Non-Extractive Spectrophotometric determination of Mo (VI) using 5-Bromosalicylaldehyde Isonicotinoyl hydrazone (5-BrSAINH)

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ABSTRACT
A highly sensitive and selective spectrophotometric method was developed for the determination of trace amount of molybdenum (VI) in aqueous DMF medium. The molybdenum ion forms a yellow colored complex with 5-Bromo salicylaldehyde isonicotinoyl hydrazone (5-BrSAINH) in an acidic buffer of pH 6.0. The complex has an absorbance maximum at 390nm, was stable for more than 48 hours. The complex shows maximum absorbance at 390nm. Beer's law is obeyed in the range 0.24-4.79 μgml^{-1}. The molar absorptivity and sandell's sensitivity of the proposed method were found as 2.0×10^4 $L.mol^{-1}$ cm^{-1} and $0.02 \mu gcm^{-2}$ respectively. The pale yellow colored complex has 1:1 (Mo (VI) - 5BrSAINH) Stoichiometry .The stability constant of the complex was determined as 1.86×10^8 by Job's method. A sensitive and selective second order derivative spectrophotometry has also been proposed for the determination of Mo(VI). The interference of various cations and anions were studied. The developed methods were successfully employed in the determination of Mo (VI) in foodstuffs and alloy steel samples.

Keywords: UV-visible sppectrophotometry, Determination of MO(VI),5-BrSAINH, foodstuffs and steel samples.

INTRODUCTION

Molybdenum is an essential trace element required by both plants and animals[1]. Molybdenum has received great attention as an alloying element in a variety of steels. It alloys with transition metals finds extensive use in industry and thus coupled with several other important applications. The main application of molybdenum is however in the manufacture of alloy steels, providing hardenability, toughness, strength and wears resistance to plain carbon steel.

Molybdenum does not occur naturally as a free metal on earth, instead being found only in various oxidation states in minerals. Molybdenum has one of the highest melting point of all pure elements It is valuable as a catalyst in the refining of petroleum. This metal has found recent applications as electrodes for electrically heated glass furnaces and fore heaths.

Many spectrophotometric methods has developed for the determination of molybdenum(VI) based on its reaction with thiocyanate in the presence of a reducing agent[2] and with toluene-3, 4-dithiol[3] are not too selective, because they are subject to interference from many other elements. Some of the recently proposed methods using thiosemicarbazones[4] are found to be less sensitive. The methods employing different organic reagents have also been reported[5]. Although several methods have been reported for the spectrophotometric determination of molybdenum[6-17] they suffer from drawbacks such as lack of reproducibility, stability, interferences and requirement of prior extraction. In the present communication, simple, rapid, selective and sensitive spectrophotometric method is reported for the micro determination of Mo(VI) complexing with 5-BrSAINH.

MATERIALS AND METHODS
Apparatus
The absorbance measurements were made on Shimadzu UV-visible spectrophotometer (Model UV-160A). pH measurements were made using

LICO pH meter Model L1-613 ELICO Private Limited, Hyderabad, India.

Reagents& chemicals
All the reagents and chemicals used in the present studies were of analytical grade.

Preparation of ligand: 0.0vf1M solution of 5-BrSAINH in dimethyl formamide was employed in the present studies.

Preparation of Metal solution: 0.01M solutions of molybdenum (VI) were prepared by dissolving requisite amount of sodium molybdate in distilled water and were standardized[18] by using standard procedure. The stock solutions were diluted appropriately as required.

Preparation of Buffer solutions: Other metal ion solutions were prepared from their nitrates or chlorides. Buffer solutions were prepared by mixing appropriate volumes of 1M CH_3COOH and 1M HCl, (pH 1.0- 3.5) CH_3COOH and CH_3COONa (pH 4.0-7.0) NH_4OH and NH_4Cl (pH 8.0-10).

Preparation of food stuffs
5g of food or fruit material (dried for about 24hrs at 70^0C in an oven) was wet ashed with nitric acid and perchloric acid. The ash was dissolved in 5ml of hydrochloric acid and evaporated to dryness. This procedure was repeated and the dried residue was dissolved in water. The solution was filtered into a 25ml standard flask, one or two drops of concentrated hydrochloric acid was added and made up to the volume with distilled water.

Preparation of alloy, steel samples
A 0.1 - 0.5 g of the sample was dissolved in a mixture of 2 ml HCl and 10 ml HNO_3. The resulting solution was evaporated to a small volume. To this 5 ml of 1:1 H_2O : H_2SO_4 mixture was added and evaporated to dryness. The residue was dissolved in 15 ml of distilled water and filtered through Whattman filter paper No.41. The filtrate was collected in a 100 ml volumetric flask and made up to the mark with distilled water. The solution was further diluted as required.

Synthesis of ligand (Scheme I)
Equimolar solutions of 5-bromo salicylaldehyde (I) and Isonicotinic acid hydrazide (II) in water were mixed and refluxed for one hour on water bath and cooled. The light yellow solid formed was separated by filtration, washed with water at room temperature. The product was recrystallized from aqueous alcohol. The product (III) showed a melting point of 238-

240^0c. $1x10^{-2}$ M solution of the reagent was prepared by dissolving 0.320gm of the reagent in 100ml 0f dimethylformamide (DMF).

