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A highly sensitive and rapid spectrophotometric method for the determination of molybdenum at nano-trace levels in some real, environmental, biological, food and soil samples using salicylaldehyde-benzoylhydrazone

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RESEARCH ARTICLE

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ABSTRACT

A very simple, sensitive and highly selective non-extractive new spectrophotometric method has been developed for the determination of molybdenum at nano-trace levels using salicylaldehyde-benzoylhydrazone (Sal-BH). The method is based on the reaction of non-absorbent Sal-BH in a slightly acidic solution (0.0025-0.0075 M H_2SO_4) with molybdenum (VI) to give a light yellowish chelate, which has an absorption maximum at 440 nm. The reaction is instantaneous and absorbance remains stable for over 24 h. The average molar absorption coefficient and Sandell's sensitivity were found to be 4.32×10^5 L/mol.cm and 5 ng/cm^2 of molybdenum, respectively. Linear calibration graphs were obtained for 0.01-60.00 mg/L of molybdenum having detection limit of 1 µg/L and RSD 0.0-2.0 %. The stoichiometric composition of the chelate is 1:1 (Mo:Sal-BH). A large excess of over 60 cations, anions and some common complexing agents (such as chloride, azide, tartrate, EDTA, SCN^- etc.) do not interfere in the determination. The method was successfully used in the determination of molybdenum in several Certified Reference Materials (Alloys, steels, water, hair and bovine liver) as well as in some environmental waters (Potable and polluted), biological samples (Human blood, urine, nails, hair, food and vegetables), soil samples, and solutions containing both molybdenum(VI) and molybdenum(V) as well as complex synthetic mixtures. The results of the proposed method for assessing biological, food and vegetables samples were found to be in excellent agreement with those obtained by ICP-OES and AAS. The method has high precision and accuracy (s = ±0.01 for 0.5 mg/L).

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1. Introduction

Molybdenum belongs to bio-elements, whose presence is essential to normal growth and development of every living system. Its biochemical role is extremely important in the nitrogen metabolism of plants. In plants, it is necessary for the fixing of atmospheric nitrogen by bacteria at the start of protein synthesis. Because either a deficiency or an excess of molybdenum can cause damage to plants, its routine control is highly recommended for healthy growth [1]. Molybdenum is added in trace amounts to fertilizers to stimulate plant growth. Up taking of molybdenum by plants is an inert process and is proportional to the presence of easily metabolize molybdenum compounds in the soil. On the other hand, excess exposure can result in toxicity to animals and humans [2]. Molybdenum poisoning causes severe gastrointestinal irritation with diarrhea, coma ruminants and death from cardiac failure [2]. Food is a source of molybdenum to humans. The element is involved in numerous biochemical processes in our body. Its daily doses acquired by an average adult with food is from 2.7 to 3.7µg [3,4]. The tolerable concentration of molybdenum in drinking water is not specified yet, in the USA it ranges from 2 to 3 µg/L [4,5]. In natural water reservoirs, its concentration level is between several to 10 µg/L.

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. Salicylaldehyde-benzoylhydrazone (SAL-BH) has been reported as a spectrophotometric reagent for copper [6] but has not previously been used for spectrophotometric determination of molybdenum. This paper reports its use in a very sensitive, highly specific spectrophotometric method of trace determination of molybdenum. The method possesses distinct advantages over existing methods [7-37] with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH/acidity range, thermal stability, accuracy, precision and ease of operation. From above mentioned literature survey, it reveals that those methods are lengthy, time-consuming, pH dependent and in most of above mentioned methods, interference was high. It is needless to emphasize further that the direct spectrophotometric method in non-extractive way is more useful if it offers high sensitivity and selectivity.

