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Rapid Solvent Extraction of Uranium(VI) with *N*-Phenylbenzohydroxamic Acid

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NOTE

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Abstract

A rapid method for the simultaneous solvent extraction and spectrophotometric determination of macro-amounts of hexavalent uranium with *N*-phenylbenzohydroxamic acid is described. The intense blood-red colored complex thus extracted from chloroform at pH ~ 4 absorbs at around 510 nm. A clean-cut separation from many commonly occurring metal ions is easily accomplished. Effects of acidity, reagent concentration, and diverse ions on the visible absorption of the extracted complex have also been investigated.

Analytical applications of *N*-phenylbenzohydroxamic acid (PBHA) have been extensively examined in recent years (*1–3*). It has been found to be an excellent reagent for the solvent extraction and colorimetric determination of many transition metal ions (*1–8*). No attempt seems to have been made for the extractive photometric determination of uranium(VI) with PBHA, especially from macroconcentrations to tracer level (only extraction). In this paper we report a rapid method for the simultaneous solvent extraction and spectrophotometric determination of macro-amounts of

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uranium with PBHA. The intense blood-red colored complex thus extracted from chloroform absorbs at around 510 nm where the reagent as well as the uranyl ion have no absorption. The advantage of the proposed method lies in the fact that a clean-cut separation from many commonly occurring metal ions is easily accomplished, and it is equally applicable for extraction of tracer amounts of uranium. Examinations on the effect of acidity, reagent concentration, and diverse ions on the absorption of uranyl-PBHA complex were carried out. Further, an attempt has been made to throw light on the stoichiometry of the extracted species.

EXPERIMENTAL

Apparatus

The spectra of the uranium(VI) complexes were scanned on a Carry-14 recording spectrophotometer and measurements at constant wavelengths were performed on a Beckmann DU quartz spectrophotometer with 10-mm matched silica cells. pH adjustments were done with a Radiometer pH meter.

Reagents and Solutions

PBHA was synthesized by the procedure of Priyadarshini and Tandon (*9*). It was recrystallized before use from a mixture of benzene and petroleum ether and was dried in vacuum over P_2O_5. Its final purity was checked by melting point, elemental analyses, UV, and IR spectra. Generally a 0.1-*M* reagent solution in ethyl alcohol-free chloroform was used for all extraction work. Ethyl alcohol was removed by washing the commercial chloroform five or six times with about half its volume of water and distilled after drying over fused calcium chloride.

An aqueous solution of uranyl nitrate, pH adjusted to 4.0, whose uranium content was determined volumetrically, was used. Solutions of diverse ions were prepared from reagent grade salts using the procedure of West (*10*).

Extraction Procedure

An aliquot of the solution containing about 7 mg/ml of uranium was taken and its pH adjusted to 4 with 0.01 *N* NaOH and 0.01 *N* HNO_3 to a total volume of 10 ml. Then 10 ml of reagent solution was added, and the contents were shaken in a separatory funnel for 10 min. The phases were allowed to settle and separate, and the organic phase was carefully transferred to a 25-ml flask after drying it over anhydrons sodium sulfate. Extraction was repeated twice to ensure complete recovery of uranium. Finally the extracts were diluted to 25 ml with chloroform. The absorbance of the red colored complex was measured at 510 nm against the reagent blank. The amount of uranium was then computed from the calibration curve.

RESULTS AND DISCUSSION

Absorption Spectrum

The visible absorption spectrum of a solution of U(VI)–PBHA complex (U = 7 mg/ml) extracted at pH 4.0 showed strong absorbance at 510 nm (Fig. 1). The reagent blank showed no absorbance at this wavelength. All absorbance measurements were therefore taken at 510 nm. Optical density–concentration graphs were plotted by carrying out measurements at 500, 510, and 520 nm; they showed that the colored chloroform extracts obey Beer's law within the usual 1 to 5% error of photometric measurements.

Extraction as a Function of pH

The liquid–liquid extraction behavior of uranium(VI)–PBHA system was studied in the pH range from 2.0 to 4.5 (Table 1, Fig. 2). The results given in Table 1 show that the extraction commenced at pH 2.0 and it was quantitative at around pH 4. Extraction sharply increased to about 80% when pH was raised by approximately 1.5 units. The extraction curve remains almost constant from pH 4.0 to 4.5. Extractions at higher pH than 4.5 were deliberately avoided as to preclude the hydrolysis of the uranyl ion *(11)*. The colored chelate was formed instantaneously and was stable at least for 24 hr if prepared in alcohol-free chloroform.

Effect of Reagent Concentration

Hexavalent uranium was extracted at pH 4.0 with varying volume and concentration of the reagent (Table 2). The results indicate that a single extraction with 10 ml of 0.1 *M* PBHA was quite adequate for quantitative extraction, while extraction was incomplete with 0.005, 0.01, and 0.015 *M* reagent solutions. Larger excesses of reagent could be used without any difficulty. In practice, 10 ml of 0.1 *M* PBHA was always used for extraction purposes.

