

## SEPARATION - SPECTROPHOTOMETRIC DETERMINATION OF Mo (vi) AND V (v) IN THE THIOCYANATE SYSTEM

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An investigation of the complexes formed between Mo(vi) and V(v) and thiocyanate in hydrochloric acid solution has been carried out. The extractability of Mo(vi) by high molecular weight amine (HMWA) in organic solvent ( $\text{CHCl}_3$ ) and its separation from V(v) was examined. The orange - coloured complex of Mo(vi) - SCN is quantitatively extractable into the organic phase containing tribenzylamine (TBA) a high molecular weight amine (HMWA), whereas the blue-coloured complex of V(v) - SCN formed under the same conditions gets separated in the aqueous phase. On the basis of selective extractability, a method has been developed for the separation and spectrophotometric determinations of Mo(vi) and V(v) in presence of many other elements. The molar extinction coefficients were found to be  $0.91 \times 10^5$  and  $0.70 \times 10^4 \text{ M}^{-2}\text{cm}^{-1}$  respectively for Mo(vi) and V(v). The extractability of the complex by HMWA suggests that the coloured species is anionic.

**Key words :** Separation, Determination, Molybdenum, Vanadium.

### Introduction

The use of high molecular weight amines (HMWA) may be said to date from 1948. More recently advantage has been taken of the use of thiocyanate as a method of chemical separation [1]. A number of analytical methods have been developed for the spectrophotometric studies of molybdenum. Khattak [2] studied the extraction and spectrophotometric determination of molybdenum as Mo(vi) - Sn (ii) - SCN complex into high molecular weight amine. Thio-compounds, such as dithiol, phenylpyrazole-1 dithiocarbamate, 2,3-dimercaptopropionic acid, 8- mercaptoquinoline, thioglycolic acid, disodium cis and 1,2- dicyanoethylene were also used for the spectrophotometric determination of molybdenum [3-8]. But very little studies have been made to separate as well as determine spectrophotometrically Mo(vi) and V(v) which always coextract as well as interfere in the spectrophotometric determination of each other. In the present studies the authors developed an analytical method which concerns not only with the spectrophotometric determination, but also the consecutive and quantitative separation of Mo(vi) and V(v) at the same acid concentration. The present studies were undertaken after a study of the extraction and separation of thiocyanate complexes of Co(ii) and Fe(iii), Co(ii) and Mn(ii) - [9-10].

### Experimental

**Apparatus.** Erma Spectrophotometer Model LS-7.  
**Reagents ;Standard molybdenum solution .** 1.5 g pure  $\text{MoO}_3$  was dissolved in a few ml of sodium hydroxide diluted with water, made acidic with hydrochloric acid, and diluted upto 1 L. The solution was further diluted to 0.001% in 0.1 N hydrochloric acid 1 ml - 10 $\mu\text{g}$ .

**Standard vanadium solution .** 1.78 g of pure  $\text{V}_2\text{O}_5$ , previously ignited at 500 $^\circ$  was dissolved in a slight excess of sodium hydroxide, acidified with a few ml of hydrochloric acid and diluted to 1 L. This solution contained 1.00 mg of vanadium per ml. The solution was further diluted to give a solution containing 0.01 mg V per ml.

**Potassium thiocyanate (aq.):** 10 M. Tribenzylamine (TBA): 5% (W/v) in pure and redistilled chloroform. All other chemicals used were of analar grade.

**Procedure.** Take equal amounts of molybdenum and vanadium in a 100 ml separating funnel. Add 1 ml of 10 M KSCN solution followed by 0.8 ml of 10 M HCl and dilute to 10 ml with distilled water. Then add 5 ml of 5% tribenzylamine (TBA)/chloroform solution and shake the contents for 2 min. Allow the two phases to separate, collect the organic phase in a dried beaker after passing it through a small (10m) Whatman filter paper to remove the suspended water droplets, and measure the absorbance at 470nm against a blank containing all the reagents except molybdenum. Determine spectrophotometrically the vanadium left in the aqueous phase under the same conditions at 760 nm.

### Results and Discussion

**Formation of Mo(vi) - SCN and V(v) - SCN complexes and the extraction of Mo(vi) - SCN by amine.** The coloured complexes of Mo(vi) - SCN and V(v) - SCN were formed by adding thiocyanate into a solution containing molybdenum and vanadium in presence of hydrochloric acid. 5 ml of tribenzylamine (TBA)/chloroform was added to the coloured solution in a separating funnel, and the two phases were shaken for 2-3 mins. The phases were then allowed to separate, and the orange-coloured complex of



Mo(vi) - SCN was quantitatively extracted into the organic phase. The blue - coloured complex of V(v) - SCN formed under the same conditions remained in the aqueous phase. The organic phase was collected in a dried beaker after passing it through a Whatman filter paper to remove the suspended water droplets. The absorption spectrum was determined with respect to a blank containing all the reagents except molybdenum and extracted in the same way. The spectrum showed the maximum absorption at 470 nm (Fig. 1). The absorption spectrum of V(v) - SCN in the aqueous phase was also measured against a blank (distilled water). The spectrum showed the maximum absorption at 760 nm (Fig. 2).