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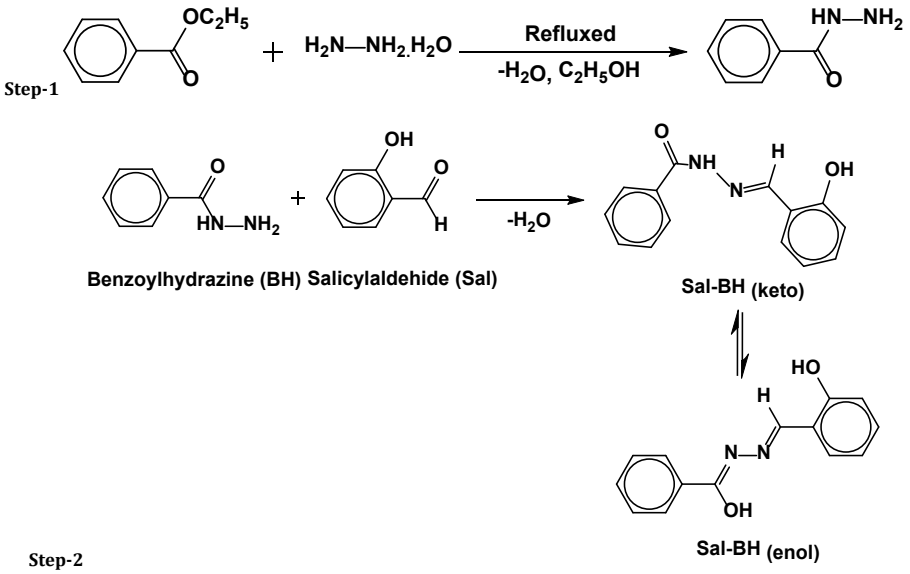

Scheme 1. Synthesis of salicylaldehyde-benzoylhydrazone (Sal-BH).

Search should be directed a new in order to develop simpler spectrophotometric method for non-extractive estimation of molybdenum in very selective and sensitive ways. The method is based on the reaction of non-absorbent Sal-BH in a slightly acidic (0.0025-0.0075 M H_2SO_4) solution with molybdenum to produce a highly absorbent pale yellowish chelate product followed by a direct measurement of the absorbance in an aqueous solution with suitable masking, the reaction can be made highly selective and the reagent blank solutions do not show any absorbance.

2. Experimental

2.1. Apparatus

A Shimadzu (Kyoto, Japan) (Model-1800) double beam UV/VIS spectrophotometer and Jenway (England, U.K.) (Model-3010) pH meter with a combination of electrodes were used for the measurements of absorbance and pH, respectively. A Shimadzu (Model: AA7000) atomic absorption spectrophotometer equipped with microcomputer controlled air-acetylene flame and A Shimadzu (Japan) (Model: 9800) Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), [λ = 418 nm, plasma gas flow rate (L/min) = 15, LOD: below 1 µg/L of Mo, RF Power (W) = 1400, Nebulizer gas flow rate (L/min) = -10] were used for comparison of the results. The elemental analyzer (Exeter Analytical Inc. Model's 440; National Center of Excellence in Analytical Chemistry, University of Sindh, Pakistan) equipped with supersensitive thermal conductivity detector for simultaneous determination of CHN was used. Infrared spectrum was recorded with FTIR Spectrophotometer, Shimadzu (Model-IR Prestige 21, Detector-DTGS KBr; Department of Chemistry, University of Chittagong) in the range 7500-350 cm^{-1}. JEOL 500SS Model (500 MHz, DMSO-d_6, TMS; Jahangirnagar University, Saver, Dhaka) four channel NMR spectrometer with signal-to-noise ratio of 5000:1 for proton were used for characterization of the ligand.

2.2. Synthesis and characterization of the reagent

2.2.1. Synthesis of the reagent

The reagent was synthesized in our laboratory according to the method of Sacconi [38] and Salam [39]. The reagent salicylaldehyde-benzoylhydrazone (Sal-BH) was synthesized by two steps (Scheme 1). First benzoylhydrazone (BH) was prepared by refluxing ethyl benzoate (700 mmol) was added to hydrazine hydrate(700mmol) in a round bottomed flask equipped with a reflux condenser. It was heated under reflux at 140 °C for about 24 hours with continuous stirring using a magnetic stirrer. Then, it was kept to stand overnight when white product separated out. The product so obtained was then filtered off, washed with ethanol and was dried first in air and then in a desiccators over silica gel. The collected crystalline product was then re-crystallized twice from the ethanol. The off-white crystalline product of benzoyl hydrazone was thus washed, dried in air and finally in a desiccators under vacuum over silica gel whose melting point 114.5 °C (Lit. 112.5 °C) [39].

