

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM(VI) WITH 2-HYDROXY-5-METHYLACETOPHENONE- ISONICOTINOYLHYDRAZONE (HMAINH)

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ABSTRACT

The extraction and spectrophotometric determination of trace amount of molybdenum(VI) with 2-hydroxy-5-methylacetophenoneisonicotinoylhydrazone (HMAINH) has been studied. The method is simple, selective, rapid and highly sensitive: reagent HMAINH forms a 1:2 yellow coloured complex with Mo(VI). The complex shows absorption maxima at 410 nm, where as absorption due to reagent is negligible. The extraction was carried out at 0.015 M-0.018 M hydrochloric acid into MIBK. Beer's law is obeyed over the concentration range of 3 - 16 ppm of molybdenum(VI) at 410 nm. Optimum range as defined by Ringbom's plot was 4 - 12 ppm. The molar absorptivity and Sandell's sensitivity of extracted species are $5.643 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and 17 ng cm^{-2} respectively. The standard deviation was found to be 0.09718. The effect of various diverse ions on the estimation of Mo (VI) has been studied. The method is applied for the determination of molybdenum in alloys.

Keywords: HMAINH, Extraction, Molybdenum(VI) determination, Spectrophotometry.

INTRODUCTION

Molybdenum is a biologically essential trace element. As a trace element

molybdenum is essential for the growth of plants and animals. In its natural occurrence, molybdenum is found in molybdenite ore at microgram level /1/. Various reagents such as 6-chloro-3-hydroxy-2-(2'-theinyl)-4H-chromen-4-one /2/, 9-methyl-2,3,7-trihydroxy-6-flurone /3/, n-octylaniline /4/, 3-hydroxy-2-(4-methoxyphenyl)-6-methyl-4-H-chromen-4-one /5/, thiocyanate and butyltriphenylphosphonium bromide /6/, 6-chloro-3-hydroxy-2-(5-methyl-2-furyl)-4H-chromen-4-one /7/, salicyladehyde 3-oxobutanoyl-hydrazone /8/, Isothipendyl hydrochloride and pipazethate hydrochloride /9/, 3-hydroxy-3-p-totyl-1-m-totyltriazene /10/ were used for spectrophotometric determination of molybdenum. Many sensitive methods, such as stopped flow injection spectrophotometry, catalytic spectrophotometry, high performance liquid chromatography, cathode and anodic stripping spectrophotometry, spectrofluorometry, X-ray fluorescence spectrometry, inductively coupled plasma emission spectrophotometry, neutron activation analysis, atomic absorption spectrophotometry have been used for determination of molybdenum. However, many of these methods are either time-consuming or require complicated and expensive instruments. Among various instrumental methods of analysis, the spectrophotometric method is preferred as a versatile technique in exploring the use of HMAINH as an effective reagent for the detection and determination of molybdenum at micro level. Therefore, it is a matter of practical interest to develop a relatively simple and sensitive method for Mo(VI) determination.

EXPERIMENTAL

Instruments and Chemicals

A digital Systronics 335 pH meter with combined glass electrode and a Systronics 106 spectrophotometer were used for pH and absorbance measurements. All chemicals used were of analytical grade. A stock solution of molybdenum(VI) (1 mg/mL) was prepared by dissolving ammonium molybdate tetrahydrate. Solutions of lower concentration were obtained by appropriate dilution as required. The stock solution of molybdenum (VI) was standardized /11/. 2-Hydroxy-5-methyl acetophenone isonicotinoylhydrazone (HMAINH) was synthesized by known method /12/ and a 0.01 M HMAINH solution was prepared by dissolving HMAINH in dimethylformamide and volume make up by ethanol in a volumetric flask.

Recommended method

An aliquot of sample solution containing 100 µg of Mo(VI) and 2 mL of 0.01 M reagent was taken and acidity was adjusted to 0.015 – 0.018 M with hydrochloric acid in 25 mL volumetric flask. The solution was transferred into 125 mL separating funnel and equilibrated for 120 sec with 10 mL MIBK solvent. The two phases were allowed to separate and dried over anhydrous sodium sulphate, the absorbance of the organic phase was measured against MIBK at 410 nm. The molybdenum(VI) content was computed from a calibration graph.