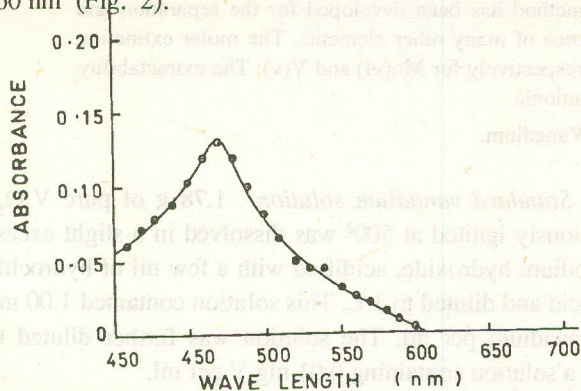


Fig. 1. Absorption curve of Mo (vi)- SCN after extraction into Tribenzylamine.

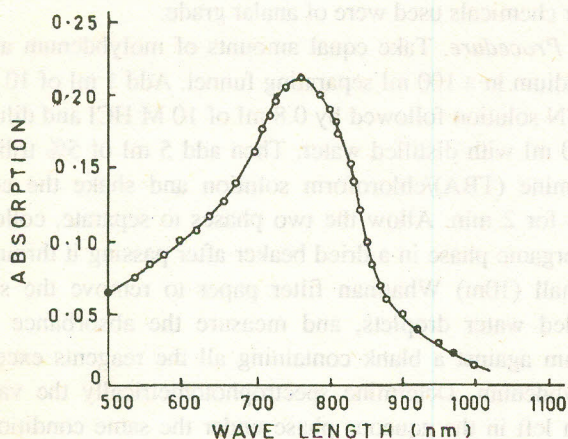


Fig. 2. Absorption curve of V (v)- SCN in aqueous phase.

**Calibration, sensitivity and Stability**. A mixture of known concentrations of molybdenum and vanadium were taken and analysed for Mo(vi) and V(v) using the foregoing procedure. Their absorbances were measured at 470 nm and 760 nm respectively. These observations are shown in Fig. 5. Beer's law was closely obeyed for the solutions containing 0.2 - 5 p.p.m. of molybdenum and vanadium. The molar absorption coefficients of molybdenum and vanadium found were  $0.91 \times 10^5$  and  $0.70 \times 10^4 \text{ M}^{-2}\text{cm}^{-1}$

respectively. The orange-coloured complex of Mo (vi)- SCN was fairly stable for a fortnight, whereas the coloured complex of V(v) - SCN was found to be stable only upto 3 hrs.

**Effect of solvents and extractants.** Two types of solvents i.e. benzene and chloroform and two types of extractants i.e. tribenzylamine (TBA) and allamine - 336 were used and their effect on the overall extraction and separation of molybdenum and vanadium was studied. When benzene solution of TBA or chloroform solution of allamine-336 was used, the complexes of molybdenum and vanadium became turbid and precipitated after shaking. When chloroform solution of tribenzylamine (TBA) and benzene solution of allamine-336 were used as extractants, no precipitation or turbidity was observed, and quantitative extraction of molybdenum and negligible extraction of vanadium was achieved. Moreover the allamine-336 solution in benzene under the same conditions quantitatively extracted both the molybdenum and vanadium complexes. This was in confirmation with our earlier work on the extraction and separation of Co(II) and Fe(III), Co(II) and Mn(II) respectively [9-10].

**Effect of hydrochloric acid concentration.** The effect of hydrochloric acid concentration in the range of 0.1 M - 1.8 M was studied on the overall extraction and separation of molybdenum and vanadium. It was observed however that 0.8 M HCL is the most suitable concentration for maximum colour intensity and efficient extraction and separation. These observations are shown in Fig. 3.

