Extraction - Spectrophotometric Determination of Microamount of Tungsten (VI) in Thiocyanate System

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Summary: Investigations were carried out to develop a sensitive and modified method for the determination of micro-amount of tungsten (VI) in presence of other trace elements. The yellow coloured tungsten (VI) Sn(II)-SCN complex formed between tungsten, thiocyanate and stannous chloride in presence of HCl is quantitatively extractable from the aqueous phase into the organic phase containing tricaprylamine (high molecular weight amine). The complex gives maximum absorption at 420 nm and is stable upto 72 hours. The system obeys Beer's law in the range 0.1-8.0 mg of tungsten in the solution, and the molar absorptivity at 420 nm is 7.8×10^{1} mol^{-1} cm^{-1}. The extractability of the complex into tricaprylamine suggests that the coloured species is anionic in nature. Most of the common cations and anions do not interfere.

Introduction

The use of alkali thiocyanate as a complexing agent for the colorimetric determination of most of the transition metals has been known for some time. Most recently, advantage has been taken of the use of alkali thiocyanate complexation as a method of chemical separation [1]. A number of analytical methods have also been used for the spectrophotometric determination of tungsten [2-11]. But these methods are cumbersome and time consuming. In the present investigations the authors after extensive studies of the spectrophotometric determination of a number of trace transitional metals [12-16], after extraction of their complexes into high molecular weight amines and tertiary alcohols, developed a sensitive and rapid method for the determination of trace/micro amount of tungsten (VI), using thiocyanate system. These studies are the modification of already reported spectrophotometric method [17], aimed at making the determination more simple.

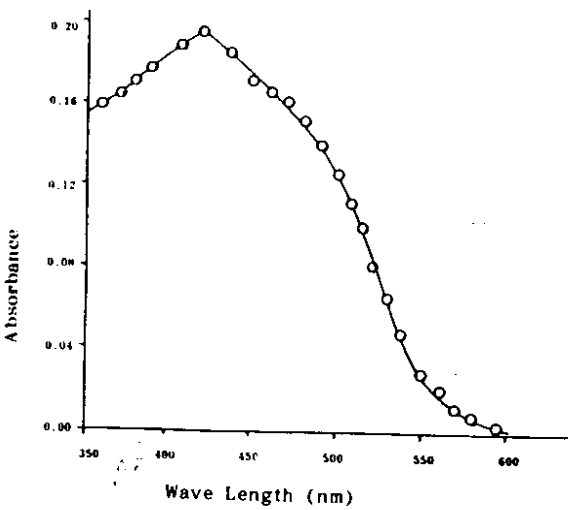

Fig. 1: Absorption spectrum of [(W)x- (CN)y]y-x system after extraction with tricaprylamine.

Results and Discussion

Effect of acid concentration

The effect of HCl concentration on the overall extraction of the complex was studied in the range of 0.10-5.0 M HCl. As is evident from Fig. 2, the concentration of 2.0 M HCl is the most suitable concentration for the efficient extraction and colour intensity of the complex.

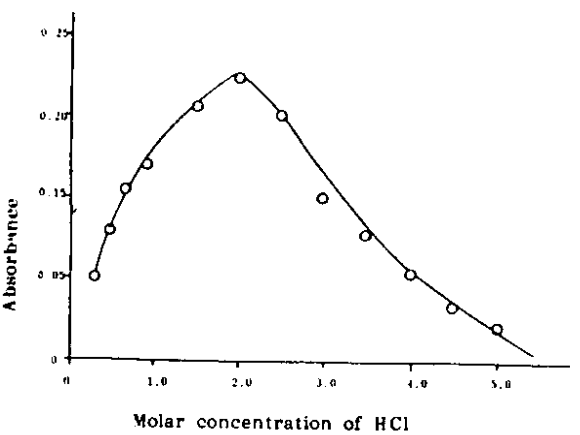

Fig. 2: Effect of hydrochloric acid concentration on extraction of tungsten thiocyanate complex.