Procedure
Aliquots of solutions containing molybdenum (VI) were transferred into a series of 10ml volumetric flasks. To these 5-BrSAINH ($5X10^{-4}$) was added and the contents were diluted to the mark with distilled water and mixed well. The absorbance was measured at 390nm against the reagent blank. The calibration graph was constructed by plotting the absorbance against the concentration of Mo (VI) ions. For the solutions as prepared above, the second derivative spectra were recorded with reference to the reagent blank in the wavelength range 385- 525nm. The second derivative amplitudes were measured at wavelength 430 and were plotted against the amount of molybdenum(VI) to obtain the calibration plot.

RESULTS AND DISCUSSION
The reaction of 5-BrSAINH with Mo (VI) at room temperature gives a yellow colored soluble complex. The absorption spectrum of [Mo (VI) - 5-BrSAINH] shows maximum absorbance at 390nm where the reagent blank does not absorb appreciably, shown in **fig 1**. Therefore, subsequent analytical studies were carried out at 390nm using the reagent blank. The preliminary investigations indicates the absorbance of the complex is maximum and stable in pH range of 5.5-6.5. Therefore, pH 6.0 was selected for further studies. The minimum amount of reagent acquired maximum color intensity with a given amount of Mo (VI) was evaluated from the absorbance measurements of the experimental solutions containing different amount of reagents. Studies on reagent (5-BrSAINH) concentration effect revelaed that a minimum of 15 fold excess reagent to get maximum and stable absorbance for the complex. From the absorption spectra of [Mo(VI) - 5-BrSAINH] the molar absorptivity and sandell's sensitivity was found as 2.0 x 10^4 $L.mol^{-1}$ cm^{-1} and 0.02 μgcm^{-2}. Various amounts of [Mo(VI) - 5-BrSAINH] were treated with suitable amounts of reagent by plotting the measured absorbance value of the prepared solutions against the concentration of Mo(VI). From the calibration plot, it was observed that Beer's law was obeyed in the concentration range 0.24-4.79 μgml^{-1} of Mo (VI). The straight line obeys the equation $A_{390}=0.2383C+0.0259$. The molar absorptivity and sandell's sensitivity of the method were found as 2.0 x 10^4 $L.mol^{-1}$ cm^{-1} and 0.02 μgcm^2, respectively. The second derivative curves recorded **(fig.2)** for experimental solutions showed the derivative amplitudes were measured at 430nm for different concentrations of Mo (VI) and plots were

made between the amount of Mo(VI) and the derivative amplitude. The plots were linear and obeyed beer's law in the range 0.49-9.52 μgml^{-1} at 430nm. The effect of various cations and anions on the derivative amplitude was studied and it was noticed that all the ions that did not interfere in the zero order determinations of Mo (VI) also did not interfere in second order derivative method.

Applications
Determination of molybdenum in foodstuffs
The amount of molybdenum present in the foodstuffs was computed from a pre-determined calibration plot and the results are presented in **Table 1.**

Determination of molybdenum in alloy steel samples
The sample solutions were prepared as described under reagent and chemicals. The amount of Mo (VI) present was determined by the following procedure.
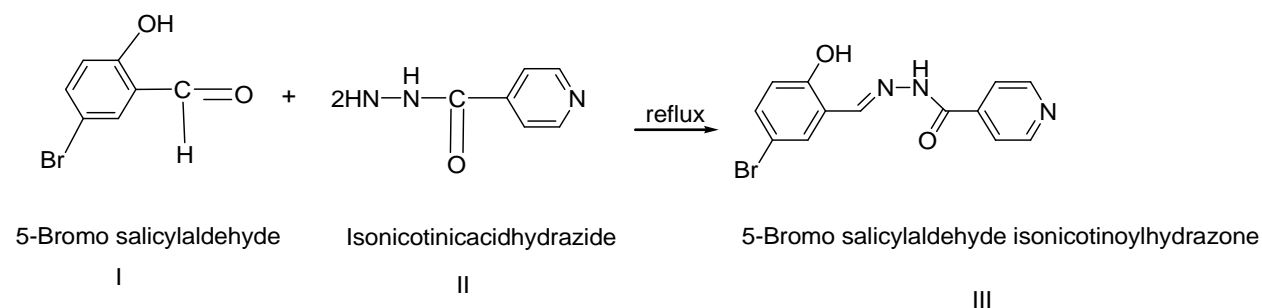
Procedure
A suitable aliquot of the sample solution was taken in a 10ml standard flask containing 5ml of buffer of pH 6.0, 1200 μg of Citrate (to mask Cu) and 1ml of $(5x10^{-4}M)$ 5-BrSAINH solution. The contents were diluted to 10ml with distilled water and its absorbance was measured at 390nm against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of molybdenum present. The results are presented in **Table 2**.