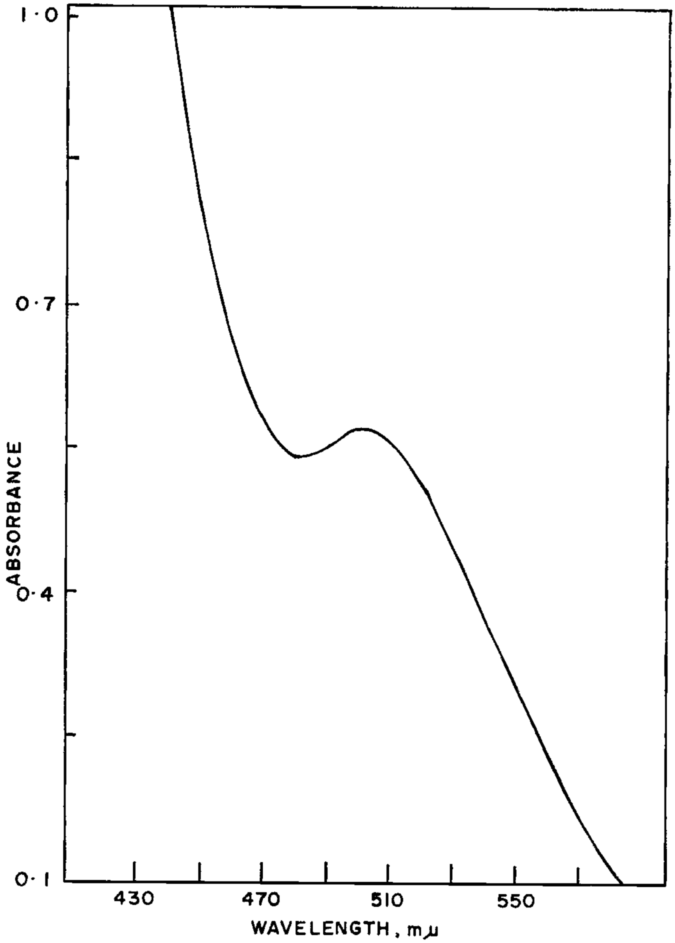

FIG. 1. Absorption spectra of U(VI)–PBHA chelate.

TABLE 1

Extraction of Uranium (VI)–PBHA Complex as a Function of pH

pH	Extraction (% E)	Distribution ratio, D
2.0	2	0.02
2.5	18	0.21
3.0	43	0.76
3.5	77	3.36
3.8	90	8.55
4.0	100	∞
4.2	100	∞
4.5	100	∞

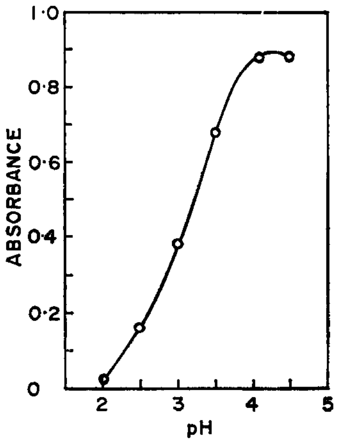

Fig. 2. Extraction as a function of pH.

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 uranyl–PBHA absorption maximum at 510 nm was investigated. Table 3 summarizes the absorbancy and the position of the absorption maximum. Moderate amounts of many commonly associated ions with uranium were tolerable. The ions showing strong interference include cerium(IV), cobalt(II), molybdenum(VI), titanium(IV), and vanadium(V).

TABLE 2

Effect of Reagent Concentration
U(VI): 10.9 mg/10 ml, pH 4.0

PBHA concentration (*M*)	PBHA added (ml)	Absorbance at 510 nm
0.005	5	0.06
0.01	1	0.05
	5	0.14
	10	0.24
0.015	5	0.20
0.10	2	0.48
	4	0.58
	6	0.60
	10	0.63
0.20	2	0.63
	5	0.62

TABLE 3

Effect of Diverse Ions. U(VI): 11.5 mg/10 ml, pH 4.0

Ion	Added as	Amount added (mg)	Absorbance	Max absorbance (nm)
Cation			0.70	510[a]
Al^{3+}	$Al(NO_3)_3$	30	0.70	510
Ba^{2+}	$BaCl_2$	30	0.71	510
Ca^{2+}	$CaCl_2$	30	0.70	510
Co^{2+}	$CoCl_2$	30	0.41	510
Ce^{4+}	$Ce(SO_4)_2$	20	Ppt	—
Ni^{2+}	$NiSO_4$	75	0.71	510
NH_4^+	NH_4Cl	50	0.71	510
Pb^{2+}	$PbCl_2$	100	0.70	510
MoO_4^{2-}	Na_2MoO_4	5	0.59	510
Ti^{4+}	$TiOCl_2$	5	0.61	510
Zn^{2+}	$ZnCl_2$	20	0.70	510
Anion				
NO_3^-	$NaNO_3$	30	0.70	510
$ClO4^-$	$HClO4$	30	0.70	510
SO_4^{2-}	Na_2SO_4	30	0.70	510

[a] Average of 3 repetitive analyses of the same sample.

Extraction Time and Stability of Color

Variation from 3 to 30 min in the shaking period revealed that 95% extraction of the colored complex from the aqueous phase occurred in 3 min whereas beyond 5 min quantitative extraction could be accomplished as per the extraction procedure. The chloroform extracts of the complex were quite stable over a week.

Nature of the Extracted Species

To understand the nature and composition of the extracted species, an attempt was made to isolate the solid complex of UO_2^{2+} with PBHA. The compound obtained by slowly evaporating off the organic phase was analyzed by microanalysis for C, H, and N, and content was determined volumetrically by Jone's reductor method. The results correspond to the formula $UO_2(PBHA)_2 \cdot 2H_2O$. The water content was also confirmed by Karl-Fischer titration as well as by thermal analysis of the solid product. The IR pattern showed the presence of water molecules and the UO_2^{2+} band at 910 cm^{-1} apart from C=O and NO stretching vibration peaks at 1590 and 925 cm^{-1}, respectively.

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