

Extraction and Spectrophotometric Determination of Molybdenum and Iron in the Thiocyanate System

¹SAEED-UR-REHAMN*, ¹SHABNAM YAMIN AND ²KAMIN KHAN

¹*Department of Chemistry, University of Peshawar,*

²*PCSIR Laboratories, Peshawar, Pakistan*

(Received 17th February, 2000, revised 2nd August, 2000)

Summary: A sensitive and modified method for the separation and estimation of microamounts of molybdenum(VI) in presence of macroamount of iron(III) in the thiocyanate system has been developed. The orange red complex Mo(VI) - SCN in the presence of HCl is quantitatively extractable to an organic phase containing tribenzylamine and chloroform whereas blood red complex Fe(III) - SCN remains in the aqueous phase. The Mo - SCN complex has maximum absorption at 470 nm while Fe - SCN complex absorbs at 460 nm. The stability of Mo - SCN complex stands for 72 hours whereas Fe - SCN complex life is for only few hours. The interference due to various ions (cations and anions) has been also carried out.

Introduction

The use of alkali metal thiocyanate as a complexing agent for the colorimetric determination of most of the transition metals has been recognized for some time. Advantage has been taken for the use of alkali metal thiocyanate complexation as a chemical separation agent [1]. In addition to thiocyanate some other complexing agents e.g. 1-nitroso-2-naphthol have also been used for the spectrophotometric determination of molybdenum [2-11]. All these methods are tedious and time consuming.

In the present work Mo(VI)* and Fe(III) were spectrophotometrically determined after separating Mo(VI) with tribenzylamine in CHCl₃ in the

presence of hydrochloric acid using thiocyanate system. This is a modification of the previously reported spectrophotometric method for the determination of molybdenum [12].

Results and Discussion

Effect of acid concentration

The effect of HCl concentration on the over all extraction and separation of the complexes was studied in the range of 0.10 - 3.0 M HCl. As is evident from figure 2, the 2.7 M HCl is the most suitable concentration for the efficient extraction, separation and measuring colour intensity of the complex.

*To whom all correspondence should be addressed.

Table-1: The effect of diverse ions on the extraction of Mo(VI) and its separation from Fe(III) (Mo(VI) and Fe(III) taken 20 µg each).

