Spectrophotometric Determination of Molybdenum(VI) Using Isothipendyl Hydrochloride and Pipazethate Hydrochloride in Alloy Steels and Soil Samples

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Molybdenum is commercially important in metallurgical and agricultural laboratories. Besides its widespread industrial uses, molybdenum is an essential trace element required by both plants and animals.¹ It is, however, harmful to both plants and animals at high concentrations.² Deficiency diseases in livestock have been recorded when soil molybdenum levels were below 1 $\mu\text{g g}^{-1}$. The increasing use of chemicals in agriculture requires more profound studies on the determination of microelements in soils and their migration. So molybdenum determination is of great interest to analytical chemists, particularly to soil and environmental chemists. The standard method available for the determination of molybdenum in soil is tedious and lengthy.³ In this method, separation of chromium, titanium and reduction of vanadium using stannous chloride is necessary prior to molybdenum determination. The method of determining molybdenum using thiocyanate and stannous chloride has several disadvantages, such as variation of absorbances with respect to the concentrations of thiocyanate, stannous chloride and acid; low sensitivity. Furthermore, other elements *viz.*, Re, V, W, U, Cr, which in their lower oxidation states formed thiocyanate complexes, are also reduced and interfere with the determination of molybdenum.⁴ Hence, a milder reductant which reduces Mo(VI) to Mo(V) quantitatively is desirable; ascorbic acid used in the present study serves the purpose. In the present investigation we are reporting two simple, adequately sensitive and accurate extractive spectrophotometric methods for the determination of Mo(VI) in alloy steels and soil samples using isothipendyl hydrochloride (IPH) and pipazethate hydrochloride (PPZ). The methods are based on the formation of chloroform-soluble mixed-ligand complexes of Mo(V) with thiocyanate and IPH or PPZ in hydrochloric acid medium. The chromogens formed in the proposed methods are more stable (more than 24 h) compared to that reported earlier⁵ (1 h) and also have higher molar absorptivity ($3.28 - 4.0 \times 10^4$) than those of the reported methods⁶⁻⁹ ($0.97 - 9.6 \times 10^3$). The methods are free from interference by a large number of metal ions unlike the reported methods.⁸⁻¹⁰ Thus the extraction of ternary complexes with chloroform led to high sensitivity, selectivity and stability compared with the methods described previously.⁵⁻¹⁰

Experimental

Apparatus

A Hitachi (Model U-2001) UV-visible spectrophotometer with 1 cm matched quartz cells was used for the absorbance measurements. Elemental analysis of the complex was performed on a Thermoquest CHN analyzer (Model EA 1110 CHN) and a Nicolet FTIR spectrophotometer (Model Impact410) was used for recording the IR spectrum.

Reagents and samples

All the chemicals used were of analytical or pharmaceutical grade and quartz-processed high-purity water was used throughout.

A stock solution of Mo(VI) was prepared using ammonium molybdate tetrahydrate (AR) in 100 ml distilled water and was standardized by a reported method.¹¹ It was diluted to give a standard solution containing 100 $\mu\text{g ml}^{-1}$ of Mo(VI). Two 0.5% solutions, one of IPH and one of PPZ, were prepared separately in distilled water and were stored in amber-colored bottles in a refrigerator. Aqueous solutions of 20% NH_4SCN and 5% ascorbic acid were prepared in distilled water. A 10 M HCl was also prepared. Solutions of diverse ions of suitable concentrations were prepared using AR grade reagents.

Determination of Mo(VI)

To a known volume of Mo(VI) solution, taken in a series of separating funnels, were added 2 ml of 10 M HCl, 2 or 3 ml of 20% NH_4SCN for IPH or PPZ and 5 or 6 ml of 5% ascorbic acid for IPH or PPZ. The mixture was set aside for 20 min and then to it were added 6 ml of IPH or PPZ. Then the mixture was diluted to 20 ml to maintain HCl concentration at 1 M. Ten milliliters of chloroform was added and the container was shaken well. The two phases were allowed to separate and the chloroform layer was passed through anhydrous Na_2SO_4 . The absorbances of the orange-red colored species were measured at 461 nm for IPH or at 465 nm for PPZ against the corresponding reagent blank. The amount of Mo(VI) in the sample solution was deduced from the calibration curve.

Analysis of molybdenum in alloy steels

About 0.5 g of alloy steel was weighed accurately, treated with aqua regia repeatedly until the sample was dissolved completely and then heated to fumes of oxides of nitrogen.

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Fig. 1 Effect of HCl concentration and standing time intervals: HCl concentration at A, 0.75 M; B, 1 M and C, 1.25 M.