RESULTS AND DISCUSSION

Absorption Spectrum

The absorption spectrum of the Mo(VI) - HMAINH complex in MIBK shows the absorption maxima at 410 nm, whereas absorption due to reagent was nearly negligible (Figure 1). Therefore, all the absorbance measurement was recorded at 410 nm against the reagent blank in spectrophotometric determination of molybdenum.

Effect of acidity

The extraction of 10 ppm of molybdenum was carried out from different acid media with 2 mL 0.01 M reagent (HMAINH) and MIBK. Since there was no complexation in H₂SO₄, HNO₃, and HClO₄ media, all of the extractions were carried out at 0.015 M HCl. The extraction of molybdenum(VI) was investigated from 0.01 M to 0.02 M hydrochloric acid. The extraction was found to be complete (Figure 2). Hence extraction of molybdenum(VI) was carried out at 0.015 – 0.018 M hydrochloric acid.

Choice of extraction solvent

Various organic solvents were examined for the extraction of molybdenum - HMAINH complex and it was observed that the extraction of molybdenum(VI) complex was quantitative in MIBK. The solvents can be arranged in the decreasing order of their extraction coefficients as MIBK >

chloroform) benzene) toluene) xylene) carbon tetrachloride) n-butenol) nitrobenzene.

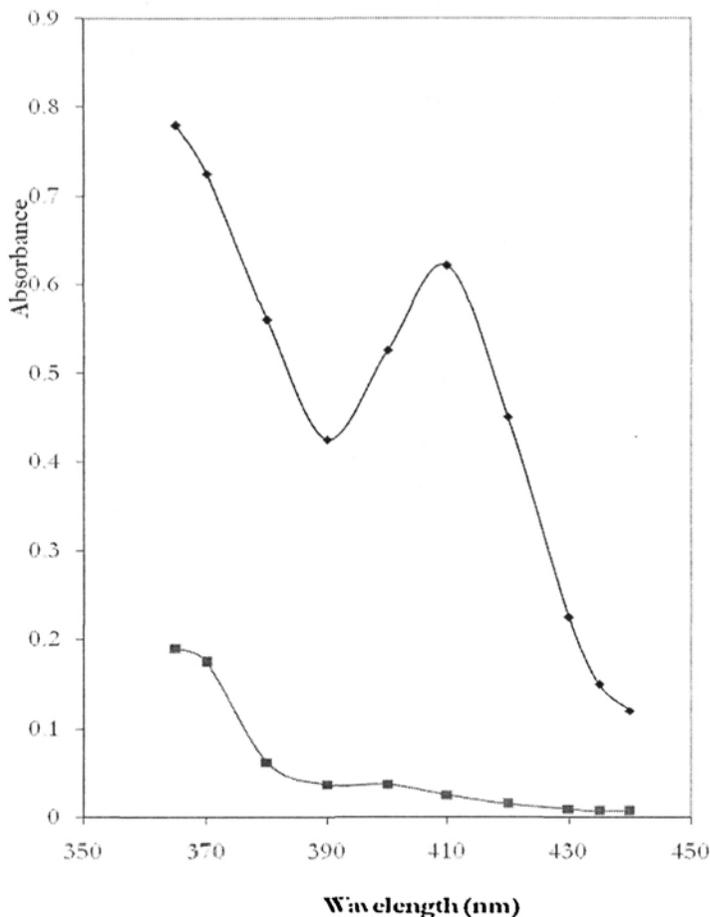


Fig. 1: A – Absorption spectrum of Mo(VI) – HMAINH against reagent blank, b -- absorption spectrum of HMAINH against MIBK

Effect of reagent concentration

The effect of reagent concentration was studied by varying the 0.01 M HMAINH concentration. It was observed that absorbance remains constant from 2 to 3 mL (Figure 3). Hence 2 mL of reagent concentration was recommended for determination of molybdenum (VI) for the further studies.

