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A highly sensitive and selective spectrophotometeric determination of molybdenum using *o*-Phenanthroline in presence of thiocyanate

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ABSTRACT

Molybdenum in the pentavalent state, forms a yellow orange colored complex with o-phenanthroline in presence of thiocyanate in hydrochloric acid medium whose absorbance is measured at 415 nm. Ascorbic acid is used as a reductant for converting Mo (VI) to Mo (V). The Ascorbic acid is used as a reductant for converting Mo (VI) to Mo (V). The molar absorptivity and Sandell's sensitivity of the method are 1.151×10^4 Imol⁻¹ cm⁻¹ and ± 0.0041 µg Mo cm⁻² respectively. Beer's law holds good up to 5.5 µg Mo ml⁻¹. A large number of cations and anions do not cause interference. The procedure worked out is quite simple, rapid, sensitive and highly selective.

Keywords: Molybdenum, o-phenanthroline, Potassium thiocyanate, Spectrophotometric determination.

INTRODUCTION

Despite the fact that several extractive methods for trace determination of molybdenum are available in literature^[1-5], but still in some cases, there are serious limitations in their applications. Also, there are reports that molybdenum, in the hexavalent state, is though stable, yet it tends to hydrolyze forming Isopoly acids and as a consequence thereof, its extraction behaviour is considered to be a complicated one and quantitative treatment of extraction equilibria is not always possible perhaps for the same reason.^[6-12] Keeping this vital aspect in mind, an attempt has been made to effect determination of molybdenum at microgram level in aqueous medium by carrying out reduction of the metal ion and its complexation with o-phenanthroline in presence of thiocyanate. The details of the method are as under:-

MATERIALS AND METHODS

A standard stock solution of molybdenum containing 1 mg/ml of the metal ion is prepared by dissolving an accurately weighed amount of sodium molybdate dihydrate, $Na_2MoO_4 \cdot 2H_2O$ in demineralized water and standardized by oxine method^[13]. Working solutions at the mircogram level are prepared by suitable dilution therefrom. Solutions of other metals ions are prepared by dissolving their commonly available chemically pure salts in distilled water or dilute acids (like HCL, H_2SO_4). o-phenanthroline reagent, 0.2% (w/v), is prepared in distilled alcohol. Ascorbic acid, 10% (w/v), and Potassium thiocyanate, 20% (w/v), are prepared in distilled water.

Sample solutions are obtained by mixing Mo(VI) solution with solution of other metal ions in suitable proportion as shown in Table-1.

Apparatus:

For absorbance measurements, a UV-visible spectrophotometer (Shimadzu-140-02) Japan is used.

(i) Synthetic Samples :

Synthetic samples are prepared by mixing molybdenum solution with solution of other metal ions in suitable proportions as shown in Table-1.

(ii) Steels:

Steel sample (0.1g) is dissolved in 3ml concentrated HCL and 1ml concentrated HNO₃by gentlewarning on a sand bath. The solution is evaporated to thick mass and treated with deionized water (10ml) and diluted HCL (1.5ml). It is then transferred into a 100ml volumetric flask and the volume made up to the mark. To an aliquot (1ml) is added ascorbic acid (50 mg) and molybdenum is determined by the proposed method.^[15,16] (Table-1)

(iii) Well water :

To a 10 ml aliquot of well water are added a known amount of molybdenum (10 μ g), 20 volume hydrogen peroxide (1ml) and aqueous ammonia (2 ml). The solution is boiled and evaporated to dryness. The residue is dissolved in 2 mol dm⁻³ CH₃COOH (3 ml) and subjected to analysis form mo by the proposed method.^[17]

(iv) Reverberatory flue dust :

Reverberatory flue dust sample (0. 1g) from copper manufacture containing no molybdenum is mixed with a solution of known Mo content and dried in an even. After fusion of the dried dust sample with sodium peroxide(0. 8g), the leach is neutralized with concentrated H_2 So₄, made slightly alkaline with aqueous ammonia boiled and the hydroxide precipitate is filtered and washed well with deionized water. The filtrate is adjusted to 0.05 mol dm⁻³ HCL and Molybdenum determined by the proposed method.^[17](Table-1)

Procedure:

To a sample solution containing 20 μ g Mo(VI) in a 10 ml measuring flask, add 1 ml, 2N HCL, 2ml ascorbic acid, 1.5 ml 20% KSCN, followed by 0.7ml, 0.2% o-phenanthroline(in alcohol) make up the volume up to the mark with distilled water. The flask is stoppered and the contents are gently mixed by turning it upside down once or twice and then allowed to stand undisturbed for 10 min. The absorbance of the yellow complex thus formed is measured at 415 nm against a reagent blank prepared similarly. Molybdenum content is determined from the standard curve drawn by plotting absorbance values obtained corresponding to varying in μ g amounts of the metal ion as per the aforesaid procedure.