**Effect of thiocyanate concentration.** The effect of thiocyanate concentration (0.1M - 2.5 M) was also examined. It was found however that maximum colour intensity and efficient extraction and separation could be achieved in the

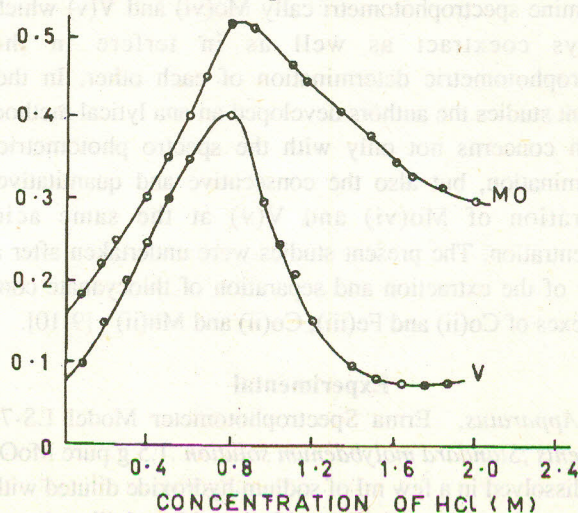


Fig. 3. Effect of HCl concentration on the extraction and separation of Mo (vi) and V (v).



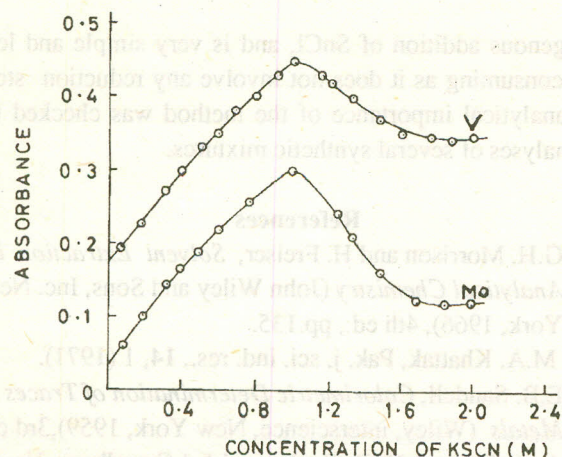


Fig. 4. Effect of KSCN concentration on extraction and separation of Mo (vi) and V (v).

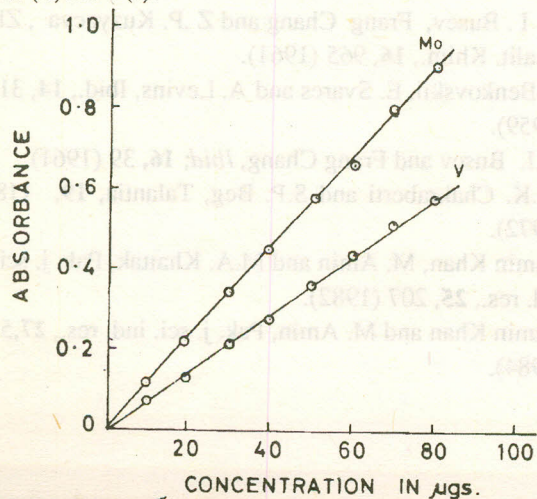


Fig. 5. Calibration curves of Mo (vi) - SCN and V (v) - SCN.

range 0.90 - 1.0 M KSCN concentration. These observations are shown in Fig. 4.

*Effect of shaking time.* Having studied the effect of HCl and KSCN concentration, efforts were also made to study the effect of shaking time and it was noted that the system attained equilibrium after 2.0 min. and no change was noted in the absorbance, by increasing the shaking time upto 5 min.

*Effect of phase volume ratio.* Keeping HCl and KSCN concentrations as 0.8 M and 1.0 M respectively the same amount of molybdenum and vanadium present in varying volumes of the aqueous phase (V<sub>aq</sub>) was extracted into 5 ml of TBA in chloroform (V<sub>org</sub>). The extraction was quantitative and the absorbance remained unchanged upto a phase volume ratio (V<sub>aq</sub>/V<sub>org</sub>) of 1:2.

*Effect of diverse ions.* The interference caused by diverse ions was studied by determining 10 µg each of molybdenum and vanadium by the foregoing procedure in presence of varying amount of interfering ions. The absorbance noted was then compared with a similar aliquot of

molybdenum and vanadium only. It was found that, three types of interferences are most frequently encountered:

- Ions which form anionic complexes with SCN<sup>-</sup> will be extracted into the amine phase e.g. Cu<sup>2+</sup>, Co<sup>2+</sup>, etc.
- Ions which form coloured anionic compounds with SCN<sup>-</sup> and which are extracted into organic solvents because of its solubility in these solvents e.g. Cr<sup>3+</sup>.
- Ions which oxidize SCN<sup>-</sup> to a coloured soluble complex of indefinite composition.

As shown in Table 1, Al<sup>3+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup> and K<sup>+</sup> did not interfere even when present in the hundredfold excess, however the interferences by Cu<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>, W<sup>6+</sup>, U<sup>6+</sup> and Zn<sup>2+</sup> are appreciable. These metals however do not interfere when present in ten-fold excess.

As a final check, one of us analysed eight number of synthetic mixtures for molybdenum and vanadium by the foregoing procedure. The results of these observations are given in Table. 2.