Finally, salicylaldehyde-benzoylhydrazone (Sal-BH) was prepared by dissolving benzoyl hydrazone (30 mmol) in 50 mL of ethanol, and salicylaldehyde (30 mmol) was added dropwise in this solution with continuous stirring. The solution was refluxed for about one hour. Then, it was cooled, allowed to stand for crystallization when a white crystalline product is separated out. A white crystalline product was obtained which then recrystallized and filtered off, washed with ethanol and dried in desiccators over silica gel and calcium chloride. Yield of product was 80%.

2.2.2. Characterization of the reagent

The reagent was characterized by taking melting point, elemental analysis, FTIR spectrum, ^{1}H NMR spectrum and thermogravimetric analysis. The melting point of the reagent was 181 °C (Lit. 182 °C) [39] which indicated the purity of Sal-BH. The results of elemental analysis (C = 49.59, N = 8.05, H = 3.34%) of the reagent was in good coincidence with the calculated values (C = 49.77, N = 8.45, H = 4.14%) [38]. The presence of FTIR peak at 1605 cm^{-1} was due to the characteristic C=N double bond ($\nu_{C=N}$, 1590-1660 cm^{-1}) [38] of the Sal-BH. The presence of ^{1}HNMR spectrum at ^{1}H=δ 6.96, ^{2}H= δ 7.57 and ^{3}H= δ 7.96 ppm was due to the characteristics [^{1}H=6.92-7.02, ^{2}H=7.35-7.88, ^{3}H=7.52-8.52] [38]. Both FT-IR and ^{1}H NMR spectrums indicated the formation of the reagent Sal-BH. The steadiness of the thermogravimetric curve obtained for about 1 g of the reagent at 80-90 °C indicated that reagent did not contain any moisture. Both FT-IR and ^{1}H NMR spectrums and elemental analysis data indicated the formation

of the reagent. The steadiness of the thermogravimetric curve obtained for about 1 g of the reagent at 80-90 °C indicated that the reagent didn't contain any moisture.

2.3. Reagent and solutions

All of the chemicals used were of analytical reagent grade or the highest purity available. Doubly distilled deionized water, which is non-absorbent under ultraviolet radiation, was used throughout. Glass vessels were cleaned by soaking in acidified solution of $KMnO_4$ or $K_2Cr_2O_7$ followed by washing with concentrated HNO_3 and rinsed several times with deionized water. Stock solutions and environmental water samples (1000 mL each) were kept in polypropylene bottles containing 1 mL of concentrated HNO_3. More rigorous contamination control was applied when the molybdenum levels in the specimens were low.

2.3.1. Sal-BH solution (3.95×10^{-3} M)

This solution was prepared by dissolving the requisite amount of salicylaldehyde-benzoylhydrazone in a known volume solution of distilled absolute ethanol. More dilute solution of the reagent was prepared as required.

2.3.2. Molybdenum (VI) stock solutions (1.49×10^{-3} M)

A 100 mL amount of stock solution (1 mg/mL) of hexavalent molybdenum was prepared by dissolving 184.0 mg of purified-grade (E. Merck ProAnalysis grade) ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_2O$ (Super special grade J. T. Baker) in doubly distilled de-ionized water, and subsequently standardized gravimetrically by the 8-quinolinol [39]. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water as and when required.

2.3.3. Molybdenum (V) stock solutions (1.49×10^{-3} M)

A 100 mL amount of stock solution (1 mg/mL) of pentavalent molybdenum was prepared by dissolving 284.7 mg of molybdenum (V) chloride, (Aldrich A.C.S. grade) in doubly distilled de-ionized water containing 1-2 mL of nitric acid (1+1). More dilute standard solutions were prepared from this stock solution as and when required.

2.3.4. 1,10-Phenanthrolin solution

A 0.1% 1,10-phenanthrolin solution was prepared by dissolving 0.1 g amount in 100 mL slightly hot de-ionized water.

2.3.5. Potassium permanganate solution

A 1% potassium permanganate (Merck) solution was prepared by dissolving in de-ionized water. Aliquots of this solution were standardized with oxalic acid. Sodium azide solution (2.5%, *w*:*v*) (Fluka purity > 99%) was also used.

2.3.6. EDTA solution

A 100 mL stock solution of EDTA (0.01%) was prepared by dissolving 10 mg of A.C.S. grade (≥90%) ethylenediamine tetraacetic acid, disodium salt dehydrate in 100 mL deionized water.

