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A highly rapid, sensitive and selective, spectrophotometric determination of Molybdenum (VI) with 5-chloro-8-hydroxy-7-iodoquinoline by extraction into chloroform

Sonia Bhardwaj and L. R. Kakkar

Department of Chemistry, Kurukshetra University, Kurukshetra, Haryana, India

ABSTRACT

A simple rapid, extractive spectrophotometric method for micro determination of molybdenum using 5-chloro-8-hydroxy-7-idoquinolene as a complexing agent has been worked out for various industrially important steel samples as well as for environmental samples. The Mo (VI) 5-Chloro-8-hydroxy-7-idoquinolene (CHIQ) complex is extracted into chloroform. The yellow colour of the complex is measured at λ_{max} 390 nm against a similarly prepared reagent blank. The 1:2 (Mo : CHIQ) complex is found to be stable for more than one hour in the extract and obeys Beer's law over the concentration range of 0-12 µg Mo ml⁻¹. The molar absorptivity and Sandell's sensitivity of the proposed method are found to be 0.7867 × 10⁴ l mol⁻¹ cm⁻¹ and 0.002439 µg Mo cm⁻² respectively. A large no. of cations, anions and complexing agents of major analytical importance such as Co (II), Pb (II), Ag (I), As (V), Bi (III), Ni (II), Zn (II), Ti (IV), Sc (IV), Cr (III), Ru (III), Ce (IV), Re (VII), Ir (III), Au (III), Pd (II) and platinum metals and chloride, bromide, sulphate, acetate, phosphate, thiourea, EDTA, iodide, citrate, nitrate, tartarate, sulphosalicylic acid, sodium dithionite, oxalate, flouride do not interfare. Only Iron, Hafnium and niobium and nitrites interfered in the procedure. The method has been satisfactorily applied for the determination of molybdenum in varieties of samples.

INTRODUCTION

There are reports in literature that Mo (VI) and (V) form chelates with oxine and its derivatives ¹⁻³, which are extractable into chloroform, leading to determination of the metal ion at μ g level. From the study of these methods, it is revealed that there are several interferences which go unchecked thereby restricting their applicability. Besides, these procedures lack sensitivity and the results too at times are also not reproducible. Keeping these aspects particularly in mind, an attempt has been made to develop a method for trace determination of molybdenum using 5-chloro-8-Hydroxy-7-Iodoquinoline as a complexing agent in perchloric acid medium, with the following details :

MATERIALS AND METHODS

Molybdenum Solution :

A Stock solution of molybdenum containing 1 mg/ml of the metal ion is prepared by dissolving an accurately weighed amount of sodium molybdate dihydrate, $Na_2MoO_4 \cdot 2H_2O$ (AR), in distilled water, which is standardized by the oxine method⁴. Lower concentrations at the µg levels are obtained by suitable dilutions.

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A suitable amount of 5-chloro-8-hydroxy-7-Iodoquinoline (CHIQ) is dissolved in distilled alcohol to give 0.1% (w/v) solution; perchloric acid (2N) is used and standardized by conventional methods⁵ Chloroform is distilled and used as solvent for extraction.

Apparatus :

A UV-visible spectrophotometer (Shimadzu-140-02, Hitachi, Japan) with 10 mm matched (quartz) cells was used for absorbance measurements.

(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 HNO₃ by gentle warning 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.⁶ (Table-1)

(*iii*) *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.^{7,8} (Table-1)

(*iv*) Well water :

To a 10 ml aliquot of well water are added a known amount of molybdenum (10 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.⁹

PROCEDURE

To a sample solution containing 50μ g Mo(VI) in a 100ml separating funnel, add 1 ml 2N HClO₄, 1 ml 5-chloro-8hydroxy-7-iodoquinoline in alcohol, (0.1%, w/v) and enough distilled water to make the final aqueous volume to 10ml. The yellow complex formed is extracted with an equal volume of chloroform by equilibrating once for 30 sec. The organic layer is filtered through a whatmann's filter paper no. 41 into a 10 ml volumetric flask in order to remove any hanging droplets of water. It is made up to the mark with the pure solvent, stoppered and gently shaken for a while just for proper mixing. The absorbance of the colored species is measured at 390 nm against a similarly prepared reagent blank. Molybdenum content in the sample is obtained from the calibration curve plotted under optimum conditions of the procedure by taking different amounts of the metal ion at the microgram level.

