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Extractive Spectrophotometric Determination of Molybdenum using *p*-Chloroisonitroso Acetophenone Hydrazone

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Separation technique like solvent extraction can be advantageously employed for the determination of metals at low concentration in micrograms using spectrophotometric methods. Hydrazoxine has been used for the extraction and spectrophotometric determination of metals at trace level as well as for the studies of transition metals in complex form. In the present paper, solvent extraction technique has been used to develop methods for the separation and spectrophotometric determination of Mo(VI) with *p*-chloroisonitroso-acetophenone hydrazone (HICAPH) prepared as per procedure reported by Dey using *p*-chloroisonitroso acetophenone. Complex formed with *p*-chloroisonitroso acetophenone hydrazone was extracted into chloroform from aqueous solution in the pH range 8 to 8.5. The absorption maxima was also tried for the extracted species and Beer's law was also studied for its applicability. In this, interference from the foreign ion has also been examined.

INTRODUCTION

A survey of literature[1-3] reveals that *p*-chloroisonitroso-acetophenone hydrazone (HICAPH) has not been investigated in details as an analytical reagent. *p*-Chloroisonitroso acetophenone is found to react with many metal ions to give the colour reactions of analytical importance. The present paper describes a sensitive and selective method for the photometric determination of Mo(VI) with (HICAP). Various methods have been reported from literature for the extraction and spectrophotometric determination of Mo(VI). The newly developed method is less time consuming.

EXPERIMENTAL

A standard solution of molybdenum Mo(VI) (1000 ppm) was prepared by dissolving 0.9201 g of A.P. grade ammonium heptamolybdate in 500 mL double distilled water. 2% HICAPH in (1 : 1) ethyl alcohol is prepared for investigation.

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Schimadzu UV-visible spectrophotometer was used for all the measurements of absorption spectra. Mettler semimicro balance was used for weighing. Elico-Li-120 model of pH-meter was used for pH measurement.

Procedure

To an aliquot containing Mo(VI) in the range 1–20 μg/mL, an ethanolic solution of HICAPH (1 : 1) was added. The mixture was adjusted to pH 8.5 and equilibrated with 25 mL distilled chloroform and shaken for 2 min. The coloured organic layer was separated which was passed through anhydrous sodium sulphate to absorb moisture if any.

The volume was made up to 25 mL by chloroform. The absorbance of chloroform extract was measured at 350 nm, against Mo free blank. The amount of Mo was found from the calibration curve.

RESULTS AND DISCUSSION

Absorption Spectra

Absorption spectrum of molybdenum(VI) complex was taken in wavelength region 300 to 440 nm containing 20 μg/mL Mo(VI). The complex has peak at 350 nm. At this wavelength reagent blank shows negligible absorbance. Therefore 350 nm has been chosen as standard for all absorbance measurements.

Effect of pH

The effect of variation of pH was studied in absorbance Mo(VI) complex at 350 nm. The result shows that pH 8 to 9.2 is suitable for complete extraction of Mo(VI).

Effect of Reagent Concentration

The reagent concentration on the absorbance Mo(VI) complex was studied by changing reagent concentration from 0.1 to 3%. The absorbance does not seem to change for reagent concentration of 2% to 3%.

Therefore 2% concentration is suitable for determination of Mo(VI).

Effect of Equilibrium Time

To determine the minimum equilibration time for the extraction of Mo(VI): HICAPH complex, various solutions containing 20 μ of Mo(VI) and 2 mL of 2% HICAPH were equilibrated for different time intervals from 0.5 min to 8 min keeping all other parameters constant.

For the complete extraction 3 min time is sufficient.

Calibration curve for Mo(VI) and molar absorptivity

pH: 8.5

Aq. phase: 20 g of Mo(VI) solution + 2 mL 2% HICAPH in arc.

Org. phase: 10 mL of chloroform.

Maximum: 350 mn.

The plotting of absorbance against concentration of molybdenum(VI) (Table-1) gave a straight line indicating that the Beer's law is obeyed over the concentration range of 0.1 to 3.0 μg/mL and Mo(VI) 350 nm.

TABLE-1
CALIBRATION CURVE

Observation No.	Concentration of metal in ppm	Absorbance
1.	0.2	0.057
2.	0.4	0.115
3.	0.6	0.175
4.	0.8	0.232
5.	1.0	0.290
6.	1.4	0.402
7.	2.0	0.574
8.	2.6	0.750
9.	3.0	0.860

Molar absorptivity = 1.9×10^4 /mole.

Effect of diverse metal ions

Various cations and anions were investigated in order to assess their tolerance in the extraction of Mo(VI).

The tolerance limit for the variation was fixed at ±2% absorbance. For 10 μg/mL working solution of Mo(VI), it was found that bromide, chlorate, iodate, sulphate, nitrate, chloride, acetate, oxalate, tartarate, citrate, thorium(IV), manganese(II), cerium(IV), aluminium(III), zirconium(IV), magnesium(II) and barium(II) did not interfere.

Thiourea, EDTA, nickel(II), selenium(IV), cobalt(II), cadmium(II), mercury(II) and tin(II) interfered seriously/copper interference was masked with sodium thiosulphate.

Masking agents required to suppress the interference by other ions

Org. Phase: 10 $CHCl_3$.

Aq. Phase: 10 mL containing 10 μg Mo(VI) + 2 mL HICAPH, interfering ion and masking agent.

λ_{max}: 350

TABLE-2

Interfering ion	Masking agent aded
Ni(II)	Interfered seriously
Se(IV)	—do—
Co(II)	—do—
Cu(II)	Sodium thiosulphate

Nature of the extracted species: Job's continuous variation method indicates ratio as 1 : 2 which was further confirmed by mole ratio method.

Application of the method

The method has been successfully applied for the determination of molybdenum(VI) in synthetic mixtures and steel.

The results are then compared with the results obtained by known standard methods. It is seen that the results obtained in the present method are in good agreement with the results from standard methods, confirming the validity of the developed method.

TABLE-3

Steel samples	Certified value	Molybdenum found	
		Present method	Known method
Carbon steel BCS 454/1	0.190	0.180	0.187
Plain carbon steel BCS-320	0.220	0.210	0.220

Here Cu was masked with thiosulphate.

TABLE-4

Synthetic mixture	Molybdenum found	
	Present method (g)	Known method (g)
Al(III) (60) + Mo(VI) (30)	29.86	30.00
Mg(II) (30) + Mo(VI) (50)	49.86	50.00

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