2.3.7. Tartrate solution

A 100 mL stock solution of tartrate (0.01%) was prepared by dissolving 10 mg of A.C.S. grade (99%) potassium sodium tartrate tetra hydrate in 100 mL deionized water.

2.3.8. Dilute ammonium hydroxide solution

A 100 mL solution of dilute ammonium hydroxide was prepared by diluting 10 mL concentration. NH_4OH (28-30% A.C.S. grade) to 100 mL with deionized water. The solution was stored in a polypropylene bottle.

2.3.9. Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their AnalaR grade or equivalent grade water soluble salts (or the oxides and carbonates in hydrochloric acid); those of niobium, tantalum, titanium, zirconium and hafnium were specially prepared from their corresponding oxides (Specpure Johnson Matthey) according to the recommended procedures of Mukherji [40]. In the case of insoluble substances, special dissolution methods were adopted [41].

2.4. General procedure

A volume of 0.1-1.0 mL of neutral aqueous solution containing 0.1-600 µg of molybdenum in a 10mL volumetric flask was mixed with a 1:8 to 1:22 fold molar excess (preferably 1 mL of 3.95×10^{-3} M) of salicylaldehyde-benzoyl hydrazone (Sal-BH) reagent solution followed by the addition of 1.0-2.0 mL (preferably 1.5 mL) of 0.025 M sulfuric acid. The solution was mixed well. After 1 minute, 2 mL of ethanol was added. The mixture was diluted up to the mark with de-ionized water. The absorbance was measured at 440 nm against a corresponding reagent blank. The molybdenum content in an unknown sample was determined using a concurrently prepared calibration graph.

2.5. Sample collection and preservation

Water: Water samples were collected in polythene bottles from shallow tube-wells, tap-wells, river, sea and drain of different places of Chottrogram region, Bangladesh. After collection, HNO_3 (1 mL/L) was added as preservative.

Blood and Urine: Blood and urine samples were collected in polypropylene bottles from effected persons of Treatment Centre and Chittagong Medical College and Hospital, Bangladesh. Immediately after collection they were stored in a salt-ice mixture and later, at the laboratory, were kept at -20 °C.

Soil: Soil (surface) samples were collected from different locations in Chottrogram region, Bangladesh. Samples were dried in air and homogenized with a mortar.

3. Results and discussion

3.1. Factors affecting the absorbance

3.1.1. Absorption spectra

The absorption spectra of a molybdenum-Sal-BH system in aqueous medium in presence of 1 mL 0.025 M sulfuric acid solution, was recorded using the spectrophotometer. The absorption spectrum of the molybdenum-Sal-BH is an asymmetric curve with maximum absorbance at 440 nm and an average molar absorptivity of 4.32×10^5 L/mol.cm (Figure 1). The reagent blank exhibited negligible absorbance despite having wavelength at 440 nm.

3.1.2. Optimization of some parameters on the absorbance

3.1.2.1. Effect of solvent

As Sal-BH is partially soluble in water, an organic solvent was used for the system, consideration of cost, availability,

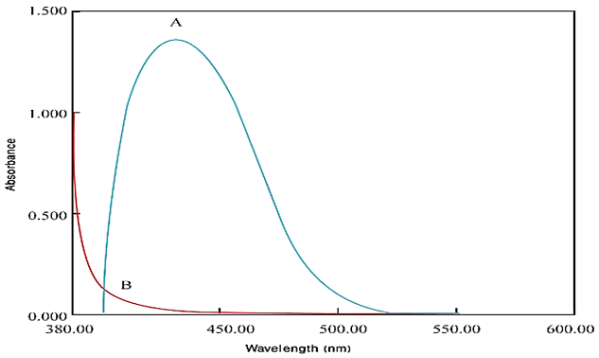

Figure 1. (A) Absorbance spectra of molybdenum^{VI}-Sal-BH (λ_{max} = 440 nm) and (B) the reagent blank in aqueous solution.