S.No.	Diverse ions	Amount µg	Mo(VI)/µg		Fe(III) µg	
			Found	Error	Found	Error
1.	Ca ⁺²	1000	23.25	+ 3.25	26.66	+ 6.66
		500	21.39	+ 1.390	21.90	+ 1.90
		100	20.00	0.00	21.90	+ 1.90
		50	17.20	- 2.80	22.85	+ 2.85
2.	Mg ⁺²	1000	20.40	+ 0.40	24.70	+ 4.70
		500	22.79	+ 2.79	20.90	+ 0.90
		100	18.60	- 1.40	18.00	- 2.00
		50	20.00	0.00	17.14	- 2.86
3.	Al ⁺³	1000	18.60	- 1.40	23.80	+ 3.80
		500	20.93	+ 0.93	24.70	+ 4.70
		100	18.60	- 1.40	22.85	+ 2.85
		50	20.93	+ 0.93	18.00	- 2.00
4.	Zn ⁺²	1000	18.10	- 1.90	22.85	+ 2.85
		500	22.30	+ 2.30	23.80	+ 3.80
		100	20.00	0.00	23.80	+ 3.80
		50	17.67	- 2.33	24.75	+ 4.75
5.	Pb ⁺²	1000	19.53	- 0.47	20.90	+ 2.95
		500	20.93	+ 0.93	22.85	+ 2.85
		100	19.00	- 1.00	22.85	+ 2.85
		50	18.60	- 1.40	20.90	+ 0.90
6.	Co ⁺²	1000	20.00	0.00	20.95	+0.95
		500	20.93	+0.93	23.80	+3.80
		100	19.53	-0.47	23.80	+3.80
		50	18.60	-1.40	22.85	+2.85
7.	Ni ⁺²	1000	16.47	- 3.26	23.80	+ 3.80
		500	18.13	- 1.87	23.80	+ 3.80
		100	16.74	- 3.26	22.85	+ 2.85
		50	25.11	+ 5.11	21.90	+ 1.90
8.	Cr ⁺²	1000	24.18	+ 4.18	20.90	+ 0.90
		500	20.93	+ 0.93	25.70	+ 5.70
		100	15.34	- 4.66	22.85	+ 2.85
		50	15.34	- 4.66	19.04	- 0.96
9.	Mn ⁺²	1000	17.20	- 2.80	24.70	+ 4.70
		500	20.93	+ 0.93	26.66	+ 6.66
		100	23.25	+ 3.25	27.61	+ 7.61
		50	25.10	+ 5.00	28.57	+ 8.57
10.	Silica	1000	24.10	+ 4.10	33.33	+ 13.33
		500	23.70	+ 3.70	25.71	+ 5.71
		100	23.25	+ 3.25	29.52	+ 9.52
		50	23.25	+ 3.25	29.57	+ 8.57
11.	V ⁺³	100	31.60	+ 11.60	31.42	+ 11.42
		50	26.90	+ 6.90	24.76	+ 4.76
12.	Au ⁺²	100	39.53	+ 19.53	30.47	+ 10.47
		50	37.20	+ 17.2	36.19	+ 16.19
13.	Sn ⁺²	1000	32.55	+ 12.55	36.19	+ 16.19
		500	31.60	+ 11.60	34.28	14.28
		100	25.10	+ 5.10	33.33	13.33
		50	28.80	+ 8.80	28.57	8.57
14.	U ⁺³	1000	21.80	+ 1.80	35.23	+ 15.23
		500	23.25	+ 3.25	30.40	+ 10.40
		100	20.00	0.00	29.52	+ 9.52
		50	24.10	+ 4.10	23.80	+ 3.8-0
15.	W ⁺⁶	1000	18.60	- 1.40	29.52	+ 9.52
		500	18.10	- 1.90	29.52	+ 9.52
		100	18.10	- 1.90	29.52	+ 9.52
		50	18.10	- 1.90	29.52	+ 9.52
16.	Cu ⁺²	1000	*		28.57	+ 8.57
		500	69.76	+ 49.76	25.71	+ 5.71
		100	37.20	+ 17.20	22.85	+ 2.85
		50	34.88	+ 14.88	19.04	- 0.96

Effect of thiocyanate concentration

The effect of potassium thiocyanate concentration between 0.10 - 2.0 M KSCN upon colour intensity was also examined. It is observed that 1.0 M KSCN is the optimum concentration for the efficient extraction and separation of the Mo(VI) complex.

Effect of extractant concentration

Having studied the effect of HCl and KSCN concentration on the extraction of the Mo(VI) complex, investigations were carried out to explore the effect of extractant (TBA) concentration. Chloroform solution of tribenzylamine was used as the extractant and its extraction efficiency was studied in the range 0.01 - 0.25 M. However 0.2M solution of tribenzylamine/chloroform suitable for complete extraction.

Effect of Phase Volume ratio

Keeping the concentration of KSCN, acid and extractant constant, the effect of phase volume ratio V_{org}/V_{aq} was studied by varying volumes of the aqueous phase. It was observed that 1:1 ratio is the most suitable for quantitative extraction and separation of Mo(VI) - SCN from Fe(III) - SCN complex.

Effect of diverse ions

In the determination of molybdenum after separation from iron, three types of interferences are almost frequently encountered (a) metal ions which form anionic complex with SCN⁻ will be extracted into organic phase e.g. V⁵⁺, W⁶⁺, Sn²⁺, Mn²⁺, etc. (b) ions which form coloured non-ionic compounds with SCN⁻ and which are extracted into solvent because of their solubility in these solvent e.g., Cr³⁺, and (c) ions which oxidize SCN⁻ to form a coloured soluble complex of indefinite composition.

With the exception of the first type, none of the remaining two interfere in the separation of molybdenum from iron by the present procedure. The ions Ca²⁺, Mg²⁺, Al³⁺, Zn²⁺, Pb²⁺, Co²⁺, and Mn²⁺ even in the concentration range of 50-100 µg added to the solution containing 20 mg each of Fe(III) and Mo(VI) did not interfere to great extent. Cr³⁺ and Ni²⁺ seriously interfere in the determination of Mo(VI) even if present in 5 fold excess. The anions i.e., SO₄²⁻, Cl⁻, CO₃²⁻, PO₄³⁻ etc. did not interfere seriously. As a final check on the validity this of method, these metal ions were determined in a number of synthetic mixtures. The results are shown in table-2.

