Int. J. Chem. Sci. : 3 (1), 2005, 115–120

SPECTROPHOTOMETRIC DETERMINATION OF Mo (VI) METAL USING CALIX(4)PYROGALLOLARENE AND ITS APPLICATION

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ABSTRACT

Calix(4)pyrogallolarene was synthesized and it was characterized using elemental analysis. FTIR and NMR data. The reagent was then used for development of a new method for the extractive spectrophotometric determination of Mo (VI) metal. The reagent forms brown coloured complex with the metal, which was then extracted with n–Butanol at pH 2.0 having maxima at 580 nm. The effect of diverse anions and cations was also studied. Sandell sensitivity and Molar Absorptivity has been calculated. The developed method was employed to determine Mo (VI) metal from analytical samples.

Key words : Calix(4)pyrogallolareve, Molybdenllun (IV), Spectrophotometry

INTRODUCTION

Molybdenum plays an important role in life processes of both; plants and animals. Its function as a catalyst in living cells are not completely understood, because the quantities involved are extremely minute. They are of the order of fraction of a part per million in soil or water and approximately one part per million in living organisms. The molybdenum requirement of plant varies with species, so that deficiency exhibited is same when its concentration is as high as 0.28 mg Kg^{-1} and in other, when its concentration is as low as 0.03 mg Kg^{-1}. Animals also require low level of molybdenum in their diets for normal growth and development.

Molybdenum has recently been found in four enzymes, two of which are nitrate reductase and the molybdenum flavoenzyme, xanthenes oxidize. Molybdenum is directly involved with nitrogen fixation, as well as nitrogen assimilation and has been classified as an essential micronutrient. Large increase in crop yield have been obtained in molybdenum deficient soil by the use of molybdenum in fertilizers, foliar spray, or by application to the seeds before sowing. Literature pertaining to the spectrophotometric determination of Mo (VI) are available recently[1–4]. In the present communication, the use of Ca for the rapid, sensitive spectrophotometric determination of Mo (VI) has been reported.

EXPERIMENTAL

In the present paper, calix(4)pyrogallolarene is synthesized and used for the extractive spectrophotometric determination of Mo (VI). Recrystallized pyrogallol (50 mmol) was taken in 100 mL round bottom flask having ethanol : water : HCl (2 : 2 : 1) as a solvent system at room temperature. The homogeneous solution was then refluxed at 80°C and slow addition of 4–chlorobenzaldehyde (50 mmol) was added to the homogeneous solution. The solution was gently refluxed for 48 hr on a water bath with stirring. During the reaction, after 3 hr the solid cyclic oligomer separates out. The reaction was cooled on an ice bath and the solid was separated by filtration and the filtrate was added to ice to obtain the second fraction of the precipitate. Both the precipitates were washed with sufficient amount of water to neutralize the acidity. After the characterization studies, both the products were found to be same and were mixed. The crude product was recrystallized from ethyl acetate. The product was solid and dark pinkish brown in colour. The cyclic oligomer was characterized by FTIR, ^{1}H NMR and elemental analysis. The elemental analysis recorded was found : C, 62.88; H, 3.65; Cl, 14.05; O, 19.38% Calcd. for $C_{52}H_{36}Cl_4O_{12}$; C, 62.78; H, 3.62 Cl, 14.26; O, 19.31%. The melting point recorded was above 320°C.

The pyragallol derivative has good solubility in DMSO for NMR spectroscopy. The ^{1}H NMR displayed single singlet at δ 5.638 for methylene bridging, singlet for aromatic protons at δ 6.338 and double doublet of proton present in 4–chlorobengalolehyde at δ 6.591 and δ 6.959, for OH, three singlets at 7.654, 7.739 and 7.780 were recorded.

The presence of intramolecular hydrogen bonding[5] between the OH groups on adjacent pyrogallol rings was confirmed by IR spectroscopy. In DMSO, the hydrogen bonded ν_{OH} was at 3480 cm^{-1}. It is noted that the hydrogen bonding in the calix(n)pyrogallolarene is much weaker than that in the calix(n)arene[6] system. A band near 400 cm^{-1} is staged to be useful in differentiating cyclic tetramer[7] from cyclic hexamer and cyclic octamer. The IR data reveals the presence of a sharp band at 440 cm^{-1} confirming the formation of tetramer oligomer.

RESULTS AND DISCUSSION

The extraction experiments for Mo (VI) by calix(4)pyrogallolarene in n–butanol from aqueous media showed that kinetics of Mo (VI) transfer to the organic phase was very fast i.e.< 1.0 minute was sufficient for attainment of equilibrium.

