Extraction - Spectrophotometric Determination of Molybdenum (V) Application to Molybdenite Ore

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Summary: A sensitive and modified method for the extraction and determination of the Mo(V) in the thiocyanate system has been developed. The orange red complex formed between Mo(V) and SCN^- is quantitatively extractable from an aqueous phase into an organic phase containing isobutyl alcohol. The complex gave maximum absorption at 470 nm and the system Obeys Beer's law in the range 0.01-7.0 ppm of molybdenum in the solution. The colour is stable for 24 hours and the molar absorptivity at 470 nm is 1.51×10^4 l $mole^{-1}$ cm^{-1}. The extractability of the complex by the tertiary alcohol suggests that the coloured species is anionic. Most of the common cations and anions do not interfere. The method developed was successfully applied to the analysis of molybdenite ores from Kohistan.

Introduction

The use of alkali thiocyanate as complexing agents for the colorimetric determination of metals has been recongized for some time. Bock [1] made an extensive study of the extractability of many metal thiocyanates into an immiscible neutral organic solvent, and it has been shown that a sizeable number of metal thiocyanates are extractable into the organic solvents. More recently advantage has been taken of the use of thiocyanate complexing as a method of chemical separation [2]. In addition to thiocyanate some other complexing agents have also been used for the spectrophotometric determination of molybdenum [3-10]. But these methods are time consuming and the applications to the analysis of ores and minerals are rarely discussed.

The present authors after a study of the extraction of thiocyanate complexes of Co(II) and Mn(II) [11], as well as Fe(III) and Co(II) [12] into high molecular weight amines (HMWA), undertook the present work of the extraction of Mo(V)-SCN complex for the spectrophotometric determination of molybdenum (V), and its application to the analysis of molybdenite ores. The present work is the modification of the existing spectrophotometric method [13] for the evaluation of geological samples.

Experimental

Apparatus

Erma Spectrophotometer Model-LS-7 was used.

Reagents

The following reagents were used.

(i) Standard molybdenum solution

2.5 g of pure MoO_3 supplied by E.Merck was dissolved in a few cm^3 of dilute sodium hydroxide, diluted with water, made slightly acidic with hydrochloric acid, and made up to 1 dm^3. The solution was further diluted to 0.001% in 0.1M hydrochloric acid, 1 cm^3 of this solution equals 10 μg of molybdenum.

(ii) Potassium thiocyanate solution

A 70% (7.2M) 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.

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(iii) Isobutyl alcohol (2-methyl-propanol-1).

The reagent used was supplied by BDH.

Analytical Procedures

Formation of Mo(V) - SCN complex and extraction by isobutyl alcohol

The orange-yellow coloured complex was formed by adding thiocyanate into a solution containing molybdenum in presence of HCl. Isobutyl alcohol (10 cm^3) was added to the coloured solution of molybdenum in a separating funnel and shaked vigorously for 2 min. The phases were allowed to separate and the coloured complex was quantitatively extracted into the organic phase as no trace of colour was found in the aqueous phase. The organic phase was collected in a dried flask after passing it through a small filter paper (5 cm) to remove the suspended water droplets. The absorption spectrum was determined using 1-cm cell 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.

Calibration, sensitivity and stability

Known concentrations of molybdenum were extracted by the foregoing procedure and the absorbance measured at 470 nm. The results are shown graphically in Fig. 4. Bear's law was closely obeyed for solutions containing 0.02-7.0 ppm. The molar absorptivity at 470 nm is 1.51 x 10^4 l $mole^{-1}$ cm^{-1}. The orange- yellow coloured complex of Mo (V) - SCN extracted into organic phase was allowed to stand overnight, but no change was observed in the optical density. After this period there is a gradual fading and lowering of the intensity of colour and reaches half of its value after 48 hours. The stability of the organic extract was found to be dependent on HCl and KCNS concentration.

Results and Discussion

Effect of acid concentration

The effect of the hydrochloric acid concentration on the overall extraction of the complex was studied in the rangte of 0.1-6.0M HCl. Maximum colour intensity and effecient extraction was achieved at a concentration of 2.5 + 0.2 HCl. The effect is shown graphically in Fig. 2.