Rapid color development, simplicity and selectivity are the advantages of the proposed method. The intensity of the colored species will not be affected by slight variation of the experimental parameters such as concentration of the reagent. The proposed method does not involve extraction, heating or any other stringent reaction conditions and offers the advantage of high color stability (48h). The commonly associated metal ions,especially Fe(III),Hg(II) & Ru(III) could be tolerated in considerable excess, which is an advantage over other reported reagents. The proposed method can be used as an alternative method for the determination of trace amounts of molybdenum in food stuffs & alloy steel samples

CONCLUSION

5-Bromo salicylaldehyde   Isonicotinicacidhydrazide   5-Bromo salicylaldehyde isonicotinoylhydrazone

I   II   III

Scheme I
Synthesis of Ligand

Table 1
Determination of molybdenum in food stuffs

Sample	Amount of molybdenum ($\sim$g ml^{-1})		Recovery (%)
	Standard method	Present method*	
Banana	0.479	0.493	101
Apple	0.239	0.228	98
Cabbage	1.439	1.42	99
Tomato	0.959	0.961	101
Rice	0.718	0.608	97
Potato	0.240	0.238	98

* Average of five determinations.

Table 2
Determination of molybdenum in steels

Sample	Compositions (%)	Amount of Mo(%) (%)		Relative error (%)
		certified	found*	
BCS 406/1	Mn(0.066); Cr(1.06); Mo(0.05); Ni (0.14); Co(0.016); Cu (0.09); V(0.19)	0.050	0.052	2.00
BCS 406	Mn(0.53); Ni(1.69);Mo(1.03); V(0.02); Cr(2.12); Cu^a(0.32)	1.030	1.000	-1.93
BCS 219/4	Mn(0.81); Cr(0.66); Mo(0.58); Ni(2.55); Cu^a(0.088); Sn (0.011); Fe(95.0)	0.580	0.598	+1.75
BCS 483	W(10.8); Cr(3.21); V(0.54); Mn (0.29); Mo(0.17); Co(1.94); Rest Fe.	0.170	0.178	+2.96

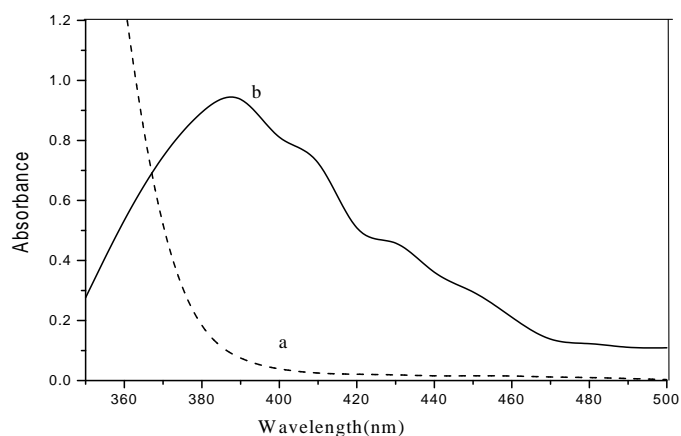* Average of five determinations.
a = masked with 1200 µg of Citrate

Fig .1
Absorption spectra of (a) 5-BrSAINH Vs Buffer blank
(b) [Mo (VI) – 5-BrSAINH] Vs reagent blank
[Mo (VI)] = 5×10^{-5} M,
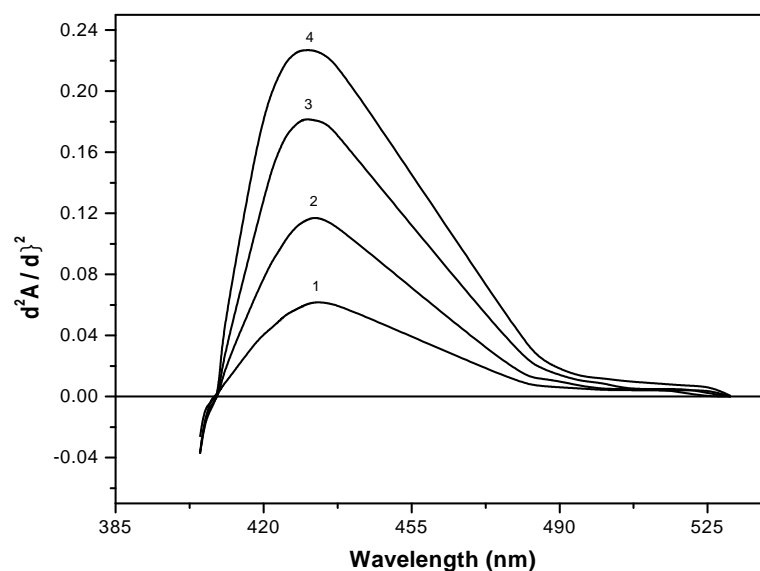[5-BrSAINH] = 5×10^{-4} M, max = 390nm

Fig. 2
Second derivative spectra of Mo(VI) – 5-BrSAINH Vs reagent blank
Mo(VI) (μg ml^{-1}) = (1) 0.4797; (2) 0.9594; (3) 0.1.4391; (4) 1.9188

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