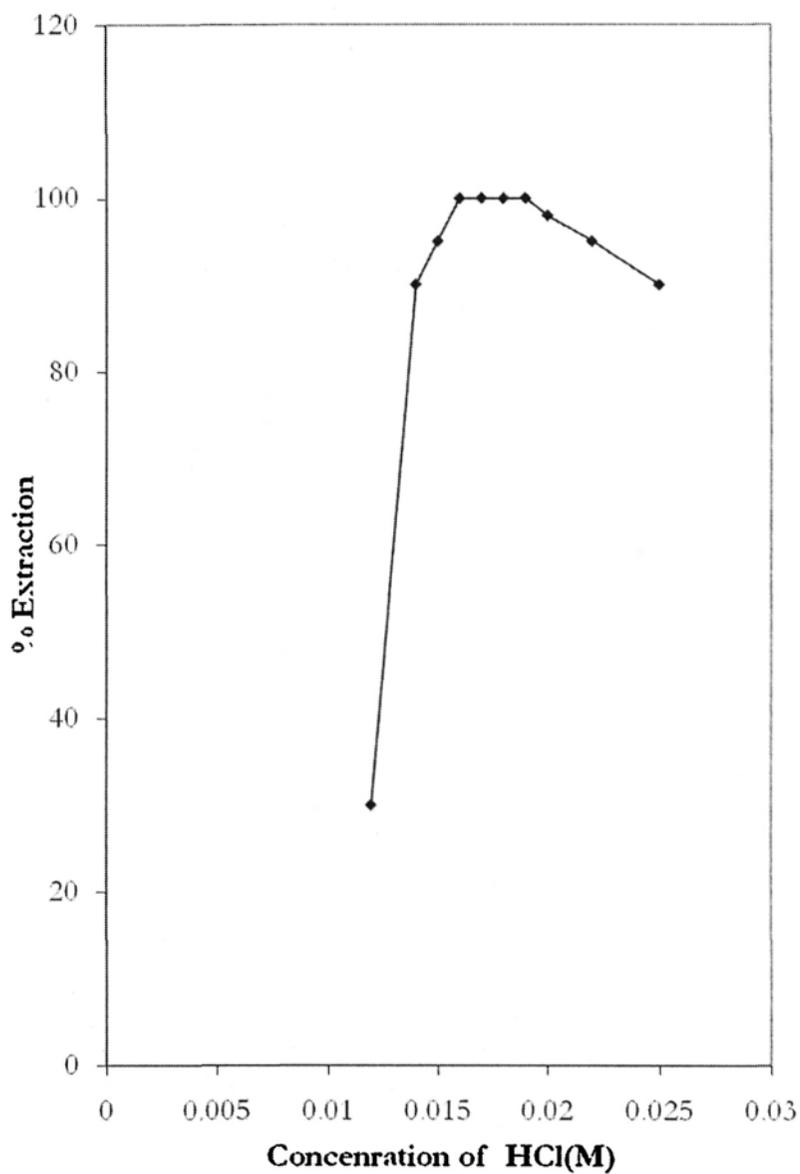


Fig. 2: Effect of acidity on extraction of Mo(VI) – HMAINH complex

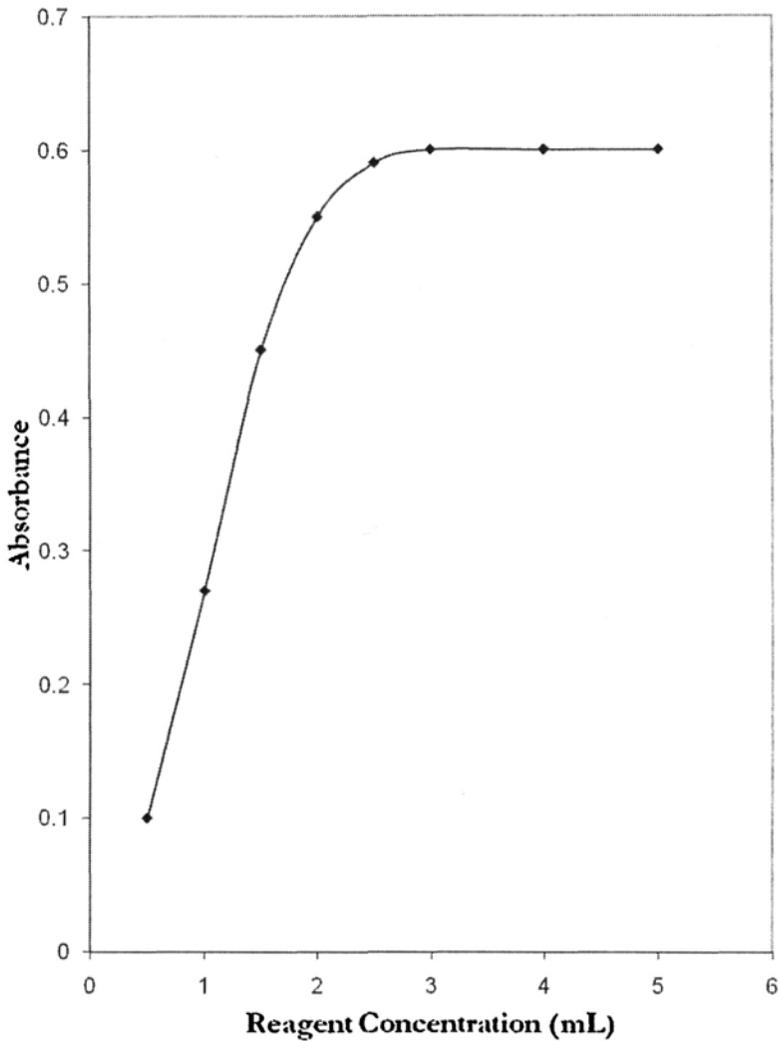


Fig. 3: Effect of reagent HMAINH concentration on the absorbance of Mo(VI) in MIBK

Equilibrium time and stability

The study of change in absorbance with variation in equilibrium time required for the complete extraction is 120 s. The extracted complex was found to be stable for 48 h.

Beer's range and sensitivity