Table-2: Analysis of synthetic mixtures

S.No.	Concentration of Molybdenum (µg)		Concentration of Iron (µg)		Other elements presents (µg)
	Added	Found	Added	Found	
1	20.00	19.90	20.00	19.80	Ca: 100, Mg: 100, SiO ₂ : 100, Al:100, Na: 100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au: 100, Ti: 100 Zn: 100.
2	20.00	19.98	20.00	19.95	Ca:100
3	20.00	19.98	20.00	19.85	Ca: 100, Mg: 100.
4	20.00	19.95	20.00	19.94	Ca: 100, Mg: 100, SiO ₂ : 100.
5	20.00	19.93	20.00	19.95	Ca: 100, Mg: 100, SiO ₂ : 100, Al: 100.
6	20.00	19.96	20.00	19.65	Ca: 100, Mg: 100, SiO ₂ : Al:100, Na: 100.
7	20.00	19.87	20.00	19.50	Ca: 100, Mg: 100, SiO ₂ : 100, Al: 100, Na: 100, K: 100.
8	20.00	19.80	20.00	19.35	Ca: 100, Mg: 100, SiO ₂ : 100, Al: 100, Na: 100, K:100, Ni:100
9	20.00	19.90	20.00	19.63	Ca: 100, Mg: 100, SiO ₂ : 100, Al:100, Na: 100 K:100, Ni: 100, Co:100.
10.	20.00	19.91	20.00	19.70	Ca: 100, Mg: 100, SiO ₂ : 100, Al: 100, Na: 100, K:100, Ni: 100, Co: 100, Mn: 100.
11.	20.00	19.95	20.00	19.45	Ca: 100, Mg: 100, SiO ₂ : 100, Al: 100, Na: 100, K:100, Ni:100, Co:100, Mn: 100, Pb: 100.
12.	20.00	19.97	20.00	19.35	Ca: 100, Mg:100, SiO ₂ : 100, Al:100, Na: 100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100.
13	20.00	19.85	20.00	19.25	Ca:, 100, Mg: 100, SiO ₂ : 1000, Al:100, Na: 100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100.
14	20.00	19.87	20.00	19.00	Ca:100, Mg:100, SiO ₂ : 100, Al:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100.
15	20.00	19.83	20.00	18.95	Ca:100, Mg:100, SiO ₂ : 100, AL:100, N:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100, Ti:100.
16	20.00	18.90	20.00	19.80	Ca:100, Mg:100, SiO ₂ : 100, Al:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100, Ti:100, Zn:100.

Experimental

Reagents

The following reagents were used:

1. Standard molybdenum solution

2.5 g of pure MoO_3 supplied by E. Merck was dissolved in a few ml of dilute sodium hydroxide, diluted with water, made slightly acidic with hydrochloric acid (pH 5-6) and made upto 100 ml. This solution equals 20 $\mu\text{g}/\text{ml}$ of molybdenum. Samples of suitable concentration were obtained by diluting this stock solution.

2. Iron solution

0.1 gm of iron wire (Analar) was dissolved in a few ml of concentrated hydrochloric acid and diluted with distilled water to 100 ml. The resulting solution containing 1000 $\mu\text{g}/\text{ml}$ of iron. The stock solution was further diluted with distilled water. So that 1 ml of this solution contained 20 μg of iron (III).

3. Potassium thiocyanate solution

5M solution was prepared from potassium thiocyanate supplied by E. Merck by dissolving the required amount in distilled water and diluting to the required concentration.

Organic reagents

1) Tribenzylamine

5% solution of tribenzylamine was prepared in chloroform. Chloroform solution of tribenzylamine is stable for some time, but every time fresh solution was prepared by dissolving the solid crystals.

All the other reagents used were of Analar grade.

Instrumentation

Spectronic-20/Hitachi U-200 spectrophotometer was used for obtaining absorption spectra of these systems. A matched pair of 10 mm cuvettes was used to obtain these spectra.