After it was cooled, 10 ml of concentrated H_2SO_4 was added and evaporated almost to dryness. We repeated the evaporation and H_2SO_4 treatment three times to remove all the HNO_3 . Finally, 20 ml of 10 M HCl was added to the residue and any insoluble material was filtered off. Then we diluted the solution to 100 ml in a calibrated flask with distilled water. Ten milliliters of the stock solution were further diluted to 100 ml with 2 M HCl. To an aliquot solution (0.5–2.0 ml) taken in a separating funnel was added HCl (1.9–1.6 ml of 10 M), followed by 2 or 3 ml of 20% NH_4SCN and 5 or 6 ml of 5% ascorbic acid for IPH or PPZ. It was set aside for 20 min; then 6 ml of IPH or PPZ was added and the mixture was diluted to 20 ml with distilled water to maintain the overall acid concentration at 1 M. The ternary complex formed was extracted into chloroform and the amount of molybdenum was deduced from the calibration curve.

Analysis of soil samples

Two grams of soil sample were placed in a platinum crucible containing about 7–8 g of anhydrous Na_2CO_3 and the contents were mixed thoroughly. The mixture was heated gently to about 500°C to burn off the soil organic matter during the first 5 to 10 min in an oxidizing atmosphere, to avoid the possibility of molybdenum loss, before the charge was fused. It was further heated to 1000 – 1100°C in an electric furnace till fusion was over. The melt was cooled and then transferred into a beaker by washing repeatedly with distilled water, and then filtered through a piece of Whatman filter paper No. 40. An aliquot solution (1–2 ml) was taken and neutralized with 10 M HCl. Amounts of NH_4SCN , ascorbic acid and IPH or PPZ were added as mentioned earlier while maintaining the overall acid concentration to be 1 M with HCl. The ternary complex developed was extracted into chloroform and the amount of molybdenum was determined from the calibration curve.

Results and Discussion

Preliminary investigations have shown that IPH or PPZ reacts with Mo(V) obtained by ascorbic acid reduction of Mo(VI) in the presence of HCl containing thiocyanate at room temperature to form chloroform soluble orange-red ternary complexes having maximum absorbance at 461 nm for IPH or at 465 nm for PPZ. The optimum reaction conditions for quantitative determination of the mixed-ligand complexes were established via a number of preliminary studies. The effect of acids on the

Table 1 Tolerance limits of diverse ions in the determination of molybdenum(VI)

Ion or species added	Tolerance limit/ $\mu\text{g ml}^{-1}$		Ion or species added	Tolerance limit/ $\mu\text{g ml}^{-1}$	
	IPH	PPZ		IPH	PPZ
Ni(II)	7500	7000	Th(IV)	1800	2000
Cu(II)	250	250	W(VI)	40	45
Co(II)	4000	4200	U(VI)	45	45
Mn(II)	2400	2500	Cd(II)	5000	5200
Cr(VI)	600	500	Zr(IV)	150	150
V(V)	1500	1300	Fluoride	2500	2200
Na(I)	6000	5500	Chloride	8000	7500
K(I)	5000	5000	Sulfate	4000	4200
Ca(II)	4500	4000	Oxalate	3000	2800
Mg(II)	4500	4000	Nitrate	1800	2000
Fe(III)	7000	7500	Citrate	5000	6000
Hg(II)	2500	2200	Acetate	5000	5500
Pb(II)	3000	2800	Tartrate	4500	4000
Al(III)	4200	4500	Bromide	1200	1500
Zn(II)	4500	4000	Phosphate	3000	3500

formation of complexes has been studied using HCl, H_2SO_4 , H_3PO_4 and CH_3COOH . As HNO_3 oxidized the ligand, it was not used for the study. It was observed that the color intensity of the complex was slow in H_3PO_4 and CH_3COOH . It was also noticed that the reduction of Mo(VI) to Mo(V) by ascorbic acid was slow below 1 M HCl. The effect of HCl concentration and standing time intervals for completion of the reaction of IPH are given (Fig. 1). The effects of different amounts of NH_4SCN (0.5–4 ml), ascorbic acid (2–8 ml) and IPH or PPZ (2–8 ml) were investigated on the formation of ternary complexes of Mo(V). The color development was slow when the volume of NH_4SCN was less than 1.5 or 2.5 ml for IPH or PPZ, while quantitative extraction of the ternary complex was not achieved with less than 6 ml of IPH or PPZ. It was also noticed that an excess of the reagents had no effect on the sensitivity or stability of the complexes. However, 2 and 3 ml of NH_4SCN respectively for IPH and PPZ and 6 ml of IPH or PPZ were used to ensure complete formation of the complex. A volume of 5 ml of ascorbic acid was found to be sufficient for the quantitative reduction of Mo(VI) to Mo(V); excess of ascorbic acid had no effect either on the stability or intensity of the colored complex. Of several organic solvents tried for quantitative extraction of the complexes, chloroform was found to be the most suitable solvent, as it was observed that only one extraction was sufficient for the quantitative recovery. The complexes were stable for more than 24 h.