Beer's law is obeyed over the concentration range of 3 - 16 ppm of molybdenum at 410 nm (Figure 4). Optimum range as defined by Ringbom's plot was 4 - 12 ppm . The molar absorptivity and Sandell's sensitivity were calculated to be $5.643 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}\text{cm}^{-1}$ and 17 ng cm^{-2} respectively at 410 nm.

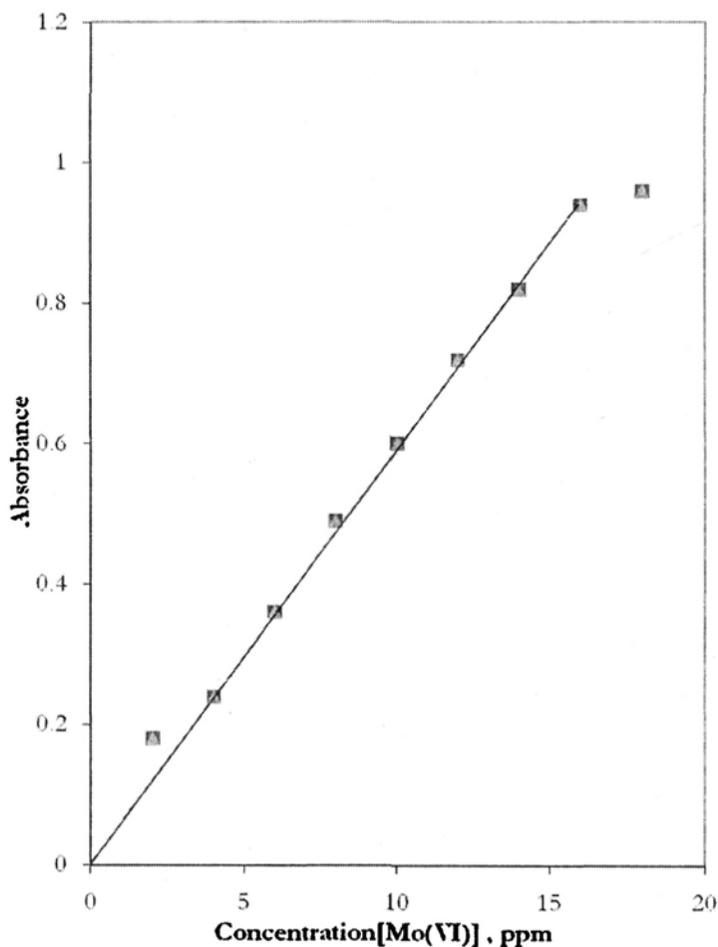


Fig. 4: Calibration plot of Mo(VI) with HMAINH (Beer's Law)