Effect of thiocyanate concentration

Various concentrations of potassiumthiocyanate in the range 0.10-5.0 M KCNS were also

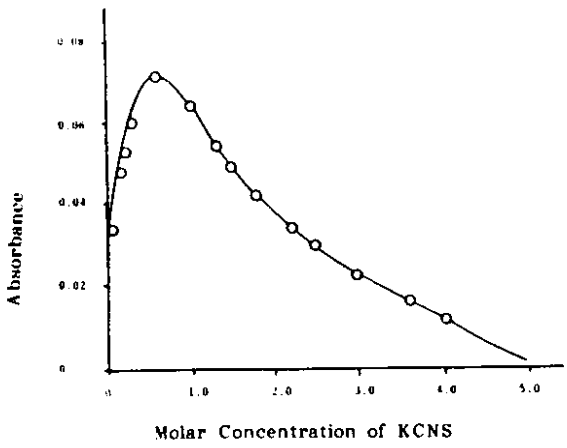

Fig. 3: Effect of KCNS concentration on extraction.

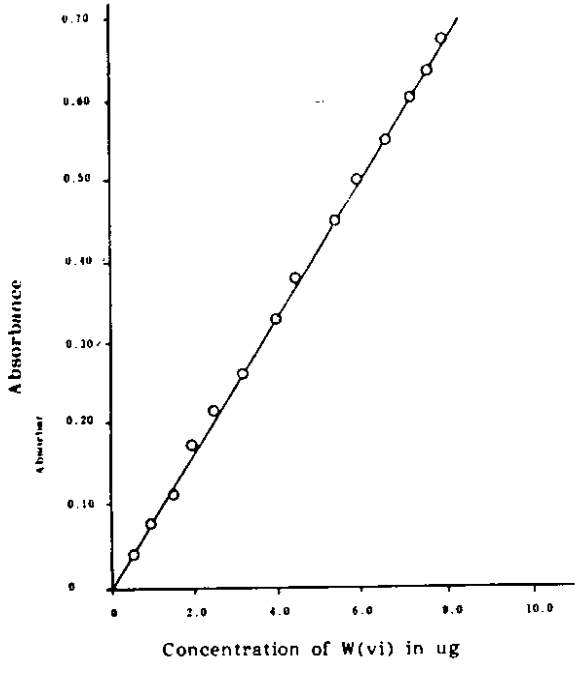

Fig. 4: Calibration curve of W(VI)-SCN complex at 420 nm extracted by tricaprylamine.

examined. It was observed that a concentration of 0.60 M KCNS is the optimum concentration for efficient extraction and colour intensity of the complex (Fig. 3).

Effect of stannous chloride concentration

Having studied the effect of HCl and KCNS concentrations on the overall extraction of the complex investigations were also carried out to study the effect of $SnCl_2$ concentration. It is evident from Fig. 5 that there is a significant variations in the dependence of the colour development and maximum extraction of the complex on the stannous chloride concentration. It is however borne out that 0.5 M $SnCl_2$ is the most suitable concentration for efficient extraction and colour intensity.

Effect of phase volume ratio

Keeping the acid and thiocyanate concentrations as constant, the same amount (10 µg) of tungsten was extracted by varying the volumes of the aqueous phase (V_{aq}) and keeping the volume of the organic phase (V_{org}) as constant. It was observed that 1:2 is the optimum ratio for the quantitative extraction.

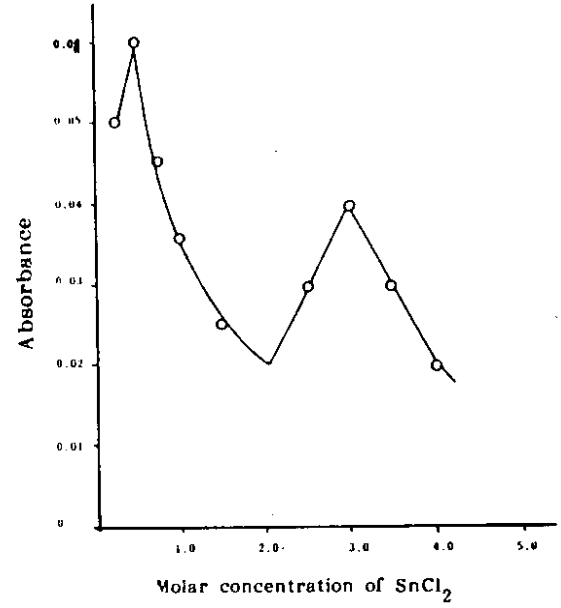

Fig. 5: Effect of stannous chloride concentration on the extraction of tungsten thiocyanate complex.

