

EXTRACTION SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF URANIUM (VI) IN THE THIOCYANATE SYSTEM

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A rapid and selective spectrophotometric method was developed for the determination of micro-amounts of uranium (VI) after extraction of its thiocyanate complex into isobutyl alcohol. The yellow coloured uranyl thiocyanate complex formed in presence of HCl is quantitatively extracted into isobutyl alcohol. The complex is stable upto a week. Beer's law is obeyed upto 50 μg of uranium and the molar absorptivity at 480 nm is $0.1 \times 10^5 \text{ l mole}^{-1} \text{ cm}^{-1}$. Most of the common cations do not interfere.

Key words: Extraction, Determination, Uranium.

Introduction

The use of alkali thiocyanates as complexing reagents for the spectrophotometric determination of metals has been recognised for some time. More recently, advantage has been taken of the use of thiocyanate complexing as a method of chemical separation [1]. A number of extractants have been used in the part for the spectrophotometric determination of uranium in the thiocyanate system [2-7]. But these methods are cumbersome and time consuming.

In continuation of our earlier studies on the thiocyanate complexes [8-10], we have developed a rapid and sensitive spectrophotometric method for the extraction and determination of U(VI) as its U(VI) thiocyanate complex.

Experimental

Apparatus. Erma-Spectrophotometer Model LS-7.

Reagents. Standard uranium solution. Dissolved 2.11 gm of pure $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water and diluted upto 1 L in a volumetric flask. 2 ml of this solution was further diluted to 100 ml in a volumetric flask so that 1 ml of final solution corresponds to 20 $\mu\text{g}/\text{ml}$.

Potassium thiocyanate(aq) 10 M. Isobutyl alcohol. (BDH). The chemical was used as such, without dilution. All other chemicals used were of analytical grade.

Procedure. To a standard uranium solution (20 μg) in a 100 ml separating funnel was added potassium thiocyanate solution (5 M) followed by HCl (5 M) and distilled water (10 ml). The whole was shaken well and extracted with 5 ml isobutyl alcohol.

Calibration, sensitivity and stability. Known concentrations of uranium were extracted by the foregoing procedure and the absorbance was measured at 480 nm. The results are shown graphically in Fig. 2. For solutions containing 10-50 $\mu\text{g}/5 \text{ ml}$ i.e. 2-10 ppm uranium obeyed Beer's law. The molar absorption coefficient is $0.1 \times 10^5 \text{ l mole}^{-1} \text{ cm}^{-1}$. The yellow

coloured thiocyanate complex was stable for a week and after this period, gradual fading of the colour intensity was noted.

Effect of HCl concentration. The effect of HCl concentration on the extraction of uranium was studied in the range of 0.03-2.0 M. As it is evident from Fig. 3., the concentration of 0.40 M HCl is the most suitable concentration for the maximum extraction and intensity of the complex.

Effect of thiocyanate concentration. Various concentrations of potassium thiocyanate in the range 0.1 - 3.0 M KSCN were also examined. It was observed that 0.7 M KSCN is the optimum concentration for efficient extraction and colour intensity. The observations are indicated in Fig. 4.

Effect of shaking time. Having studied the effect of HCl and KSCN concentrations, efforts were also made to study the effect of shaking time on the overall extraction. It was noted that the system attained equilibrium after 2 mins. and no specified change was noted in absorbance by increasing the time upto 7 mins.

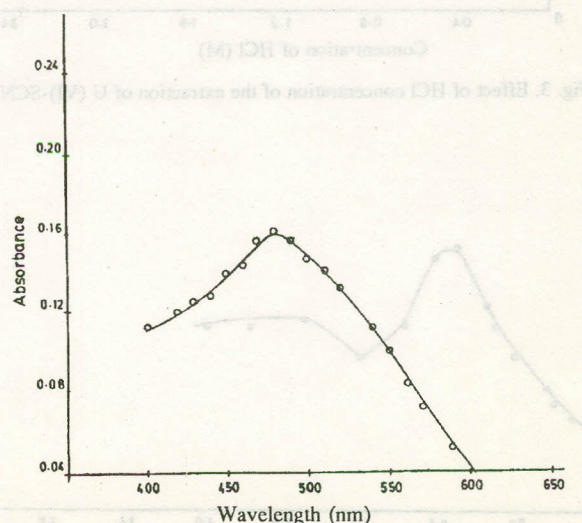


Fig. 1. Absorption curve of U(VI)-SCN after extraction into isobutyl alcohol.