Nature of extracted species

The composition of the extracted species was determined by carrying out Job's continuous variation method (Figure 5) and was further confirmed by mole ratio method (Figure. 6). It was found to be 1 : 2.

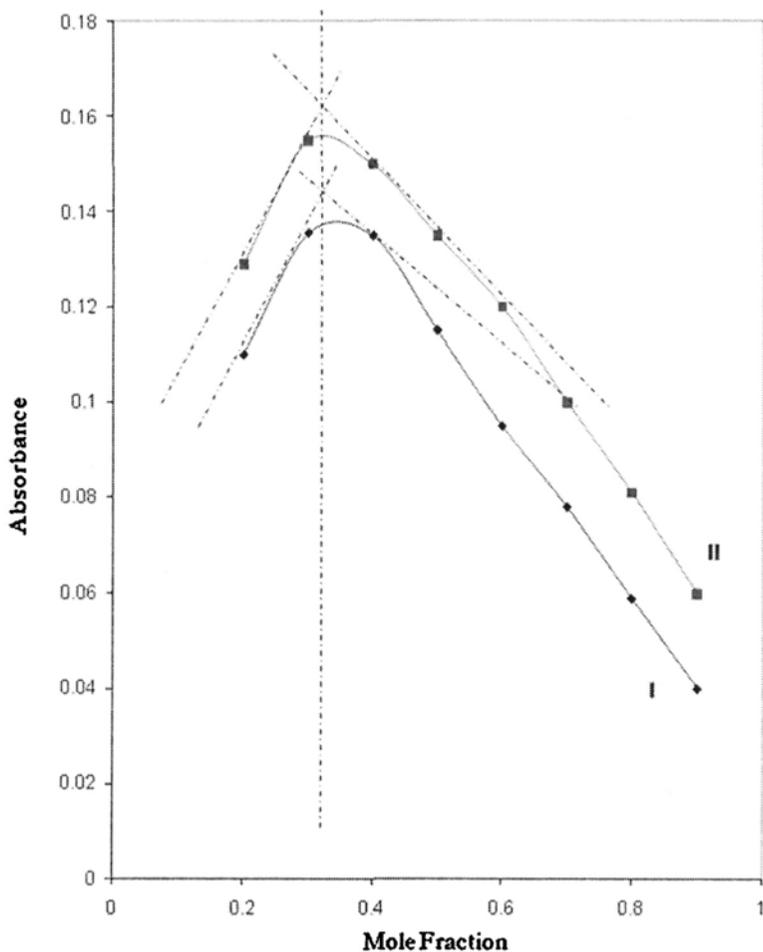


Fig. 5: Mo(VI) : HMAINH species by Job's continuous method.