RESULTS AND DISCUSSION

In perchloric acid solution, molybdenum, in the hexavalent state, reacts with 5-chloro-8-hydroxy-7-iodoquinoline forming an extractable yellow colored complex into chloroform, whose absorption max. lies at 390 nm. (Figure A)

Effect of varying experimental conditions on the absorbance of Mo (VI) CHIQ complex:

Effects of Different Acid Medium :

Under identical conditions, the extraction of the molybdenum complex has been effected in different acid7 media at 1N, and absorbance values are measured. The absorbance is maximum at 0.410 in $HClO_4$ followed by H_2SO_4 (0.400), HCl (0.380), CH₃COOH (0.370) and H_3PO_4 (0.370) in the order. Hence $HCIO_4$ medium is preferred. (Table-2)

Effect of Various Solvents :

The extraction of the complex has been tried with several solvents. It shows a maximum constant value at 0.410 in chloroform; whereas, it displays a downward trend with carbontetrachloride (0.400), benzene (0.380), amlyl acetate (0.300), cyclohexane (0.290), amyl alcohol (0.180). The complex is not extractable in isobutyl methyl Ketone and is

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not found to be stable in dichloromethane. Therefore, chloroform is chosen as an extractant for the complex. (Table-2)

The absorption spectrum of the complex (figure A) indicates that λ_{max} lies at 390 nm, where the blank shows minimal absorbance.

The effect of various parameters namely perchloric acid, 5-chloro-8-hydroxy-7-iodoqunioline, equilibration time on the extraction and absorbance of the complex is shown in Table-2. It is inferred from the data given in table–2 that for 50 μ g Mo 0.5-2.0 ml 2M HClO₄, 0.7-1.7 ml of 0.1% CHIQ reagent in 10ml aqueous volume, contacting for 10-50 sec with an equal volume of chloroform and measuring absorbance at 390 nm, are the optimum conditions for the system.

Effect of Diverse Ions :

The absorbance of the molybdenum complex is unaffected if the aqueous solution (10 ml) containing 50µg Mo, also contains individually chloride, bromide, sulphate, acetate, phosphate, thiourea, EDTA, each 10mg/ml; iodide, citrate, each 0.9 mg/ml; nitrate, 0.8 mg/ml; tartarate, 0.7 mg/ml; sulphosalicylic acid and sodium dithionite, each 0.5 mg/ml; oxalate, fluoride, each 0.3 mg/ml. Nitrite interfere in the method. Amongst the cations, in 10 ml aqueous volume, Ca (II), Co (II), Pb (II), Ag (I), As (V), Bi (III), each 10 mg/ml; Ni (II), Zn (II), each 9 mg/ml; Ti (IV) 6mg/ml; Se (IV), Cr (III), each 5mg/ml; U (VI), 4mg/ml; Cu (II), W (VI), Th (IV), each 1 mg/ml; do not show any absorbance under conditions of the procedure. Pt (IV), Cr (VI), each 0.5 mg/ml; Ru (III), 0.4 mg/ml; Ce(IV), Re (VII), each 0.3 mg/ml; Ir (III), Au (III), each 0.1 mg/ml; Pd (II), 20 µg/ml; are without effect. Fe (II, III), Hf (IV), Nb (V) show some interference.

CONCLUSION

The complex shows a linear response in absorbance value in chloroform upto 120µg Mo in 10 ml aqueous volume and thus maintains a Beer's Law range of 0-12 µg Mo ml⁻¹ (Figure – 1). The optimum concentration range that can be measured accurately, as evaluated from Ringbom plot ¹⁰ is 1.91 to 8.71 µg/cm⁻². (Figure-2). Molar absorptivity and Sandell's sensitivity of the method are 0.7867×10^4 1 mol⁻¹ cm⁻² and 0.002439 µg Mo cm⁻², respectively. Standard deviation of the method is ±0.010.