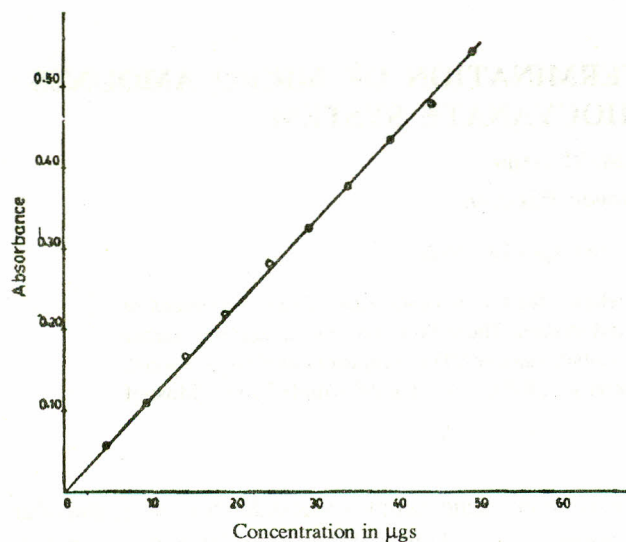


Fig. 2. Calibration curve of U (VI)-SCN.

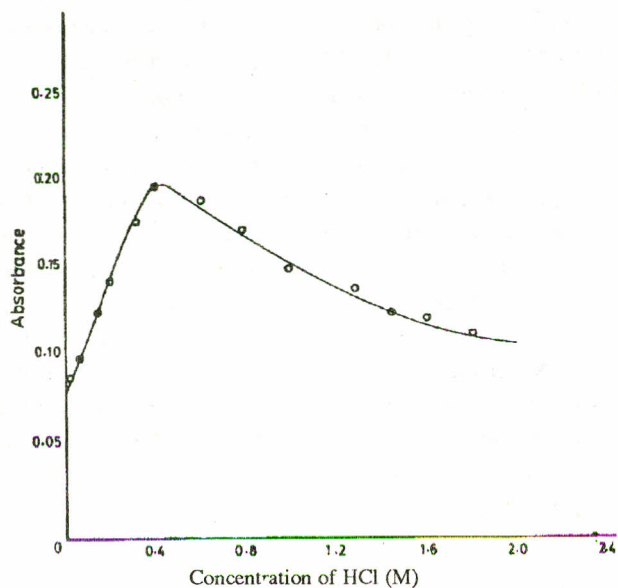


Fig. 3. Effect of HCl concentration of the extraction of U (VI)-SCN.

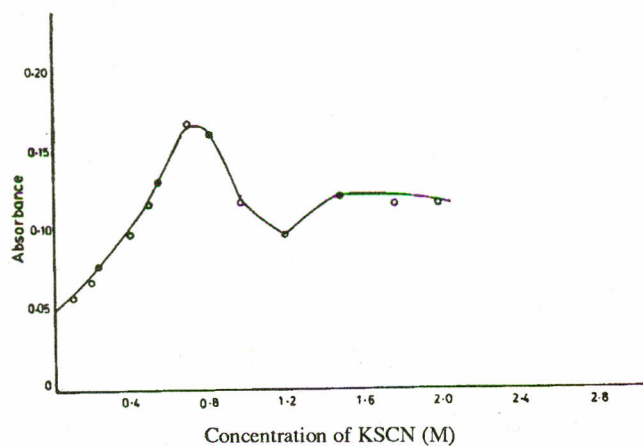


Fig. 4. Effect of KSCN concentration on the extraction of U (VI)-SCN.

TABLE 1. EFFECT OF DIVERSE IONS (URANIUM TAKEN, 10 µg EACH).

Diverse ions	Amount (µg)	Uranium (µg)	
		Found	Error
Al ³⁺	100	10.05	+0.05
	500	10.50	+0.05
	1000	11.20	+1.20
Cu ²⁺	10	11.30	+1.30
	25	Infinity	Not measurable
Ni ²⁺	100	10.03	+0.03
	500	10.63	+0.63
	1000	12.20	+2.20
Co ²⁺	25	10.12	+0.12
	50	11.20	+1.20
	100	Infinity	Not measurable
Mn ²⁺	25	Infinity	Not measurable
Sb ⁵⁺	10	10.80	+0.80
	25	Infinity	Not measurable
Mg ²⁺	100	9.95	-0.05
	500	10.02	+0.02
	1000	10.10	+0.10
V ⁵⁺	10	10.55	+0.55
	25	Infinity	Not measurable
Cr ³⁺	25	11.30	+1.30
	50	Infinity	Not measurable
Zn ²⁺	50	10.06	+0.06
	100	10.80	+0.80
	500	Infinity	Not measurable
Pb ²⁺	50	10.03	+0.03
	100	10.25	+0.25
Fe ³⁺	500	Infinity	Not measurable
	5	11.25	+0.25
	10	Infinity	Not measurable
Ti ⁴⁺	10	10.08	+0.08
	25	10.12	+0.12
	50	Infinity	Not measurable
Mo ⁶⁺	10	11.43	+1.43
	25	Infinity	Not measurable
Ba ²⁺	100	9.94	-0.06
	500	10.02	+0.02
	1000	10.09	+0.09
Sn ²⁺	10	9.96	-0.04
	25	10.06	+0.06
	50	10.48	+0.48
Eu ³⁺	100	Infinity	Not measurable
	100	10.02	+0.02
	500	10.08	+0.08
Er ³⁺	1000	10.08	+0.08
	100	10.08	+0.08
	500	9.56	-0.44
Sm ³⁺	1000	10.01	+0.01
	100	9.82	-0.18
	500	10.01	+0.01
Yb ³⁺	1000	9.65	-0.35
	100	10.01	+0.01
	500	9.52	-0.48
	1000	9.52	-0.48

