lower concentrations; i.e. 0.005, 0.01, and 0.02 *M* reagent solutions. Larger quantities of reagent could be used without any difficulty and had no effect on absorbance of the extracted species.

Recovery and Shaking Time

It was confirmed by the following experiment that uranium is extracted quantitatively into the organic phase: 5 ppm of uranium was extracted according to the recommended procedure, and the remaining aqueous phase was again extracted by adding 10 ml of reagent solution. It was observed that there was no difference between the absorbance value of the second organic phase and the reagent blank.

Effect of Diverse Ions

In order to examine the utility of this method in the presence of other ions, their interference was studied. At first, the effect of various ions on the U(VI) *N*-*m*-T-*o*-MBHA complex absorption maximum at 515 nm was investigated. Table 3 summarizes the absorbance values of 7.5 ppm U(VI) in the presence of diverse ions. Moderate amounts of many ions commonly associated with uranium did not interfere except for cerium(IV), molybdenum(VI), titanium(IV), and vanadium(V).

Acknowledgment

The author is indebted to Professor A. B. Biswas of Indian Institute of Technology, Powai, Bombay for his valuable advice and discussion. He is grateful to Professor T. S. Ma, Department of Chemistry, City University of New York for his valuable suggestion and criticism. He wishes to thank C.S.I.R., New Delhi for the award of a Senior Research Fellowship.

TABLE 3
Effect of Diverse Ions[a]

Ions	Added as	Amount added (mg)	Absorbance
Al^{3+}	$Al(NO_3)_2$	30	0.68
As^{3+}	$AsCl_3$	30	0.68
Ba^{2+}	$BaCl_2$	40	0.69
Ca^{2+}	$CaCl_2$	40	0.67
Cd^{2+}	$CdSO_4$	40	0.68
Ce^{4+}	$Ce(SO_4)_2$	Ppt	0.68
Co^{2+}	$CoCl_2$	40	0.67
Ga^{3+}	$Ga(NO_3)_3$	40	0.67
Ge^{4+}	$GeCl_4$	40	0.68
Hg^{2+}	$HgCl_2$	40	0.69
NH_4^+	NH_4Cl	50	0.69
Ni^{2+}	$NiCl_2$	70	0.69
Mn^{2+}	$MnCl_2$	40	0.68
Mg^{2+}	$Mg(NO_3)_2$	70	0.68
MoO_4^{2-}	Na_2MoO_4	1	0.66
		5	0.56
Pb^{2+}	$PbCl_2$	75	0.68
Ti^{4+}	$TiOCl_2$	1	0.67
		5	0.59
Zn^{2+}	$ZnCl_2$	30	0.68
Zr^{4+}	$Zr(NO_3)_4$	5	0.62
ClO_4^-	$HClO_4$	40	0.68
NO_3^-	$NaNO_3$	40	0.68
SO_4	Na_2SO_4	40	0.68

[a]Uranium, 7.5 ppm; pH, 5.3 to 5.5; 510 nm.

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Received by editor June 26, 1974