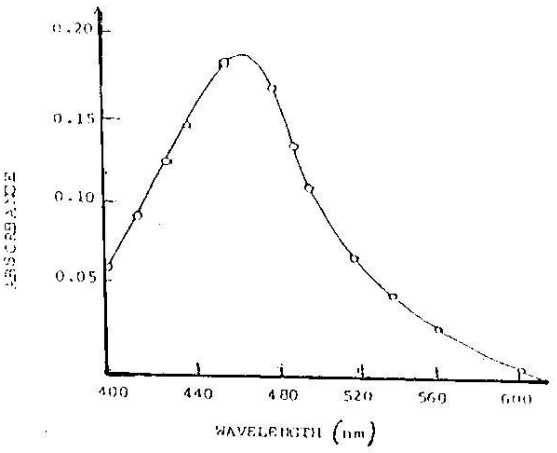

Fig.1: Absorption spectrum of $[(Mo)\eta\text{-}(CNS)Y]^{Y-X}$ system after extraction with isobutyl alcohol.

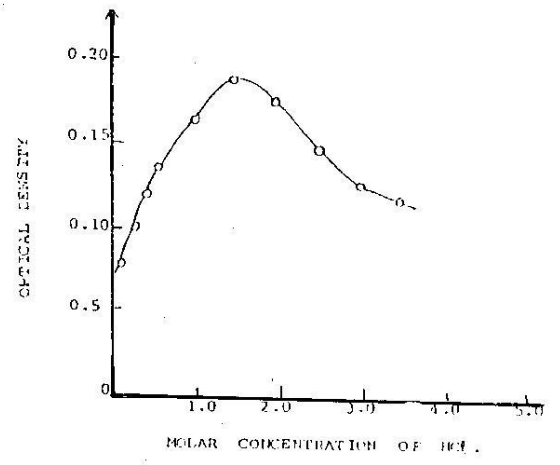

Fig.2: Effect of Hydrochloric acid concentration on extraction.

Effect of shaking time

The absorbance of the extract from 10 μg molybdenum in the aqueous phase was measured as a function of shaking time. The system attained equilibrium within 2 min. and increasing the shaking time up to 20 min. there was no notable change in the absorbance.

Effect of phase volume ratio

Keeping the acid and thiocyanate concentrations as 1.5 M and 3.5 M respectively, the same amount (10 μg) of molybdenum present in varying volumes of the aqaueous phase (Va) was extracted into 10 cm^3 of isobutyl alcohol (Vorg). The ratio 1:1 was found to be the optimum, and the extraction was quantitative.

Effect of the diverse ions

In the determination of molybdenum by the above procedure, three types of interferences are almost frequently encountered (a) metal ions which form anionic complexes with SCN will be extracted into the organic phase e.g. Fe^{3+}, Pb^{2+}, V^{5+}, W^{6+}, Mn^{2+} etc. (b) ions which form coloured nonionic compounds with SCN^- and which are extracted into neutral solvents because of their solubility in these solvents e.g. Cr^{3+}, and (c) ions which oxidize SCN to a coloured soluble complex of indefinite composition.

With the exception of the first type, none of the remaining two types interfere in the determination of molybdenum by the present procedure. As can be seen from Tabl-1 the first type also did not interfere seriously in the determination of molybdenum provided these ions are present in moderate amounts. Co^{2+} which also forms an extractable anionic greenish blue complex [10] and gave the absorption maxima at 620 nm did not interfere with Mo(v) though present in 50 fold exess. Similarly Cu^{2+} did not interfere even in 100 fold excess.

Table-1: Determination of molybdenum in the presence of diverse ions (molybdenum taken 20 μg)

No.	Diverse ions	Amount (μg)	Molybdenum (μg) Found	Error
1.	Co^{2+}	1000	21.00	+ 1.00
2.	Ni^{2+}	2000	20.10	+ 0.10
3.	Ca^{2}	1500	20.30	+ 0.30
4.	Mg^{2+}	2000	19.87	- 0.13
5.	Fe^{3+}	500	--	
6.	Cr^{3+}	1000	19.75	- 0.25
7.	Pb^{2+}	1000	20.50	+ 0.50
8.	Cu^{2+}	2000	20.00	0.00
9.	Zn^{2+}	1000	19.00	- 1.00
10.	Al^{3+}	1000	20.00	0.00
11.	Ti^{4+}	2000	19.53	- 0.47
12.	V^{5+}	1000	22.00	+ 2.00
13.	W^{6+}	1000	20.24	+ 0.24
14.	U^{3+}	2000	20.00	0.00
15.	Sn^{2+}	2000	19.70	0.30
16.	Sb^{3}	500	21.50	+ 1.50
17.	Si^{4+}	500	21.62	+ 1.62
18.	Mn^{2+}	500	25.00	+ 5.00
19.	SO_4^{2-}		20.41	+ 0.41
20.	Cl^-		20.00	0.00
21.	CO_3^{2-}	-*	20.00	0.00
22	PO_4^{3-}		19.89	- 0.11
23.	NO_3^-		2.50	+ 0.50