Stoichiometry of the Complex :

The ratio of Mo (VI) and the reagent CHIQ in the extracted species is found out to be 1:2 as determined by mole ratio method (Figure-3) job's method of continous variations as modified by vosburg and cooper 11,12 (Figure-4). The probable structure of the complex is as under :



APPLICATIONS

The wide applicability of the method is straightway shown by the analysis of a wide variety of natural samples, (different types of well water) synthetic and technical samples, (including various types of steels) reverberatory flue dust (Table – II). The method takes less than 5 min. for single determination. The method has better sensitivity 0.002439 μ g Mo cm⁻² giving 0.001 absorbance value as compared to that using 8-hydroxyquinoline (0.12), 8-mercapto quinoline (0.0112), 5,7-dibromo-8-hydroxyquinoline (0.0124), 8-hydroxy-7-Iodoquinoline-5-sulphonic acid (Ferron) (0.0174)^(1,2,3) and a wider Beer's law range i.e. 0-12 μ g Mo ml⁻² as compared to 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone¹³ (HMBATSC) (0.24 – 4.32 μ g ml⁻¹), 9-(2, 4-dihydroxyphenyl)-2, 3, 7-trihydroxyl-6-Fluorone (DHPTHF)¹⁴ (0.6 μ g Mo ml⁻¹), Alizarin Red S¹⁵ (0.05-5.50 g Mo ml⁻¹) 4-dihydroxybenzaldehyde isonicotinoyl hydrazone¹⁶ (0.3-6.0 μ g Mo ml⁻¹).

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Sr. No.	Composition of sample Matrix (a)	Mo(VI) added (µg)	Mo(VI) found (µg)
1.	Ca(1), Co(1), Ni(1)	50	51.2
2.	Ni(1), Ag(2), Ca(1)	70	70.0
3.	Co(2), Ag(1), Cr(III) (0.1)	100	98.8
4.	As(1), Bi(2), U(0.1)	10	9.9
5.	Pt(0.05), Pd(0.001), W(0.2)	60	58.8
6.	Th(0.2), W(0.1), Re(0.15)	40	40.0
7.	Well water (i)	50	50.0
8.	Well water (ii)	100	99.4
9.	$[Fe (0.264), W(0.068), Cr(0.04)]^{b}$	10	10.0
10.	[Fe (0.35), Cu (0.005), Ni (0.0456), Cr (0.095)] ^c	5	5.0
11.	[Fe(2.665), Ni(0.033), Cr(0.466), Mn(0.033)] ^d	15	14.98
12.	[Fe(0.004), Ni(0.252), Cr(0.08), Cu(0.026), W(0.008), Al(0.004), Mn(0.004)] ^e	20	20.1
13.	[Fe(0.25), Ni(2.5), Cr(0.75), W(0.2)] ^c	0.71	0.69
14.	Reverberatory flue dust	15	14.98

Table – 1 Analysis of different samples by the proposed m	ethod
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• Figure in brackets shows the amount of metal ion in mg.

• Sample No. 9 is analogous to steel CA-15.

• Sample No. 10 is analogous to stainless steel-U.

• Sample No. 11 is analogous to cast steel.

• Sample No. 12 is analogous to cristite.

• Sample No. 13 is analogous to Hastelloy-C.

Table - 2 Effect of various parameters on the absorbance of Mo-CHIQ complex

1.	HCIO ₄ (2N),ml	0	0.2	0.5	0.7	1.0	1.2	1.5	2.0	2.5	
	Absorbance	0.170	0.405	0.410	0.410	0.410	0.410	0.410	0.410	0.370	
2.	5-chloro-8-hydroxy-7-Iodoquinoline (0.1% w/v in ethanol), ml	0	0.2	0.5	0.7	1.0	1.2	1.5	1.7	2.0	
3.	Absorbance	-	0.150	0.370	0.410	0.410	0.410	0.410	0.410	0.390	
	Equilibration time, sec	5	10	20	30	40	50	60	75	90	120
	Absorbance	0.400	0.410	0.410	0.410	0.410	0.410	0.390	0.370	0.350	0.320

• Mo (VI) 50 μ g, HCIO₄ (2N) variable, 5-chloro-8-hydroxy-7-Iodoquinoline (0.1% w/v in ethanol) 1 ml, aqueous volume = solvent volume = 10 ml, equilibration time – 30 sec, No. of extraction – 1.

• HCIO₄ (2N) 1 ml, other conditions are the same excepting addition of 5-chloro-8-hydroxy-7-Iodoquinoline (0.1% w/v in ethanol) reagent.

• 5-chloro-8-hydroxy-7-Iodoquinoline (0.1% w/v in ethanol) 1ml, other conditions are the same excepting variation in equilibration time.

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