SELECTIVE EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM (V) WITH N-HYDROXY–N (4-METHYL) PHENYL N'(4-FLUORO) BENZAMIDINE HYDROCHLORIDE AND THIOCYANATE

Dr. (SMT.) RUBINA ALVI AND Dr. HEMLATA MOHABEY

Department of Chemistry, Govt. Digvijay College, Rajnandgaon (C.G.)

RECEIVED : 22 February, 2016

N-Hydroxy N-(4 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride is newly synthesised reagent Mo (VI) is reduced to Mo (V) with ascorbic acid in hydrochloric acid solution and then complexed with thiocyanate. The orange red complex is extracted with benzene solution of N-hydroxy N (4 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride and thiocyanate. The coloured mixed chelate absorbs at 470 nm, with molar absorptivity 3840/mole^{-1} cm^{-1}. Beer's law is obeyed in the range is 5.0-20ppm of molybdenum.The optimum acidity range is 2.2 to 3.5 MHCl. Most of the common ions including Al (III), Cr (III), Fe (III), Fe (II), Ni (II), Zr (IV), V(V), Ti (IV), Zn (II) etc do interfere. The method has been used for the determination of molybdenum for steel.

KEY WORDS : Solvent Extraction, Mixed Ligand Complex, Spectrophotometer, Absorbance.

INTRODUCTION

Molybdenum is a trace elements distributed widely in nature which plays an important role in plants and animal nutrition and in our industrial society. While there are areas in the world where optimum growth of crops is not possible because of the deficiency of molybdenum, these are also many areas where naturally occurring high levels of molybdenum in forage lead to livestock [1] health problems. This needs study of environmental effects of molybdenum.

Many methods have been published for colorimetric determination of Molybdenum. The most important thiocynate method [2] with is stated to be the most reliable for trace molybdenum analysis [3] or thedithiol method [4] have some drawbacks such as low stability, extraction of coloured complex, interference of ions and low sensitivity.

The N. Hydroxy N. (4 methyl) phenyl N' (4 fluoro) phenyl benzamidinehydrochloride and thiocyarate method is very effective [5]. It is very simple, rapid and highly selective. It is free from, volume ratio of aqueous phase, concentration of reagents, order of addition of reagents, temperature, standing time etc.

EXPERIMENTAL

1. Chemicals

0-1% solution of HMPFBH in benzene was used for the extraction and spectrophotometric determination of molybdenum. Freshly prepared 10% solution of ascorbic acid and 2% solution of NH4SCN thiocyanate were employed. Standard solution was prepared. The solution was standardised with β. Hydroxy quinoline [6].

2. Apparatus –

A Carl-Zeise-Zena spectrophotometer spekol was used for colorimetric determination of complex and the pH values were determined with systronic pH type 321.

3. Colour Reaction –

Molybdenum (VI) is reduced to Mo (V) with ascorbic acid in hydrochloric acid medium & complexed with thiocyanate ions. The orange complex formed is then extracted with benzene solution of hydroxyamidine.

Procedure –

The aliquot of solution containing 200 µg of molybdenum was taken in a 125 ml separatory funnel To this 5ml of ascorbic acid solution was added. Then added 2.5 ml ammonium thioryanate solution. The acidity of solution was adjusted between 2.2 -3.5 M with hydrochloric acid keeping the total volume of aqueous phase to 25 ml. Then add 25ml of benzene solution of the reagent and equilibrated for 5 minutes. The benzene layer was separated dried over anhydrous sodium sulphate and the absorbance was measured at 470 nm.

RESULT AND DISCUSSION

Choice of solvent – Chloroform, CCl_4, benzene, toluene etc were found to extact the mixed complex quantitatively. Benzene found to be best extracting solvent as in this the sensitivity of the complex is enhanced and complete extraction is relatively rapid.

Effect of acidity – Acidity of the solution was maintained with hydrochloric acid. Optimum acidity range was found to be 2.2 to 3.5 M HCl.

Choice of reducing agent – Stannous chloride, hydroxyl amine hydrochloride, ascorbic acid were tried as reducing agents But ascorbic acid was found to be the best to reduce Molybdenum (VI) to molybdenum (V) stannous chloride and hydroxylamine hydrochloride results low and erratic. Crouthamel, Johnson [7-13] reported this.

Effect of Reagents –

(A) Effect of HMPFBH – A 1 : 20 molar ratio of metal to reagents was found to give maximum colour intensity. In practice a 50 fold molar excess of reagent over that of molybdenum was used for colour development.