Extraction as a function of pH

In order to obtain the optimum extraction for molybdenum, the extraction was carried out at various pH values (2.0–10.0) using various buffer solutions. The percentage extraction of Mo (VI) with calix(4)pyrogallolarene increased from 1.6 and maximum extraction was observed at 2.0 pH and further, the percentage extraction of the complex decreases.

Absorption spectrum

The absorption spectrum of Mo : Calix(4)pyrogallolarene in n–butanol shows an intense absorption peak at 580 nm and the absorbance due to the reagent is negligible at this wavelength. Hence, the absorption measurements were taken at 580 nm using a reagent blank.

Effect of solvent

The suitability of the diluents was investigated using organic solvents such as chloroform, methyl isobutyl ketone, n–butanol, carbon tetrachloride, toluene, hexane, nitrobenzene and diethyl ether. The extraction of molybdenum was quantitative with calix(4)pyrogallolarene, when both were dissolved in aqueous solution taking n–butanol as diluent. n–Butanol was used for further extraction studies as it gave better and quick phase separation.

Effect of salting out agents

The presence of 0.1 M solution of alkali and alkaline metal salts does not show any improvement over the absorbance value of Mo : Calix(4)pyrogallolarene extract. Hence, these salts have not been added in the aqueous phases before extraction for subsequent studies.

Effect of reagent concentration

The effect of variation in concentration of calix(4)pyrogallolarene shows that 1.0 mL of 0.1% methanolic solution of calix(4)pyrogallolarene is sufficient for colour development and extraction of 1.0 mL of 0.1 mg/mL of molybdenum solution.

Effect of equilibrium time

The study of change in absorbance with variation in equilibrium time for the extraction of molybdenum shows that equilibrium time of one minute is sufficient for the quantitative extraction of Mo (VI).

Stability of the complex with time

The study of stability of the colour of the extracted species with time shows that the absorbance of the extracted species is stable up to 72.0 hr. Throughout the experiment, for the reason of practical convenience, the absorbance measurements have been carried out within one hour of the extraction of molybdenum.

Calibration plot

The calibration plot of absorbance against concentration of Mo (VI) gives a linear reproducible graph in the concentration range 10–400 μg of molybdenum indicating that the Beer's law is obeyed in this range. The molar absorptivity and Sandell sensitivity were calculated to be 2.02×10^2 L mol^{-1} cm^{-1} and 0.202 μg cm^{-2} (Fig. 1)

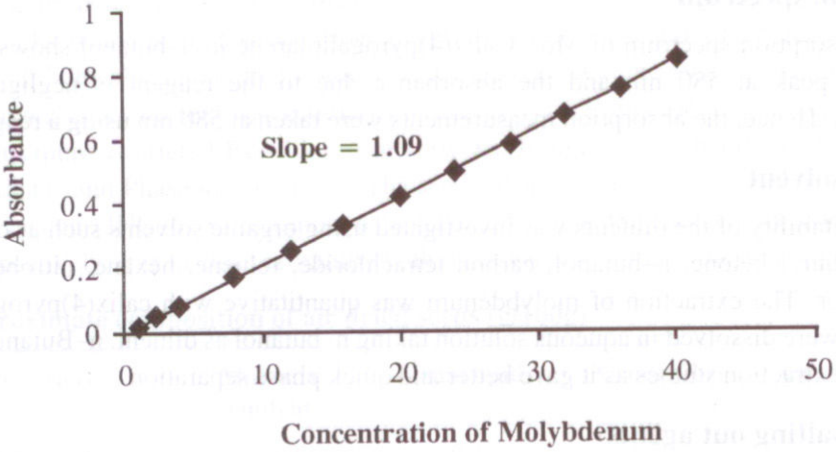

Figure 1. Calibration Plot of Mo (VI) with C(4)PA

Nature of extracted species

The composition of extracted species has been determined by Job's continuous method. Slope ratio method, and Mole ratio method indicating the composition of Mo (VI): Calix(4) pyrogallolarene complex is 1 : 1 (Fig. 2).