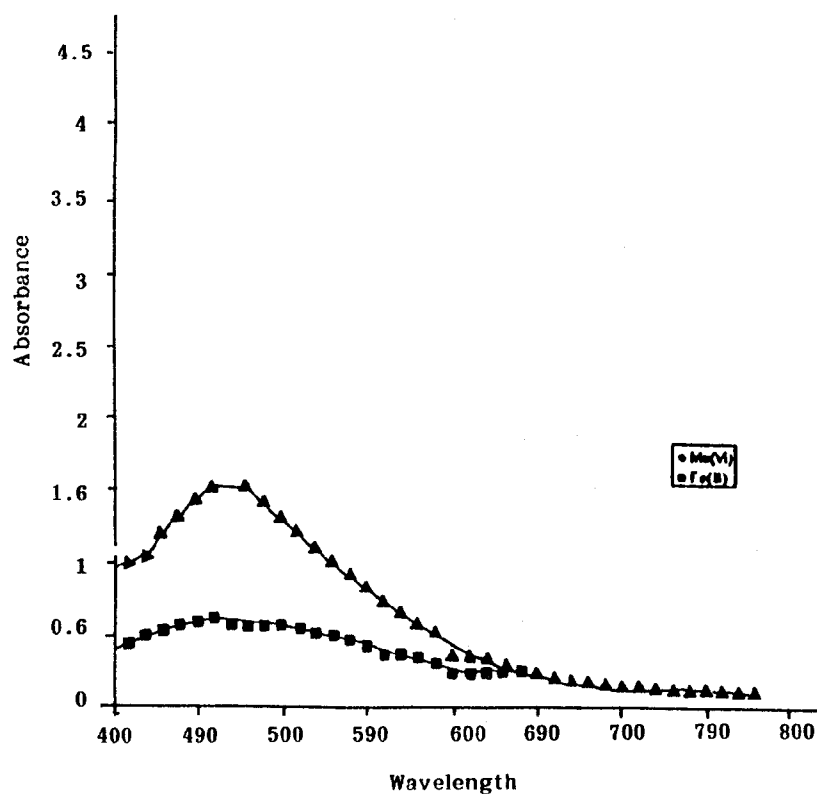


Fig. 1: Absorption spectrum of Molybdenum (VI) thiocyanate and Iron (III) thiocyanate systems.

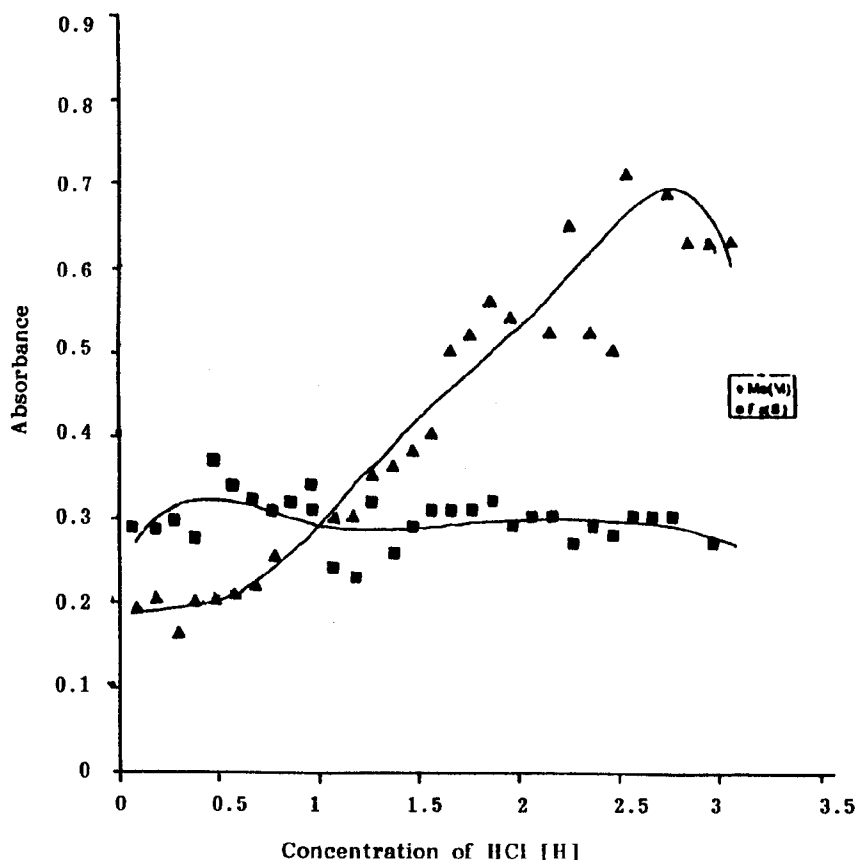


Fig. 2: Effect of HCl concentration (M) of Molybdenum (VI) from Iron (III) thiocyanate system.

