Determination of Molybdenum (VI) as Complex with Bromopyrogallol red in Micellar Media of Tween 80

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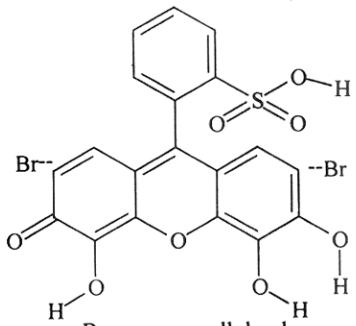
Summary: Molybdenum (VI) was determined spectrophotometrically with bromopyrogallol red as complexing reagent in aqueous phase in presence of a non-ionic surfactant Tween 80. Beer's law is obeyed, over the concentration range 0.6-1.0 μgmL^{-1} with the detection limit 0.12 $ngmL^{-1}$. The λ_{max}, molar absorption, molar absorptivity and Sandell's sensitivity were 480 nm; ε_{max} = ($\times 10^4$ $mol^{-1}cm^{-1}$) 0.6 and (15.9) $ngcm^{-2}$. Validation of this method has been made by comparing the results with those obtained by flame AAS, no significant difference was noted between the two methods at 95 % confidence interval. The method is simple, accurate and economical and has been applied for the determination of molybdenum (VI) in industrial waste water samples

Introduction

Molybdenum (VI) is a bio-essential trace element for both plants and animals [1]. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions [2,3] due to both rapidity, simplicity and wide applications. Several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surfactant [4,5]. Due to the solubility of several compounds in micelles (aggregates of surfactants), many analytical techniques for the determination of metal ions in aqueous system have been developed and modified [6-16]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the toxic organic solvents. The use of polyoxyethylene sorbitan monooleate (Tween 80) is reported for the determination of metal ions using 1-nitroso-2-naphthol as a complexing agent [17]. The determination of metal complexes of 1-(2-pyridylazo)-2-naphthol in micellar media has been reported recently [18-20]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants. The bromopyrogallol red is used as chelating agent in the determination of metal ions by spectroscopy. However bromopyro-gallol red metal complexes are water insoluble and therefore a solvent extraction with either chloroform or carbon tetrachloride is required. Xirong *et al.* [21, 22] reported a spectrophotometric determination of Mo (VI), W (V) and Sb (III) as complexes of bromo-pyrogallol red in aqueous media. Bromopyrogallol red has a hydrogen atom of hydroxyl group that is replaceable by a metal, and oxygen atom, which forms stable complexes with several metal ions.



Bromo-pyrogallol red

In the present work, a spectrophotometric determination of Mo (VI) as their bromopyrogallol red complex in micellar aqueous surfactant Tween 80 is described. The method was successfully applied for the determination of Mo (VI) in waste water samples.

Results and Discussion

Fig. 1 shows the absorption maxima (λ_{max}) spectra of (a) bromopyrogallol red at 431 nm and for (b) Mo (VI)- bromopyrogallol red complex at 480 nm. The Mo (VI)- bromopyrogallol red complex

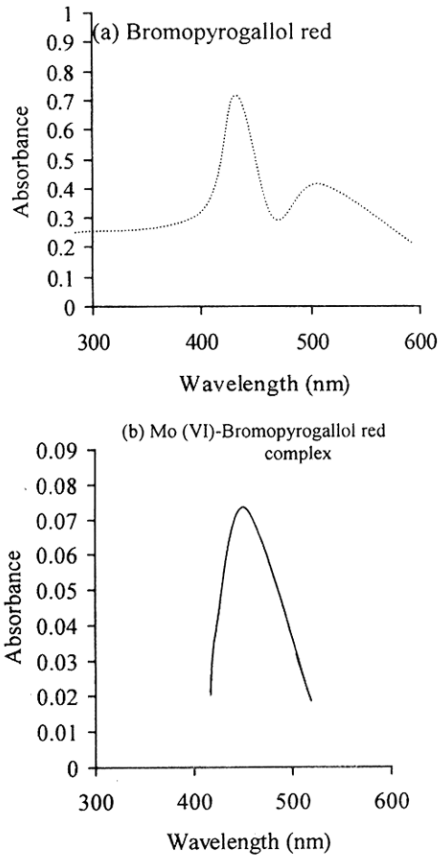


Fig. 1 Absorption spectra of (a) Bromopyrogallol red (b) Mo (VI)-bromopyrogallol red complex in 5 % Tween 80.

shows the enhancement in the absorption in the micellar method than absorption spectra in CCl_4 at 480 nm. The optimized 0.01 % reagent concentration was used throughout the complex study. It seems that micelle in solution was formed because 5 % Tween 80 solution was above (cmc) critical micellar concentration (0.0013 % w/v) [24]. 5 % Tween 80 surfactant was used throughout the metal-complex formation. The maxima absorbance was observed at optimized pH 2.0. Fig. 2 shows a calibration graph of metal complex. The Beer's law holds in the range 0.6-1.0 μgmL^{-1}. There is a slight improvement in the determining range of metal ion as compared to the method reported by Xirong Huang *et al.* [14].

