Extraction Spectrophotometric Determination of Molybdenum(V) with N^1-(*o*-Chlorophenyl)-N^1-hydroxy-N^2-(*o*-methylphenyl)benzamidine Hydrochloride and Thiocyanate

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A highly selective method has been developed for the extraction and spectrophotometric determination of molybdenum(V) using N^1-(*o*-chlorophenyl)-N^1-hydroxy-N^2-(*o*-methylphenyl)benzamidine hydrochloride and thiocyanate. The reagent reacts with molybdenum(V) in the presence of thiocyanate ion and forms orange red complex in strongly acidic medium. Which can be extracted with benzene. The extract shows a sharp maximum at 470 nm, having molar absorption coefficient 3770 $cm^3 mol^{-1} cm^{-1}$. The system obeys Beer's law from 3 to 22 ppm. A large number of metal ions associated with matrix of Mo, such as Ni, Co, Cu, V, Nb, Ti, Zn, etc. do not interfere with the determination. The applicability of the method has been tested with various alloys. The stoichiometry of mixed complex is found to be 1 : 2 : 2 (metal : reagent : thiocyanate).

Molybdenum(VI) is frequently determined spectrophotometericaly with the thiocyanate in the presence of reducing agent forming a molybdenum(V) thiocyanate complex.[1] A number of methods[2—4] have been developed for determination of molybdenum but these methods suffer from interferences of tugsten ion. The present method describes a simple rapid and selective method for the extraction spectrophotometric determination of molybdenum using hydroxyamidine and thiocyanate. The method is free from volume ratio of aqueous phase, concentration of reagent, order of addition of reagent, temperature, standing time, and correlation of color intensity with molybdenum concentration. The method is applicable to the analysis of ores and alloys.

Experimental

Apparatus: A carlzeiss Jena specol grating spectrocolorimeter was employed for measuring absorption values. The pH value were determined by systronic pH meter type 322.

Reagents: The reagents used were of A. R. grade. Standard molybdenum solution was prepared dissolving A. R. ammonium molybdate in glass distilled water and diluted to 1 dm^3. The solution was standardized with 8-quinolinol.[5] Purified benzene was used for preparation of reagent solution and extraction work. 1% w/v solution of the reagent in benzene was used. Freshly prepared 10% solution of ascorbic acid and 5% solution of potassium thiocyanate were employed. The reagent was prepared by condensation of equimolar quantities of *N*-(*o*-methylphenyl)-benzimidoyl chloride and *N*-(*o*-chlorophenyl)hydroxylamine in ether medium. The resulting hydrochloride was recrystallized from absolute ethanol, yield 86% and mp 197 °C.

Procedure: An aliquot of solution containing 200 µg of molybdenum was taken in a 125 ml separatory funnel. To this 5 ml of ascorbic acid and 2.5 ml of potassium thiocyanate solution were added. The acidity was adjusted between 2—4.5 molar with hydrochloric acid keeping the total volume of the aqueous phase to 25 ml. 15 ml of the benzene solution of the reagent was added and shaked for 2 min. The benzene layer was transfered to a 50 ml beaker containing anhydrous sodium sulfate. The aquous phase was washed with 2×4 ml fresh portion of benzene and the washings were added to the contents of the beaker. The dry extract was transfered to a 25 ml volumetric flask and volume was adjusted with benzene. The absorbance was measured at 470 nm against benzene blank.

Table 1. Determination of Molybdenum in BCS Steels[a)]

Sample	Certified value/%	Molybdenum found/%	Average value/%	Standard deviation
64A	4.11	4.055		
		4.050		
		4.050	4.050	± 0.0014
		4.060		
		4.050		
64B	4.95	4.900		
		4.850		
		4.850	4.850	± 0.0195
		4.910		
		4.850		
60B	0.430	0.415		
		0.410		
		0.420	0.420	± 0.0147
		0.420		
		0.420		

a) British Chemical Standard.

Application of the Methods: As the method is highly selective. The scope of the method has been further extended to the determination of molybdenum(V) in BCS steel samples. The results are shown in Table 2.

Results and Discussion

The absorption spectra of molybdenum-hydroxyamidine complex was plotted in presence of thiocyanate and of reagent, complex shows a peak at 470 nm with molar absorption coefficient 3770±50 $mol^{-1} cm^{-1}$ (Fig. 1).

Effect of Variables: Benzene, toluene, carbon tetrachloride etc. were found to extract the mixed com-

Table 2. Comparision of Reagents for Colorimetric Determination of Molybdenum

Reagent	Color/wave-length/nm	pH/acidity	Sensitivity µg-Mo cm^{-2}	Ion interfere	Remarks
Thiocyanatetin(II) chloride	Orange-red 465	1.0 M[a] HCl	0.010	W, Pt	The method suffer from limitation of analytical variables like concentration of thiocyanate standing time etc.
Dithiol	Dark green 680	6—14 M HCl H_2SO_4	0.005	Fe, Cu, W	The reagent reacts with many metal ions hence selectivity is poor.
Thiocyanate potassium methylxanthate	Red 470	4—7 M HCl	0.0068	W, V, Rh	The method is not specific to molybdenum.
Thioglycolate	Yellow 370	—	0.049	Cu, Sn, Ni, Co, Bi, Fe, Hg, W	—Do—
Thiocyanate monooctyl-*α*-anilinobenzyl phosphonate	Red 470	—	0.016	Cu, Ti, Zr, Nb, U, Fe	—Do—
Thiocyanate 2-(2-mercaptobenzoyl)-4*H*-thiopyran-4-one	Orange-red 470	—	0.005	Fe, Co, Ni, Ag, Au, F, Thiosulphate	—Do—
HCPMPBH+Thiocyanate	Orange-red 470	1.8—4.2 M HCl	0.026	None	Highly selective

a) 1 M=1 mol dm^{-3}.