Effect of phase-volume ratio. Keeping HCl and KSCN concentration as constant, the same amount (20 μ gs) was extracted, varying the volumes of the aqueous phase (Vaq) and keeping the volume of isobutyl alcohol (Vorg) as constant. The extraction was quantitative and the absorbance remained unchanged upto a phase volume ratio (Vaq/Vorg), of 1:2.

Effect of diverse ions. In the determination of uranium by the foregoing procedure three types of interference were frequently encountered: (a) ions which form anionic complexes with SCN^- will be extracted into the organic phase, e.g. Cu^{2+} , Co^{2+} , Mo^{6+} etc. (b) ions which form coloured anionic complexes with SCN^- and which are extracted into organic solvents because of their solubility in the solvent e.g. Cr^{3+} , (c) ions which oxidized SCN^- to a coloured soluble complex of indefinite composition.

With the exception of the first type the later two types do not interfere in the determination of uranium by the foregoing procedure. As shown in Table 1. Mg^{2+} , Ba^{2+} , Eu^{3+} , Er^{3+} , Sm^{3+} did not interfere seriously even present upto 100 folds excess, however the tolerance limit of Yb^{3+} is 500 mg/10 μ g of U(VI). Sn(IV) , Cu(II) , Mn(II) , V(VI) , Sb(V) , Fe(III) and Mo(VI) Interfered seriously, however the diverse action of some of these ions (Co^{2+} , Ti^{4+} , Sn^{4+}) is tolerable if present in moderate concentrations (i.e. upto 2 fold excess). Moreover the effect of Al(III) , Ni(II) and Pb(II) is tolerable upto the concentrations of 100-500 mgs/10 μ gs of U(VI). The limits of tolerance are given in Table 1. As a final check on the validity of the method developed a number of synthetic mixtures for determination of uranium by the foregoing procedure were analysed and the results are shown in Table 2.

TABLE 2. ANALYSIS OF SYNTHETIC MIXTURE.

S. No.	Uranium (μ gs)			
	Present	Found	Error	Error%
1.	4.00	4.00	0.00	0.00
2.	7.00	7.02	*0.02	+0.28
3.	12.00	11.95	-0.05	-0.42
4.	16.00	16.12	+0.12	+0.75
5.	22.00	22.08	+0.08	+0.36
6.	26.00	25.75	-0.25	-0.96
7.	32.00	31.87	-0.13	-0.41
8.	35.00	35.09	+0.09	+0.26
9.	42.00	41.79	-0.21	-0.50
10.	48.00	48.03	+0.03	+0.06

Approx $\pm 0.9\%$

Conclusion

As indicated above, the complex formed between U(VI) and SCN^- in presence of HCl is readily extracted into isobutyl alcohol. The isobutyl alcohol behaves as a strong basic/oxonium solvent and occupies all the coordination positions. The possible structures of the yellow complex of uranium (VI) with thiocyanate are $\text{UO}_2(\text{SCN})^+$, $\text{UO}_2(\text{SCN})_2$ and $\text{UO}_2(\text{SCN})_3$ [11]. It is assumed that the coloured complex of $\text{UO}_2(\text{SCN})_3$ is possibly extracted into isobutyl alcohol to form an ion association pair $\{\text{UO}_2(\text{Bui OH})_2\}^{++}\{\text{SCN}\}_3^-$.

Results of the analyses of the synthetic mixtures indicate that the extraction of uranium (VI) into isobutyl alcohol and its estimation as U(VI)-SCN, seems to depend upon acid and thiocyanate concentrations. The analytical importance of the method is valid from the results of the analyses of various synthetic mixtures because, a minor error has been noted in the estimation of uranium (VI) as its thiocyanate complex.

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