RESULTS AND DISCUSSION

In hydrochloric acid medium, hexavalent molybdenum is reduced to pantavalance with ascorbic acid.^[14] Mo(V) thus formed reacts with o-phenanthroline in presence of thiocyanate forming a yellow colored species, whose absorption maximum lies at 415 nm. As the complex is not well extracted into various organic solvents and hence the determination are made in aqueous solution.

Under the same set of aqueous conditions, in 2N acid solution, absorbance is maximum with HCL (0.165); whereas, it is low in H_2SO_4 , H_3PO_4 , CH_3COOH media in the same order. Thus hydrochloric acid is the suitable medium for the system.[Table-II]

The effect of hydrochloric acid concentration, ascorbic acid, thiocyanate and o-phenanthroline on the absorbance of the complex is shown in Table-II. It is evident form the data that the absorbance is maximum and constant at 0.165 for 0.5-1.5 ml of 2N HCL in 10 ml solution under the conditions as indicated in Table II for different variables. Hence, 1 ml HCL (2N) is recommended for the procedure. For the quantitative reduction of Mo(VI) to Mo(V), 1.4-2.2 ml ascorbic acid (10%) considered sufficient. The requirement of 20% KSCN and 0.2% o-phenanthroline (in alcohol) for obtaining maximum absorbance is 1.4-1.8 ml and 0.65-0.85 ml respectively for each operation.

The color the complex is fully developed in 10 min does not show any change for about 30 min. Hence 10 min color development time is necessary.

The complex is not extractable into carbontetrachloride, cyclohexane, chloroform, dichloromethane and hardly shows any absorbance with benzene. It does show absorbance on extraction with amyl acetate, ethyl acetate, but the readings oftenly are erratic. Hence, it was preferred to carry out measurements of absorbance in aqueous solution only.

Beer's law, Sandell's sensitivity stoichiometry of the complex

To sum up optimum conditions for the system, it is inferred that for 20 μ g Mo, 1ml 2N HCL, 2ml 10% (w/v) ascorbic acid, 1.5 ml, 20% (w/v) thiocyanate, and 0.70 ml, 0.2% (w/v) o-phenanthroline in alcohol in 10ml aqueous

volume with a color development time of 10 min are needed for the formation of the complex, whose absorbance is measured at λ_{max} -415 nm. (Figure-A)

The complex obeys Beer's law range of 0.0–6.0 μ g Mo ml⁻¹ (Figure-1) and the optimum concentration range that can be measured, as evaluated from Ringbom plot,^[18] is 2.14 to 4.38 μ g mol⁻¹. (Figure-2) Molar absorptivity and Sandell's sensitivity of the complex are 1.151×10^4 1 mol⁻¹ cm⁻¹ and 0.0041 μ g Mo cm⁻² respectively. For eight replicate determination, containing 20 μ g Mo each time, the standard deviation comes out to be \pm 0.021. Employing equimolar solutions, the ratio of molybdenum, o-phenanthroline and thiocyanate in the complex is determined as 1:2:2 by job's method of continuous variations^[19] (Figure 3-4), which is further confirmed by mole ratio method as well.^[20] (Figure 4-5).

Effect of Diverse ions:

The presence of chloride (10mg); oxalate, EDTA (disodium salt), citrate (20 mg each); tartarate (40 mg); phosphate (50 mg); thiourea (80 mg); flouride, nitrate (90 mg each); Sulphate, acetate (100 mg each); in 10ml aqueous solution containing $20\mu g$ of Mo, does not have any effect on the absorbance of the complex and are therefore non-interfering.

Amongst the cations, in 10ml aqueous volume, Zn (II), 20mg; Pt (IV), As (V), 10mg each; Cu (II), 7mg; Pb (II), Be(II), La(III), Ce (IV), 5mg each; Ni(II), Cr (III), U(VI), 2 mg each; W(VI), 1.2 mg; V(V), Cr(VI), Zr(IV), 1 mg each; Bi(III), 0.5mg; Fe (III), 0.45 mg; Re (VII), 300µg ; Pd (II), 220µg ; Ir (III), Ru (III), 100µg each; Au (III), 90µg; Ti (IV) 50µg; Fe (II), 20µg; do not show any absorbance under conditions of the procedure. Ce (IV), Co (II), 0.5mg each; give turbidities while Nb(V), Th(IV), Bi(III) interfere by lowering absorbance.