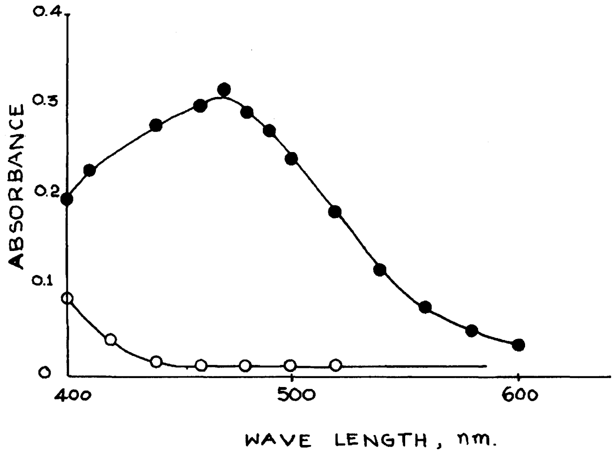

Fig. 1. Absorption spectra of HCPMPBH (0.003 M) and Mo(V)-SCN$^-$-HCPMPBH mixed complex in benzene.

$C_{Mo} = 8.33 \times 10^{-5}$ M.

plex quantitatively. Benzene was found to be the best as in this the complete extraction is relatively rapid. The acidity of the aqueous phase was adjusted between 2—4 molar HCl. Below 2 molar and above 4 molar lower absorbance values were obtained. In practice generally the acidity was adjusted to 3.0 molar. (Fig. 2) Tin(II) chloride, hydroxylamin hydrochloride, ascorbic acid were tried as reducing agents to reduce Mo(VI) to Mo(V). Among them, ascorbic acid was found to be the best. When ascorbic acid is used as reducing agent a stable and reproducible maximum color intensity was obtained without interference from thiocyanate. Excess of reagents did not affect color intensity. The system obeys Beer's law from 2 to 20 ppm. The method is precise and the standard deviation of the method corresponds to ±0.003 absorbance unit and relative standard deviation of 1.06% (at concentration of 8 ppm.).

Influence of Diverse Ions: Most of the common ions including iron(III), vanadium(V), and tantalum do not interfere with the determination. The stoichiometric ratio of metal to ligand in molybdenum(V)–SCN$^-$–hydroxyamidine complex was established by a curve fitting method.[6]

The result indicates that the ratio of the complex is

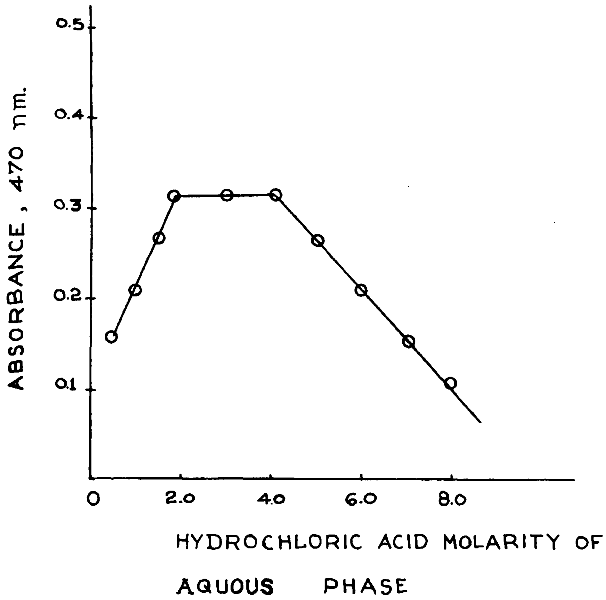

Fig. 2. Effect of acidity on the extraction of Mo(V)-SCN^--HCPMPBH mixed complex in benzene.

$$C_{\mathrm{Mo}} = 8.33 \times 10^{-5}\ \mathrm{M},$$
$$C_{\mathrm{HCPMPBH}} = 0.003\ \mathrm{M},$$
$$C_{\mathrm{SCN^-}} = 0.05\ \mathrm{M}.$$

1 : 2 : 2 (metal : thiocyante : reagent).

Comparision with Other Methods: A wide variety of reagents have been reported for the spectrophotometric determination of molybdenum in various complex materials. The method using thiocyanate[1)] is the oldest and most extensively used. Although the thiocyanate method is simple and cheap, it requires careful regulation of the many variable to achieve analytical reproducibility. It also lacks stability making its use rather difficult. In recent years dithiol[2—4)] has received much attention. Although it is more sensitive than the thiocyanate method, yet this reagent reacts with a number of metal ions iron, copper, tin, and tunguston give precipitate and interfere seriously with the determination of molybdenum. Catechol, mercaptoacetic acid, phenylhydrazine, potassium ethylxanthate, 8-quinolinol, *o*-hydroxyphenylacetohydroxamic acid, diphenylcarbazone, chloranilic acid, tannic acid, 1,10-phenanthroline, monooctyl (α-anilinobenzyl) phosphonate thiocyanate, and many other reagents have been reported for spectrophotometric determination of molybdenum. All the methods reported suffer from various draw backs like reproducibility of the color, standing time etc. The stability of the thiocyanate method and its complex can be enhanced by adding a second ligand to form a new mixed complex which can be extracted into water immiscible organic solvents. The proposed method is simple rapid and highly selective. Most of the common ions including iron(III) and vanadium(V) do not interfere with the determination as these are reduced with ascorbic acid in hydrochloric acid solution i.e. under the conditions applied for the determination of molybdenum. The methods are summarized in Table 1.

References

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