(B) Effect of Thiocyanate – 1 to 275 fold molar ratio of metal to thiocyanate is necessary for complete extraction of molybdenum (V) as mixed complex.

Influence of diverse ions –

To study the effect of various anions and cations on the determination of molybdenum, a fixed amount of molybdenum (8 ppm) was mixed with known quantity of foreign ion under study and the acidity of the solution was adjusted to 3.0 M Mo (V) was extracted and

determined according to procedure, a reasonable amount of many anions and cations are tolerated.

Comparison with other Methods -

A number of reagent such as thiocyanate in (II) chloride [14-16], chloranilic acid [17], mercapto acetic acid [18-19], dithio oxamide [20], 4-methly λ-bentanol [21] etc have been reported for extraction spectrophotometric determination of molybdenum.

Sample	Certified Value %	Average Value %	Standard deviation
60B	0.430	0.410	± 0.0061
64A	4.11	4.070	± 0.0071
153 [Tool Steel]	8.38	8.372	± 0.0042
111B	0.255	0.259	± 0.0027

The disadvantages are overcome successfully in the present N-hydroxy-N (4 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride and thiocyanate method.

Conclusion

N – Hydroxy N (4 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride is proposed as a newly synthesizedreagent for selective extraction and spectrophotometric determination of molybdenum with thiocyanate. The brown red mixed complex of these reagent is extractable into benzene. The extraction is quantitative at 2.2 to 3.5 M Hydrochloric acid. The wave length of maximum absorption, molar absorptivity and Sandell's sensitivity of 1 : 22 (Mo : SCCN : HMPFBH) mixed complexes are 470 nm 3840/mole^{-1} cm^{-1} and 0.0285 µg of the molybdenum/cm^2 respectively. The colour system obey's Beer's law in the range 5ppm to 20ppm of the metal and is stable over 24 hrs. The method is suitable for the determination of molybdenum in steel samples, ores and alloys.

Acknowledgement

I am thankful to the Principal of Digvijay College Dr. R.N. Singh for providing me the laboratory for my work and also I am very thankful to the head of the Department of chemistry for their guidance.

References

1. Sauchelli, V., *Trace Elements in Agriculture*, Van Nostrand Reinhold, New York, p. 134, (1969).
2. Sandell, E.B., "*Colorimetric Determination of Traces of Metals*", **3rd Ed**., Interscience Publiishers, p. 640.
3. Hillebrand, W.F., Lundell, G.E.F., Bright, A. and Hoffman, J.E., *Applied Inorganic Analysis*, John Willey and Sons, Inc. New York, **2nd Ed**., p. 314 (1953).
4. Bickford, C.F., Jones, W.S. and Keene, J.S., *J. Am. Pharm, Asso. Sci. Ed*., **31**, 255 (1948).
5. From *Ph. D. Thesis*.
6. Vogel, A.I., "*A Text Book of Quantitative Inorganic*."
7. Crouthamel, C.E. and Johnson, C.E., *Anal. Chem*., **26**, 1284-91 (1954).
8. Disck, A.T., Bingley, J.B., *Nature*, **158**, 516 (1946).
9. Vogel, A.I., "*A Text Book of Quantitative Inorganic*".
10. Perrin, D.D., "Organic Complexing Reagent : Structural Behaviour and Application to Inorganic Analysis", *Interscience*, New York, p. 293 (1964).
11. Hobert, E.W. and Hurley, E.P., *Anal. Chem. Acta*., **27**, 144 (1942).

12. Marshell, M.J., *Econ. Geol*., **59**, 142 (1964).
13. Hope, R.P., *Anal. Chem*., **29**, 1053 (1957).
14. Bankovski, J., Svares, E. and Levins, A., *Zh. Anal. Khim.*, **14**, 313 (1959).
15. Busev, A.I. and Chang, F., *Zh. Anal. Khim.*, **16**, 39 (1961).
16. Chakraborty, A.K. and Bag, S.P., *Talenta*, **19**, 1187 (1972).
17. G.R. Waterbury and C.E. Bricker, Anal. Chem. 29, 129 (1957).
18. Will, F. and Yoe, J.H., *Anal. Chem*., **25**, 1363 (1953).
19. Roy, H.N., Roy, S.K. and Chakraborty, M.M., *Chemist Analyst*, **55**, 42 (1966).
20. Willian, D.A., Holcomb, I.J. and Boltz, D.F., *Anal. Chem.*, **47**, 2025 (1975).
21. Patil, S.P. and Shinde, V.M., *Anal. Chem. Acta*, **67**, 473 (1973).

❑