Effect of the diverse ions

The investigations carried out revealed that in the determination of tungsten by the foregoing procedure, three types of interferences are almost and usually encountered (i) metals ions which form anionic complexes with SCN^- will be extracted into the organic phase *e.g.*, Fe(III), Co(II), Mn(II), Cu(II), V(V) etc. (ii) those ions, which form coloured anionic species with SCN^- are extracted into the neutral solvents, *e.g.* Cr(III) and (iii) ions which oxidize the SCN^- to a coloured soluble complex of indefinite composition. As can be seen from Table-1

Table 1: Determination of tungsten (VI) in the presence of diverse ions (tungsten taken 10 µg each.

No.	Diverse ions	Amount (g)	Found	Error
1.	Al^{3+}	100	10.04	+0.04
		500	10.50	+0.50
		1000	11.40	+1.40
2.	Ba^{2+}	100	10.03	+0.03
		500	10.05	+0.05
		1000	10.08	+0.08
3.	Pb^{2+}	25	10.06	+0.06
		50	10.40	+0.40
		100	10.80	+0.80
4.	Sb^{3+}	5	10.50	+0.50
		10	11.8	+1.80
		25	Infinitely not measureable	
5.	Mg^{2+}	100	9.96	-0.04
		500	10.03	+0.03
		100	10.60	+0.60
6.	Co^{2+}	25	10.15	+0.15
		50	11.40	+1.40
		100	Infinitely not measureable	
7.	Cu^{2+}	10	11.80	+1.80
		25	Infinitely not measureable	
8.	Cr^{3+}	25	11.70	+1.70
		50	Infinitely not measureable	
9.	Fe^{3+}	5	11.60	+1.60
		10	Infinitely not measureable	
10.	Mn^{2+}	10	11.80	+1.80
		25	Infinitely not measuremenable	
11.	Mo^{6+}	10	11.50	+1.50
		25	Infinitely not measureable	
12.	Ni^{2+}	100	10.50	+0.05
		500	10.70	+0.70
		1000	12.50	+2.50
13.	Ti^{4+}	10	10.09	+0.09
		25	10.25	+0.70
		50	Infinitely not measureable	
14.	V^{5+}	5	10.50	+0.50
		10	10.65	+2.50
		25	Infinitely not measureable	
15.	Zn^{2+}	50	10.05	+0.05
		100	10.65	+0.65
		500	Infinitely not measureable	
16.	Eu^{3+}	100	10.03	+0.03
		500	10.08	+0.08
		1000	11.02	+1.02
17.	Er^{3+}	100	9.93	+0.07
		500	10.02	+0.02
		1000	10.05	+0.05
18.	Sm^{3+}	100	9.89	-0.11
		500	10.03	+0.03
		1000	10.06	+0.06
19.	Yb^{3+}	100	9.97	-0.03
		500	10.08	-0.04
		1000	10.08	+0.08

that Ba(II), Mg(II), Eu(III), Er(III) and Tb(III), do not interfere seriously though present in 50-100 fold excess. However the tolerance limits of Ni(II) is 100 mg/10 mg of W(VI), and those of Fe(II), Ti(IV), Zn(II) is 10-50 µg/10µg. Cr(III), Fe(III), and Mn(II), which form coloured anionic species with SCN^- are co-extracted [12-16] easily alongwith W(VI) Sn(11)-SCN complex and thereby interfere seriously. It is also obvious that the interference of the anions *e.g.* SO_4^{2-}, Cl^-, CO_3^{2-}, HCO_3^-, PO_4^{3-} etc. is not encountered so seriously. As a final check on the validity of the method developed, a number of synthetic mixtures were analysed to determine the tungsten content by the foregoing procedure. The results obtained has been shown in Table 2.