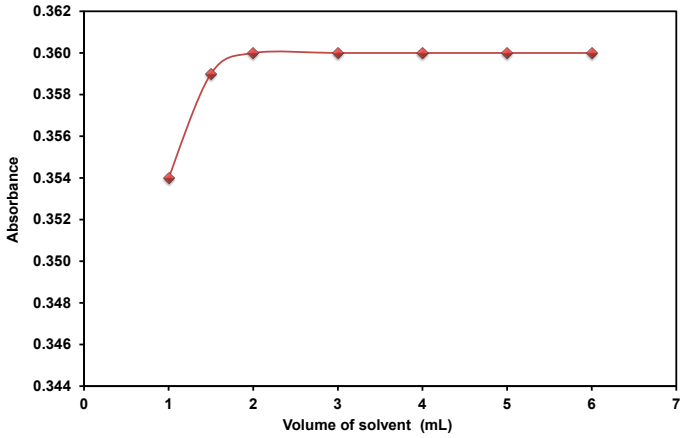

Figure 2. Effect of solvent (ethanol) on the absorbance of Mo^{VI}-Sal-BH system.

toxicity and volatility of the solvent etc. Of the various solvents (Acetone, benzene, carbon tetrachloride, chloroform, ethanol, 1-butanol, isobutyl methyl ketone, dimethyl formamide, methanol and 1,4-dioxane) studied, ethanol was found to be the best solvent for the system. Different volumes (0-6 mL) of ethanol were added to fixed metal ion concentration and the absorbance were measured according to the general procedure. Maximum absorbance was observed in 30±2% (*v*:*v*) ethanol:water medium, hence, a 30% ethanol solution was used in the determination procedure. It was observed that 20-60% (2-6 mL) ethanol produced a constant absorbance of the Mo-chelate (Figure 2). For all subsequent measurements, 30% (3 mL) of ethanol was added.

3.1.2.2. Effect of acidity

Among the various acids (nitric, sulfuric, hydrochloric and phosphoric) studied, sulfuric acid was found to be the best acid for the system. The variation of the absorbance was noted after the addition of 0.05-3.0 mL of 0.025 M sulfuric acid to every 10 mL of test solution. The maximum and constant absorbance was obtained in the presence of 1.0-3.0 mL of 0.025 M sulfuric acid at room temperature 25±5 °C. Outside this range of acidity, the absorbance decreased (Figure 3). For all subsequent measurements 1.5 mL of 0.025 M sulfuric acid was added.

3.1.2.3. Effect of time

The reaction is very fast. A constant maximum absorbance was obtained just after dilution within few seconds to volume and remained strictly constant for over 24 h (Figure 4); a longer period of time was not studied.

3.1.2.4. Effect of temperature

The Mo-Sal-BH system attained maximum and constant absorbance at room temperature (25±5 °C). Outside this range of temperature, the absorbance decreased.

3.1.2.5. Effect of reagent concentration

Different molar excesses of Sal-BH were added to a fixed metal ion concentration and the absorbance was measured according to the general procedure. It was observed that molybdenum metal, the reagent molar ratio of 1:8 to 1:22 produced a constant and maximum absorbance of Mo-chelate. Outside this range of reagent, the absorbance decreased (Figure 5). For different (0.5 and 1.0 mg/L) molybdenum concentrations an identical effect of varying the reagent concentration was noticed. For all subsequent measurements, 1 mL of 3.95×10^{-3} M Sal-BH reagent was added.

3.2. Calibration graph (Beer's law and sensitivity)

The well-known equation for a spectrophotometric analysis in a very dilute solution was derived from Beer's law. The effect of the metal concentration was studied over 0.01-100 mg/L distributed in four different sets (0.01-0.1, 0.1-1.0, 1.0-10 and 10.0-100.0 mg/L) for convenience of the measurement. The absorbance was linear for 0.01-60.00 mg/L at 440 nm for representing four graphs (0.01-0.10, 0.1-1.0, 1-10 and 10-100 mg/L) as shown in Figures 6-9, respectively. Of the four calibration graphs, one showing the limit of the linearity is given in Figure 9. The Figures 6-8 were straight-line graphs passing through the origin (r^2 = 0.9998).