Molar absorptivity is ε_{max} ($\times 10^4$ $mol^{-1}cm^{-1}$) 0.6. Where as Sandells' sensitivity calculated was 15.9 $ngcm^{-2}$. There is a slight improvement in the Sandells' sensitivity of metal ion as compared to the method reported by Xirong Huang *et al.* [14].

All other analytical parameters such as wavelength, surfactant, reagent concentration are given in Table-1.

Table-1: Analytical characteristics of Mo (VI)-bromopyrogallol red complex in the presence of surfactant Tween 80

Characteristics	Mo (VI)
Beer's law range (μgmL^{-1})	0.6 - 1
Absorption maxima (λ_{max} nm): in micellar	480
Absorption maxima (λ_{max} nm): in CCl_4	486
Molar absorptivity in micellar $\times$ (10^4 $mol^{-1}cm^{-1}$)	0.6
Sandell's sensitivity ($ngcm^{-2}$)	15.9
Detection limit ($ngmL^{-1}$)	0.12
pH	2.0
5 % Tween 80 used in mL	3.0
0.0 1% bromopyrogallol red used in mL	2 .0
RSD ±	0.02

Detection limit

Detection limit was found 0.12 $ngmL^{-1}$ using the present method. There is a slight improvement as compared to the method reported by Xirong Huang *et al.* [14].

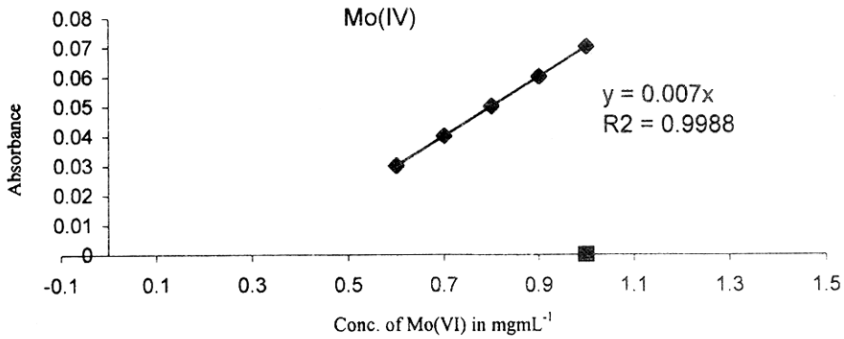


Fig. 2: Calibration graph of Mo (VI)-bromopyrogallol complex in 5 % Tween 80.

Interference

As we can see from Table-2 interferences of metal ions of Zr (IV), Sn (IV), Ti (IV), Bi (III), V (V) and Sn (III) was serious. The interference was removed using EDTA and ascorbic acid as masking agents.

Table-2: Effects of foreign ions on the determination of 5 μg of Mo (VI)

Foreign Metal ions	Tolerance limits μgmL^{-1}	Foreign non metal ions (0.01 M)	Tolerance Limits (mL)
As (III) Cr (III)	>100	Nitrite	1.0
Co (II) Ca (II) Mg (II)	>100	Silicate	1.0
Cu (11) Pb (II)	80	Phosphate	1.0
Mn (II)	60	Oxalate	0.25
Zn (II) Al (III)	40	Citrate	0.5
Sb (V) Fe (II)	20	Fluoride	>2.5
Sn (IV) Cr (VI) Fe (III)	10	Ascorbate	>2.5
Zr (IV) Sn (11) Ti (IV)	4	EDTA	>2.5
V (V)	2		
Sb (III)	1		

With a relative error being less than ± 5%

Composition

Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. From Fig. 3 it can be inferred that metal: ligand ratio is 1:2.

Validation of method

Proposed method was verified by percent recovery of known amount of metal ion by standard addition method and the results were compared with AAS, which are in good agreement as given in Table -4.

Application

The proposed spectrophotometric method was applied for the determination of Mo (VI) in industrial waste water samples. Results are shown in Table-4.