Table 2: Analyses of synthetic mixtures

S.No	Tungsten (µ g)			
	Present	Found	Error	% Error*
1.	2.50	2.50	0.00	0.00
2.	2.00	2.01	+0.01	0.50
3.	2.50	2.52	+0.02	0.80
4.	3.00	2.99	-0.04	-0.33
5.	4.00	3.98	-0.02	-0.56
6.	5.50	5.53	+0.03	+0.45
7.	7.00	6.96	- 0.04	-0.57
8.	7.80	7.85	-0.05	-0.64
9.	8.20	8.23	+0.03	+0.36
10.	9.00	9.06	+0.06	+0.06
11.	10.00	10.03	+0.03	+0.03
12.	10.50	9.89	-0.61	-0.06

*Approx. ± 0.43%.

Conclusion

The method developed is the modification of the existing spectrophotometric method for the determination of tungsten (VI) in the thiocyanate system [17] and is considerably advantageous over the is previous recommended procedure, because of its selectivity, and wide tolerance to solution parameters. Moreover the tolerance limits of a number of diverse ions were studied, and series of synthetic mixture were analysed so as to check the reproduceability, accuracy, and validity of the method developed. The cumbersome boiling, cooling and the extragenous addition of two acids at a time as recommended in the previous existing method [17] is also avoided.

Experimental

Erma spectrophotometer Model I S-7 was used.

Reagents

The following reagents were used.

(i) Standard tungsten solution [17]

Sodium tungstate (0.276 g, 72.5% tungsten) is dissolved in water containing a few tenths of gram of sodium hydroxide and then diluted to 2 litres. A tungsten concentration of 0.10 mg by weight per ml

is obtained. This solution was further diluted with distilled water so that 1 ml of the solution corresponds 10 µg.

(ii) Potassiumthiocyanate solution

A 70% (7.2 M) solution was prepared from potassium thiocyanate supplied by E. Merck, by dissolving the required amount in distilled water and then diluting to the required concentration.

(iii) Stannous chloride solution

Stannous chloride solution (5 M) is prepared by dissolving 112.8 g of stannous chloride dihydrate in 3.5 M hydrochloric acid and making upto 100 ml in a volumetric flask.

All the other reagents used were of Analar grade.

Procedure

Formation of W(VI)-Sn(II)-SCN complex and extraction by tricaprylamine

The yellow coloured complex was formed by adding thiocyanate and stannous chloride into a solution containing tungsten in the presence of hydrochloric acid. Tricaprylamine (5 cm^3) in benzene was then added to the coloured solution of tungsten in a 100 cm^3 separating funnel and shaked the contents for 2-3 minutes. The phases were allowed to separate and the coloured complex of W(VI)-Sn(II)-SCN formed was found to be quantitatively extracted into the organic phase, because, even a trace of colour could not be found in the aqueous phase. The organic phase was collected in a 10 cm^3 dried flask after passing it though a small (0.5 cm) filter paper to remove the suspended water droplets. The absorbance of the coloured complex was measured with respect to the blank containing all the reagents, except tungsten and extracted in the same manner. The absorption maxima (λ_{max}) was noted at 420 nm (Fig. 1).

Calibration, sensitivity and stability

Known concentrations of tungsten were extracted by the foregoing procedure and the absorbance measured at 420 nm. Their results are shown graphically in Fig. 4. Beer's law was closely obeyed for solutions containing 0.10 - 10.0 µg tungsten. The molar absorptivity at 420 nm is 7.8 x 10^5 $mole^{-1}$ cm^{-1}. The yellow coloured complex of W(VI)-Sn(II)-SCN extracted into the organic phase was allowed to stand overnight, but no change was observed in the absorbance with lapse of time. After this period there seemed a gradual fading of colour and lowering of the colour intensity till reaching half of its value after 48 hours. The stability of complex however, was found to depend on the $SnCl_2$, HCl and KCNS concentrations.

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