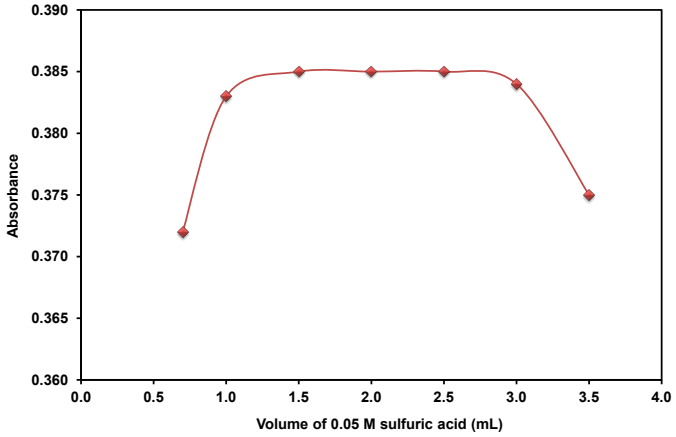

Figure 3. Effect of acidity on the absorbance of Mo^{VI}-Sal-BH system.

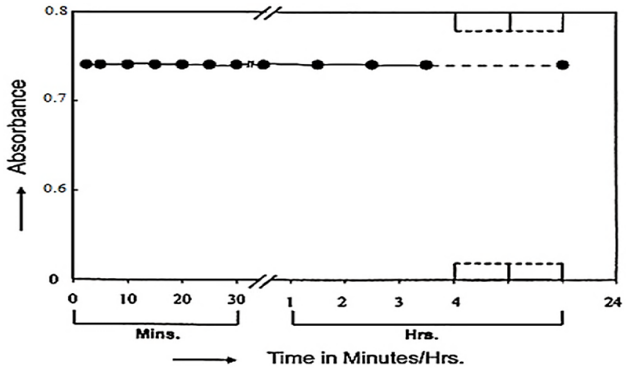

Figure 4. Effect of time on the absorbance of Mo-Sal-BH system.

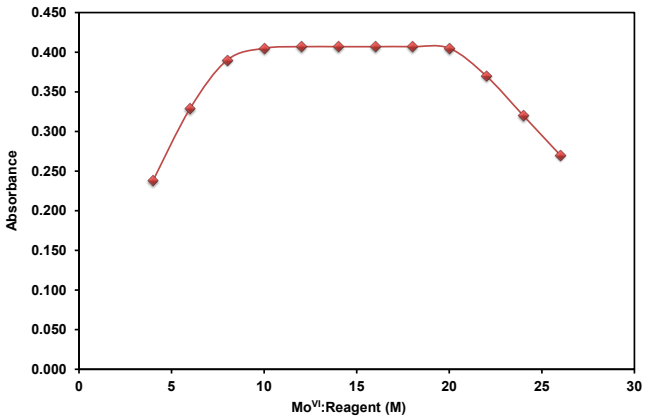

Figure 5. Effect of reagent Mo^{VI}:Sal-BH molar concentration ratio on the absorbance of Mo^{VI}-Sal-BH system.

The molar absorption co-efficient and the Sandell's sensitivity [42] were found to be 4.32×10^5 L/mol.cm and 5 ng/cm^2 of molybdenum, respectively. The selected analytical parameters obtained with the optimization experiments are summarized in Table 1.

3.3. Effect of foreign ions

The effect of over 60 anions, cations and complexing agents on the determination of only 1 mg/L of molybdenum was studied. The criterion for interference [43] was an absorbance value varying by more than 5% from the expected value for molybdenum alone. The results are summarized in Table 2. As can be seen, a large number of ions have no significant effect on the determination of molybdenum. The interference were from Cr(VI), Fe(III)and V(V) ions. Interference from these ions is probably due to complex formation with Sal-BH. The greater tolerance limits for these ions can be achieved by using several masking methods. In order to eliminate interference of Cr(VI), Fe(III) and V(V), EDTA, 1,10-phenonthroline and tartrate used as masking agents, respectively. During the interference studies, if a precipitate was formed, it was removed by centrifugation. The amount mentioned is not the tolerance limit but the actual amount studied. However, for those ions whose tolerance limit has been studied, their tolerance ratios are mentioned in Table 2.