*Amount expressed in grams

Fe^{3+} however seriously interferes even if present in traces, because the extractable species also absorbs, strongly in the region 450-500 nm. The strong interference of Mn^{2+} is due to its reddish coloured Mn(II) - SCN complex formation which absorbs at 480 nm [11]. As is evident from the Table-1 the effect of anions i.e., SO42-, Cl-, CO32-, PO43- etc. were also studied but they did not interfere seriously.

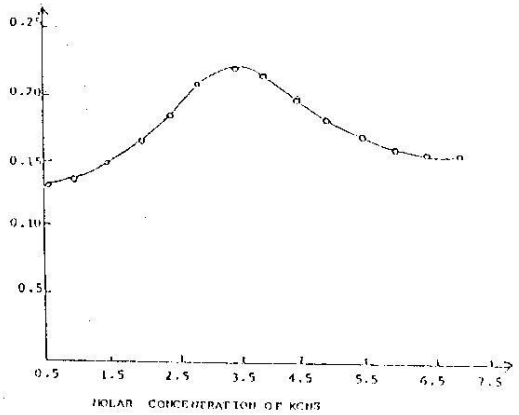

Fig.3: Effect of KCNS concentration on extraction.

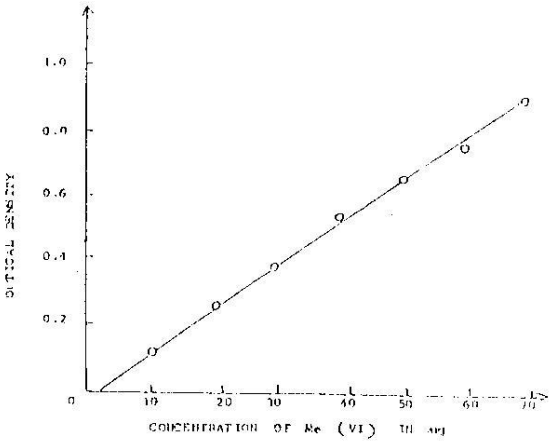

Fig.4: Calibration curve of Mo(VI) at 470 nm extracted by isobutyl alcohol.

Analysis of molybdenite ores

Fused 0.5 g of well agated sample into platinum crucible with fusion mixture (Na_2CO_3 + K_3CO_3) and KNO_3 in the ration 1:4:0.4. The fused mass is leached out with distilled water at 60°C using an electric water bath. The soluble part is fil-

tered through a Whatman filter paper and the filtrate is then diluted to 250 cm^3. Keeping the acid concentration as 1.5M HCl, 5 cm^3 of this solution is transfered to a 100 ml separating funnel and KCNS solution is added in sufficient amount so that the final concentration is 3.5M KCNS. Isobutyl alcohol 10 cm^3 is added to this solution and the two phases are then shaken for 2 min. on a mechanical shaker. The two phases are allowed to separate and after the equilibrium is attained the organic phase is drawn into a dried flask after passing it through a small filter paper (5 cm) to remove the suspended water droplets. The absorbance is noted at 470 nm, the amount of molybdenum is calculated from the calibration curve and is expressed as % concentration. Accurate and encouraging results were achieved which were then compared with the already established colorimetric methods [13-14]. These comparative results are shown in Tabl-2.

Table-2: Comparative analysis report of molybdenite Ores of Kohistan using thiocyanate and other standard methods

Sample No.	Molybdenum (%) Benzoine-oxide method [14]	Mo (VI) - Sn (II) - CNS method [13]	Present method
Lahor-1	0.50	0.45	0.51
Lahor-2	0.75	0.70	0.72
Pazang-1	0.30	0.28	0.29
Pazang-2	0.45	0.50	0.49

Conclusion

The method developed is the moldification of the existing method [12], aimed at avoiding the extragenous addition of $SnCl_2$ and Mohr's salt and to apply it successfully for the evaluation of the indigenous molybdenite ores.

The information obtained from the extraction parameters and the spectrophotometric determination of Mo(V) reveal that thiocyanate complex formed is anionic in nature and is readily extracted into isobutyl alcohol.

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