Analytical features

The ternary complexes obeyed Beer's law in the concentration range of 0.5–5.9 and 0.5–6.9 $\mu\text{g ml}^{-1}$ of Mo(VI) with molar absorptivity values of 3.28×10^4 and 4.0×10^4 $\text{l mol}^{-1} \text{cm}^{-1}$ for IPH and PPZ, respectively. Sandell's sensitivity values, as calculated from Beer's law data were found to be 9.8 and 10.9 ng ml^{-1} for IPH and PPZ, respectively. Regression analyses of Beer's law plots at their respective λ_{max} values revealed a good correlation ($r = 0.9987$ and 0.9992). Graphs of the absorbance versus the concentration showed low intercept values (0.02453 and 0.03188) and slope (0.1211 and 0.1437) and are described by a regression equation, $Y = a + bX$ (where Y is the absorbance of a 1 cm layer, b is the slope, a is the intercept and X is the concentration of the drug in $\mu\text{g ml}^{-1}$), obtained by the least-squares

Table 2 Determination of molybdenum in alloy steels and soil samples, and comparison with the standard method

Sample	Certified value	Found ^a by the proposed method		RSD		Comparison with the standard method			
		IPH	PPZ	IPH	PPZ	IPH		PPZ	
						F	t	F	t
MSREMo ₁ ^b	4.56%	4.57%	4.55%	1.05	0.97	—	—	—	—
MSREMo ₂ ^b	3.82%	3.79%	3.80%	1.00	1.05	—	—	—	—
BSS ^c	0.85%	0.86%	0.84%	0.91	0.91	—	—	—	—
S ₁ ^d	2.54 µg g ⁻¹	2.55 µg g ⁻¹	2.54 µg g ⁻¹	0.94	1.02	1.21	1.23	1.42	1.11
S ₂ ^d	1.91 µg g ⁻¹	1.90 µg g ⁻¹	1.92 µg g ⁻¹	1.02	1.07	1.34	1.11	1.31	1.12

a. Average of five determinations. b. Obtained from Visweshwaraiah Iron and Steels Ltd., Bhadravati, India. c. Obtained from Bhilai Steels, Bhilai, India. d. Obtained from University of Agricultural Sciences, Dharwad, India.

method. The low relative standard deviation values (0.88 and 0.95) and the range of error at 95% confidence level (0.51 and 0.62) for the analyses of six replicates of 4 µg ml⁻¹ of Mo(VI) indicated good precision and accuracy of the proposed methods.

Stoichiometry of the complexes

The stoichiometry of Mo(V) complexes with IPH or PPZ and SCN⁻ in solution was studied spectrophotometrically by Job's method¹² of continuous variations and equilibrium shift method.¹³ The results indicated that the mole ratio between Mo(V), SCN⁻ and IPH or PPZ was 1:4:1. The solid complexes were isolated from chloroform layer by evaporating on water bath and were analyzed for analytical data. The data correspond to (IPH/PPZ-H) [MoO(SCN)₄]. The coordination of IPH/PPZ and SCN⁻ to molybdenum was also confirmed by IR spectral data.

Effect of diverse ions

The effects of some diverse ions in the determination of 4 µg ml⁻¹ of Mo(VI) in the presence of a number of foreign ions were studied. The results presented in Table 1 clearly indicate that the proposed methods could be effectively applied for the determination of Mo(VI) when many foreign ions were present in large excess.

Statistical analysis of the results in comparison with the standard methods

The results of the analysis of soil samples were compared statistically by the Students t-test and by the variance ratio F-test with those obtained by the standard method.³ The students t-values at 95% confidence level did not exceed the theoretical values, indicating that there was no significant difference between the proposed and standard method. It was also noticed that the variance ratio F-values calculated for $p = 0.05$ did not exceed the theoretical values, indicating that there was no significant difference between the precision of the proposed methods and the standard method. The results are shown in Table 2.

The proposed methods could be used as alternative methods for the investigation of micro amounts of molybdenum in alloy steels and soil samples, as they are simple and sensitive and free from the interferences of commonly associated substances in these materials.

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