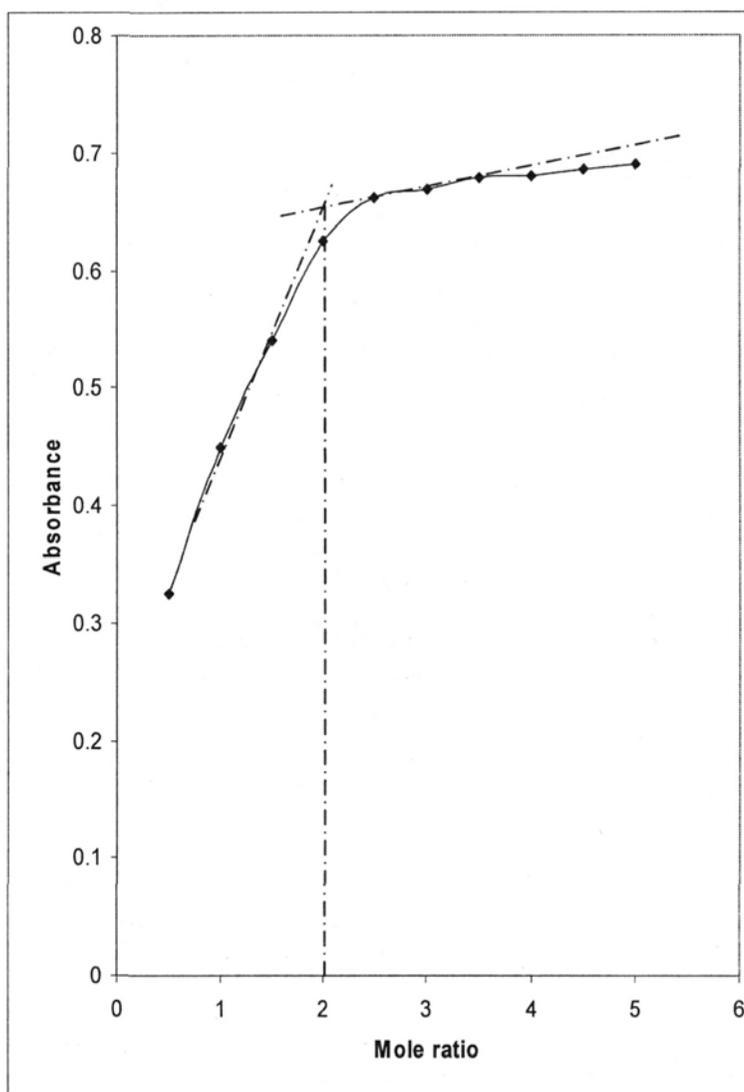


Fig. 6: Mole ratio for Mo(VI) – HMAINH species

Effect of diverse Ion

The effect of the various foreign ions were investigated in order to find tolerance limit of these ions in the extraction of Mo(VI). No interference was observed in the presence of following ions at the amounts (mg mL^{-1}) shown

as Zn(II) (5) ,Al(III) (10), Ni(II) (5), Cu (II) (5), Co (II) (5), Thiocyanate (200), Oxalate (100), Tartrate (50), Acetate (100).

Precision and accuracy

For the study of reproducibility and accuracy of the method, absorbance measurement with ten different identical solutions containing 10ppm of molybdenum was determined. Average of these ten readings and standard deviation was calculated. The standard deviation was found to be 0.09718. From standard deviation reproducibility of results with 95% confidence limit was 19.77 ± 0.06945 .

APPLICATION

Procedure for determination of molybdenum in alloys

Three samples of alloys were analysed separately. A known weight (1g) of the sample was dissolved in 9 mL of concentrated sulphuric acid and 50 mL of water. After the initial reaction was over, the solution was heated with 5 ml of nitric acid and evaporated to white fumes. The extract was boiled to dissolve soluble matter, filtered it and diluted to 100 mL with distilled water. An aliquot of this solution (1 to 2 mL) was analysed by proposed method. Results of analysis are reported in Table No 1. The result of molybdenum in alloys is in agreement with the certified values.

CONCLUSION

2-hydroxy-5-methylacetophenoneisonicotinoylhydrazone (HMAINH) was used as the reagent for the extractive spectrophotometric determination of molybdenum(VI) from hydrochloric acid media. The above reagent provides a simple, rapid and accurate method for spectrophotometric determination of molybdenum (VI). It has the advantages of high sensitivity, selectivity and easy availability.

Table 1

Sr. No.	Sample	Composition in %	Molybdenum		
			Declared value (%)	Found (%)	Relative error %
	ALLOYS				
1	Standard sample 1	C 0.35, Mn 0.3, Si 0.91 , Cr 3.32 , V 0.33	1.36	1.343	1.25
2	AISI 4140 (En-19)	C 0.4, Mn 0.80 , Si 0.25 , Cr 0.8 – 1.10	0.2	0.1964	1.8
3	En -24	C 0.40, Mn 0.50, Si 0.25, Cr 0.9 - 1.40, Ni 1.30 –1.80.	0.20 – 0.35	0.26	5.45

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