Procedure

Formation of Mo(VI) - SCN complex and Fe(III) - SCN complex

An orange yellow complex ion solution was formed by adding 5M thiocyanate into a solution containing molybdenum (VI) and iron (III) in presence of HCl (2.7 M). Tribenzylamine was added to the coloured solution of molybdenum and iron in a (100 ml) separating funnel and shaken vigorously for 2-3 minutes. The phase were allowed to separate. The coloured (yellow - orange) complex of Mo(VI) - SCN was quantitatively extracted into the organic phase Fe(III) - SCN (Red) complex remained in the aqueous phase. The organic phase was collected in a dried flask after passing it through a small filter paper to remove the suspended water droplet. The aqueous phase was collected in an other flask after passing it through a small filter paper. The

absorption spectrum was determined with respect to a blank of Mo- SCN complex. TBA/chloroform was used as blank for Fe - SCN complex. The spectrum showed the maximum absorption [Mo(SCN)_n] at 470 nm and [Fe(SCN)] at 460 nm (Fig. 1).

Calibration, sensitivity, and stability

Molybdenum (VI) and iron (III) were extracted into TBA/CHCl₃ by the foregoing procedure from the synthetic samples of known concentrations of these elements. The results are shown in Fig. 1. Beer's law was closely obeyed for solution containing 0.02 - 80 ppm. The orange - yellow complex of Mo(VI) - SCN was extracted into organic phase while red coloured Fe(III) - SCN complex remained in aqueous phase. Both complexes were allowed to stand overnight. No change in colour was observed in Mo (SCN)

complex, but the red colour due to Fe (SCN) complex gradually faded and completely disappeared after few hours. The stability of the organic extract was found to be dependent on HCl and KSCN concentration.

Conclusion

This method is a modification of the existing spectrophotometric method for separation and determination of molybdenum (VI) and iron (III) in the thiocyanate system. This is considerably advantageous over the previous methods, because of its selectivity and wide tolerance limits in the presence of a number of diverse ions. The effect of diverse ions were studied in a series of synthetic mixture, so as to check the reproducibility, accuracy and validity of this method.

References

1. G.M. Morrison and H. Frieser, "Solvent Extraction in Analytical Chemistry" 4th edition, Wiley Interscience, New York, p. 43 (1966).
2. V.M. Peshkova, E.K. Invanova, S. Memon, *Zh. Anal. Khim.*, **35**, 486 (1980).
3. E.B. Sandell, "Colorimetric Determination of Traces of Metals, 3rd edition, Wiley Interscience, New York, p. 195 (1959).
4. A.I. Busev, F. Chang and Z.P. Kuzyaeva, *ZH. Analit. Khim.*, **16**, 695 (1961).
5. A.I. Basev, B.B. Byrko and I.I. Grandderg, *Vestnik, Moskov, Univ. Ser. II, Khim.*, **15**, 76 (1960).
6. J. Benkovskii, E. Svares and A. Levins, *Ibid*, **14**, 313 (1959).
7. A.I. Burev and F. Chang, *Ibid*, **16**, 36 (1961).
8. A.K. Chakrabarti and S.P. Bag, *Talanta*, **19**, 1187 (1972).
9. S.C. Liang and P.Y. Hsu, *Huo Hsueh Hsueh Pao*, **22**, 171 (1959).
10. M.K. Arunachalam and M.K. Kumaran, *Talanta*, **21**, 355 (1974).
11. K. Khan and M. Amin, *Pak. J. Sci. Ind. Res.*, **27**, 263 (1984).
12. K. Khan, T.A. Khan and H. Rashid, *J. Chem. Soc. Pak.*, **12**, 4 (1990)