Sr. No.	Composition of the sample	Mo added µg	Mo found µg		
1	Ni(0.5), Ir (0.01),Re(0.05)	10	0.90		
2	Ni(0.50), Pb(0.4), Ir (0.01)	30	30.04		
3	Re(0.01), Pb(0.5), As(1)	20	20.0		
4	Re(0.01), As(1), U(0.5)	25	25.65		
5	As(1), Ir(0.01), Fe(0.2)	40	40.0		
6	Cr(0.1), V(0.4), Be(0.5)	10	10.0		
7.	[Fe(0.29), Ni(0.075), Cr(0.1), Cu(0.005), Mn(0.01), Co(0.0005), Si(0.005), Pt(0.00025)] ^c	20	19.8		
8.	[Fe(1.05), Cu(0.015), Ni(0.1368), Cr(0.285), Cu(0.003)] ^c	15	15.1		
9	$[Fe(0.66), W(0.17), Cr(0.1)]^{c}$	25	25.65		
10	Well water I	50	50.0		
11	Well water II	45	45.0		
12	Reverberatory flue dust	35	34.05		

1. Figure in brackets shows amounts in mg.

2. Composition of sample-7 is analogous to stainless steel.

3. Composition of sample–8 is analogous to cristite.

4. Composition of sample-9 is analogous to steel CA-15.

Table-II: Effect of various parameters of	n the absorbance of Mo complex
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1	HCI (2N),ml	0.2	0.5	0.7	1.0	1.2	1.5	1.7	2.0	2.2									
	Absorbance	0.090	0.165	0.165	0.165	0.165	0.165	0.160	0.150	0.140									
2	Ascorbic Acid(10%), ml	0.2	0.5	0.7	1.0	1.2	1.4	1.5	1.7	2.0	2.2	2.5							
	Absorbance	0.180	0.190	0.210	0.230	0.240	0.240	0.240	0.240	0.240	0.235	0.230							
3	Pot. (20%) thiocyanate, ml	0.2	0.5	0.6	0.8	1.0	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.2	2.5		
	Absorbance	0.190	0.190	0.190	0.190	0.210	0.220	0.230	0.240	0.240	0.240	0.240	0.240	0.240	0.210	0.210	0.180		
4	o-Phenanthroline (0.2% in alcohol), ml	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6	0.65	0.7	0.75	0.8	0.85	0.90
	Absorbance	0.140	0.140	0.140	0.145	0.150	0.160	0.180	0.185	0.190	0.200	0.220	0.230	0.240	0.240	0.240	0.240	0.240	0.230

1. Mo(VI) 20 µg, HCL(2N) variable, Ascorbic acid 10%(w/v) 1ml, KSCN 20% (w/v) 1ml, o-phenanthroline 0.2%(w/v) 1ml, aqueous volume=10 ml, λ_{max} -415 nm).

2. Mo(VI) 20µ, HCL(2N) 1 ml, Ascorbic acid variable, KSCN 20% (w/v) 1ml, o-phenanthroline 0.2%(w/v) 1 ml, λ_{max} -415nm, aqueous volume=10ml.

3. Mo(VI) 20 μ g, HCL(2N) 1 ml, Ascorbic acid 10% (w/v) 2 ml, KSCN 20% (w/v) variable, o-phenanthroline 0.2% (w/v) 1ml, λ_{max} 415 nm, aqueous volume=10 ml.

4. Mo(VI) 20 μg, HCL (2N) 1 ml, Ascorbic acid 10% (w/v) 2 ml, KSCN 20% (w/v) 1.5 ml, o-phenanthroline 0.2% (w/v) variable, λ_{max}-415 nm, aqueous volume=10ml.



Figure A: Absorption spectra of Mo(V)-KSCN-o-phenanthroline (Complex against Blank)







complex at 415 nm.





Conc. of Mo -1.042×10^{2} M Conc. of O phen. -1.042×10^{2} M





CONCLUSION

The proposed method of Molybdenum determination in trace amounts is simple, sensitive and free from the interference of a large number of metal ions. The validity of the method is tested by analyzing a wide variety of samples of varying complexity [Table-1]. The results obtained are quite satisfactory and reproducible.

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