Results of the analyses of synthetic mixtures of Mo(vi) and V(v) by the foregoing procedure indicate that the extraction of Mo(vi) into tribenzylamine (TBA)/ chloroform, its estimation as Mo(vi)-SCNS as well as E. seems to depend upon acid and thiocyanate concentrations.

TABLE 1. EFFECT OF DIVERSE IONS (MOLYBDENUM AND VANADIUM TAKEN, 10 µg EACH).

Diverse ions	Amount (µg)	Molybdenum (µg)		Vanadium (µg)	
		Found	Error	Found	Error
Fe <sup>3+</sup>	1000	10.50	+0.50	infinity	not measurable
Co <sup>2+</sup>	100	11.00	+1.00	10.00	0.00
Ni <sup>2+</sup>	5000	9.00	-1.00	10.00	0.00
Cr <sup>3+</sup>	2000	10.50	+0.50	10.10	+0.10
Zn <sup>2+</sup>	1000	10.00	00.00	10.50	+0.50
W <sup>6+</sup>	100	10.50	+0.50	10.00	0.00
Cu <sup>2+</sup>	1000	10.30	+0.30	10.00	0.00
Mn <sup>2+</sup>	5000	10.00	0.00	9.00	-1.00
Ti <sup>4+</sup>	2000	10.00	0.00	9.20	0.80
U <sup>6+</sup>	5000	11.00	+1.00	9.80	-0.20
Na <sup>+</sup>	5000	10.00	0.00	10.00	0.00
K <sup>+</sup>	5000	10.00	0.00	10.00	0.00
Pb <sup>2+</sup>	500	10.00	0.00	10.00	0.00
Mg <sup>2+</sup>	1000	9.94	-0.06	10.00	0.00
Al <sup>3+</sup>	2000	9.98	-0.02	10.00	0.00
Ba <sup>2+</sup>	2000	9.82	-0.18	9.80	-0.20
Sulphate	1.0g	10.50	+0.50	10.6	+0.60
Nitrate					
Chloride					
Phosphate					



TABLE 2. ANALYSIS OF SYNTHETIC MIXTURES

S. No	Molybdenum ( $\mu\text{gs}$ )			Vanadium ( $\mu\text{gs}$ )		
	Present	Found	Error	Present	Found	Error
1.	10	10.00	0.00	10	10.00	0.00
2.	20	20.00	0.00	20	9.90	-0.10
3.	30	30.10	+0.10*	30	29.80	-0.20
4.	40	39.90	-0.10	40	40.20	+0.15
5.	50	50.05	+0.05	50	49.85	-0.15
6.	60	60.00	0.00	60	60.25	+0.25
7.	80	79.85	-0.15	80	79.50	-0.50
8.	100	100.20	+0.20	100	100.05	+0.05

The maximum extraction and separation of molybdenum and vanadium occurs at 0.8 M HCl and 1.0 M KSCN. The complex formed between Mo(vi) and SCN<sup>-</sup> is readily extracted into tribenzylamine in chloroform solution and the blue-coloured complex of V(v) - SCN remains in the aqueous phase. Although these observations were no guarantee that V(v) was not extracting at all in the organic phase under the specified conditions, yet it does not obscure the coloured complex of Mo(vi) - SCN, and therefore, no interference was noted in the estimation and separation of Mo(vi) and V(v).

The spectrophotometric method developed was also the modification of the existing methods [3-4] to avoid the

extraneous addition of SnCl<sub>2</sub> and is very simple and less time consuming as it does not involve any reduction step. The analytical importance of the method was checked by the analyses of several synthetic mixtures.

#### References

1. G.H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry* (John Wiley and Sons, Inc. New York, 1966), 4th ed., pp.135.
2. M.A. Khattak, Pak. j. sci. ind. res., **14**, 1 (1971).
3. E.B. Sandell, *Colorimetric Determination of Traces of Metals* (Wiley, interscience, New York, 1959), 3rd ed.
4. A. I. Busev, V. B. Byrko and I. I. Grandberg, Vestn. Mosk. Univ. Ser. Khim., **15**, 276 (1960).
5. A. I. Busev, Frang Chang and Z. P. Kuzyacva, Zh. Analit. Khim., **16**, 965 (1961).
6. J. Benkovskii, E. Svares and A. Levins, *Ibid.*, **14**, 313 (1959).
7. A.I. Busev and Frang Chang, *Ibid.*, **16**, 39 (1961).
8. A.K. Chakraberti and S.P. Beg, Talantia, **19**, 1187 (1972).
9. Kamin Khan, M. Amin and M.A. Khattak, Pak. j. sci. ind. res., **25**, 207 (1982).
10. Kamin Khan and M. Amin, Pak. j. sci. ind. res., **27**, 5 (1984).