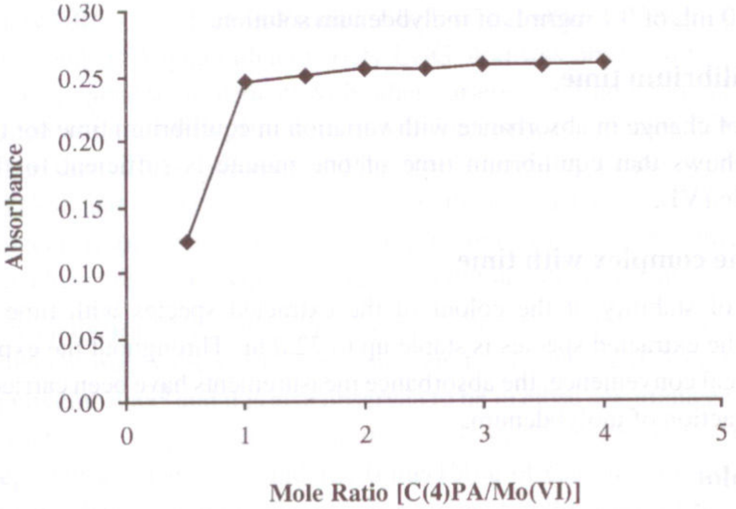

Figure 1. Mole ratio method of Mo (VI)

Effect of other ions

Varying amounts of foreign ions were added in the fixed amount (200 μg) of molybdenum to study the interference in the recommended extraction and subsequent determination procedure. The tolerance limit was set at the amount of foreign ion required to cause 2.0% error in the recommended procedure.

Precision and accuracy

The precision and accuracy of the spectrophotometric determination method have been studied by analyzing five solutions each containing 240 μg of molybdenum.

Percentage recovery

Recovery of the molybdenum from different acid media using standard catechol method containing 200 μg of molybdenum and 1.0 mL of 0.1% calix(4)pyrogallolarene solution has been studied (Table 1). The maximum recovery has obtained at 1 M HCl i.e. 98.5%.

Table 1. Percentage recovery

Total amount of molybdenum taken : 200 μg
Aqueous phase : 10.0 mL containing 1.0 mL of 0.1% C(4)PA in methanol.
Organic phase : 10.0 mL (2 x 5) of n–butanol

Stripping Agent	1 M	2 M	3 M	4 M
HCl	98.5%	72.0%	52.0%	51.5%
$HClO_4$	28.0%	24.0%	23.0%	21.0%
HNO_3	25.0%	77.0%	95.0%	25.0%
H_3PO_4	–	–	–	–
H_2SO_4	15.0%	23.0%	–	–

APPLICATION

Procedure for determination of molybdenum in analytical samples

(i) Steel samples : 25 mg of carbon steel (BCS 454/11), plain carbon steel (BCS 320) and Mn–Mo steel (BCS 214/2) obtained from Ita Labs., Mumbai, were dissolved separately in aqua–regia followed by addition of 5 mL of perchloric acid. The solutions were evaporated to dryness, leached with water and diluted with 25 mL distilled water. From the diluted solutions, an aliquot was taken for extraction and determination of molybdenum from each of the sample stock solution.

(ii) Synthetic mixtures : The separation of Mo (VI) from synthetic mixtures of associated metals containing Al (III), Zr (IV), Ce (IV) and Mg (II) with varying combinations was carried out. A definite aliquot of this solution was taken and often the adjustment of acidity of the aqueous solution was made to 0.8 N with respect to HNO_3 and addition of solution. The molybdenum complex formed was extracted in 10 mL of toluene. The amount of molybdenum present was computed from the calibration curve. The results obtained were compared with those obtained by using standard Dithol method (Table 2).

Table 2. Determination of molybdenum in analytical samples

Sample	Certified Value	Mo found* (µg)	
		Present method	Known method#
Synthetic mixtures[a]			
Al (III) [60] + Mo (VI) [30]	–	29.00	30.00
Zr (IV) [50] + Mo (VI) [20]	–	20.00	20.00
Ce (IV) [25] + Mo (VI) [50]	–	49.00	50.00
Mg (II) [30] + Mo (VI) [50]		50.00	50.00
Steel samples[b]			
Carbon steel (BCS 454/1)[a]	0.19	0.19	0.20
Plain carbon steel (BCS 320)[a]	0.22	0.22	0.22
Mn–Mo steel (BCS 214/2)[a]	0.25	0.26	0.25

*An average of three determinations; # Dithiol method; [a]value in parentheses [ ] are in µg; [b]value are in % ; @ copper masked with thiosulphate

CONCLUSION

The results obtained show that calix(4)pyrogallolarene in n–butanol can be effectively used for quantitative extraction of Mo (VI) from aqueous media. The extraction requires minimum equilibrium time i.e. one minute and the complex is stable for 72 hr. The method is sensitive, precise and reproducible. The method has a detectable range from 10–400 µg for molybdenum. The results show good agreement with the standard method.

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Accepted : 22.10.04