Table-3: Percent recovery of known amount of metal ion added to tap water.

Metal ions	Amount added ($\mu g\ mL^{-1}$)	Amount found ($\mu g\ mL^{-1}$)	Recovery (%)
Mo (VI)	1.0	0.99 ± 1	99 ± 1

Table- 4: Determination of Mo (VI) ions in industrial waste water samples

Sample	Amount of Mo(VI) determined (μg)		
*Industrial waste	Present method	AAS	C.V %
	0.49 ± 0.32	0.50 ± 0.22	2.57

Experimental

All chemicals used were analytical grade reagents (Merck and Fluka A.G) unless otherwise stated. Standard stock solution (100 μgmL^{-1}) of Mo (VI) was prepared using their ammonium molybdate salt. Five- percent (w/v) Tween 80 solution was prepared dissolving in a 100 mL volumetric flask, and diluting to the mark with double distilled water.

Buffer solution of pH 2 was prepared by taking 0.2 M KCl (25 mL) and 0.2 M HCl (6.5 mL) mixtures by adjusting the volume to 100 mL according to Perrin and Dempsey [23].

Apparatus

A UV / Vis Spectrometer Perkin Elmer model Lambda 2 was used throughout this study. Atomic

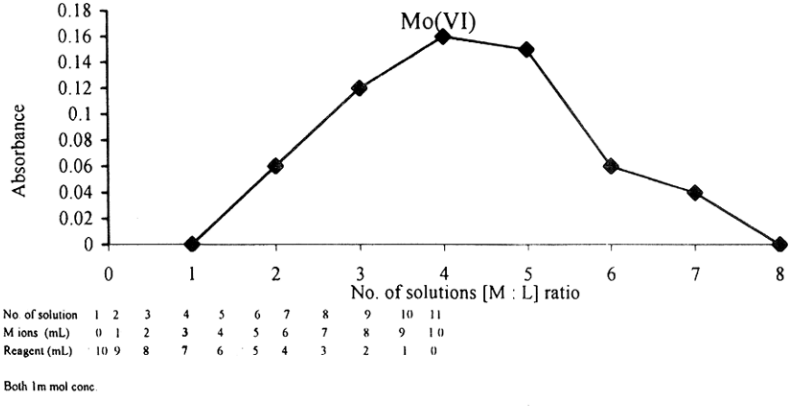


Fig. 3: Job's plot of metal : ligand ratio.

absorption spectrometer model Spectra AA. 20 Varian was used for metal ion determination. The Pye Model 292 pH meter was used.

Spectrophotometric metal ion determination in micellar solution

Appropriate volumes of stock solution of metal ion, bromopyrogallol red, surfactants 5 % Tween 80 was added to a series of 25 mL calibrated flasks and made up to volume with distilled water. The following concentration ranges of Mo (VI) ions 0.12-2 μgmL^{-1}, concentration of bromopyrogallol red 0.01 % and 5 % Tween 80 optimized values were used. The surfactant concentration, pH values and analytical wavelength used are listed in Table-1.

Spectrophotometric metal ion determination after extraction with CCl_4

Appropriate volumes of stock metal, buffers and bromopyrogallol red aqueous solutions were placed into a separating funnel and 10 mL of CCl_4 was added. The organic layer was transferred to a 25 mL volumetric flask. In order to obtain complete extraction, the process was repeated twice with 10 mL and then once with 5.0 mL of CCl_4. For the 25.0 mL total volume of the organic layer the absorbance was measured at the appropriate wavelength 486 nm for metal ion.

Determination of Mo (VI) in industrial waste samples

The industrial waste

Industrial wastewater sample, 1L obtained from industrial effluent collected from Kotri site area was filtered using Whatman filter paper. Concentrated nitric acid (4 mL) and 30 % hydrogen peroxide (2 mL) were added to the filtrate. The resulting solution was concentrated in an oven at 110°C to a final volume of 25 mL. Appropriate amounts of 5 % Tween 80 and bromopyrogallol red was added to a 25 mL calibrated flask. Then 5 mL of the sample was added and the absorbance was measured against blank reagent prepared under the same conditions. The same sample 5-mL was diluted to 25 mL with double distilled water for AAS analysis (Table-4).

Conclusions

Determination of trace amount of Mo (VI) is carried out directly using bromopyrogallol red in nonionic micellar media of Tween 80 in aqueous solution. The method is simple and rapid with greater sensitivity, better selectivity and improved precision and replaces difficult step of extraction with toxic organic solvents. Mo (VI) content in various matrixes can be determined by the present method.

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