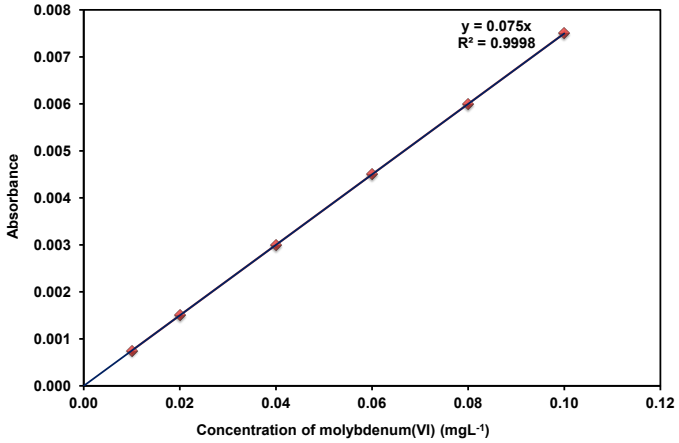

Figure 6. Calibration graph of A: 0.01-0.10 mg/L of molybdenum (VI).

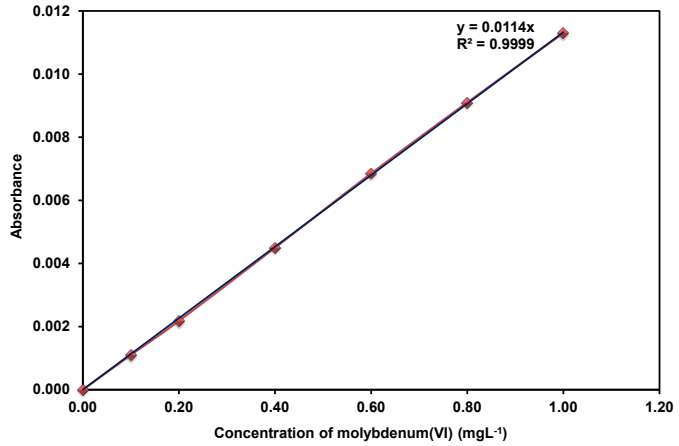

Figure 7. Calibration graph of B: 0.1-1.0 mg/L of molybdenum (VI).

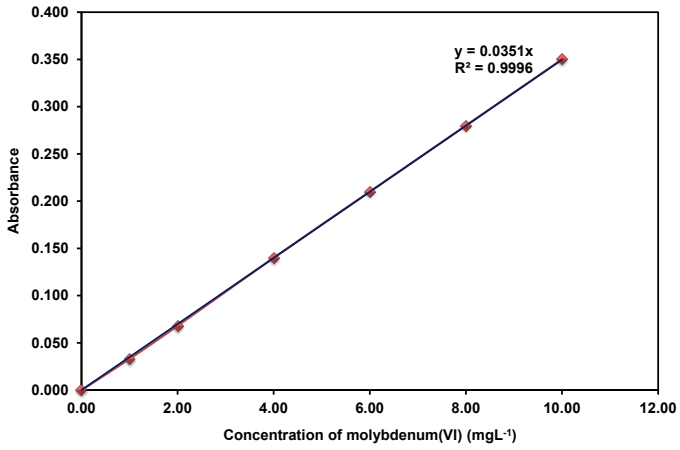

Figure 8. Calibration graph of C: 1-10 mg/L of molybdenum (VI).

3.4. Composition of the absorbent complex

Job's method [44] of continuous variation method was applied to ascertain the stoichiometric composition of the complex under the optimum conditions (Table 1). A Mo-Sal-BH (1:1) complex was indicated by this method. The molar-ratio method [45] was also applied to ascertain the stoichiometric composition of the complex. A Mo-Sal-BH complex was indicated by both methods and the stoichiometry was also found to be 1:1 (Metal: Ligand).Job's method of continuous variation was applied to ascertain the stoichiometric composition of the complex according to the general procedure. Experimental data has been shown graphically in Figure 10 and the stoichiometry was found to be 1:1 (Metal: Ligand).

3.5. Precision and accuracy

The precision of the present method was evaluated by determining different concentrations of molybdenum (each

Table 1. Summary of selected analytical parameters obtained with optimization experiments.

Parameters	Studied range	Selected value
Wavelength, λ_{max} (nm)	200-800	440
Solvent (mL)	0-8	2.5-6 Preferably (25-60%)
Acidity, (M) H_2SO_4	0.000125-0.00105	0.0025-0.0075 (Preferably 0.00395)
pH	5.0-2.5	3.90-3.05 (Preferably 3.4)
Time (h)	0-72	1min - 24 h (Preferably 5 min)
Temperature (°C)	10-90	20-70 (Preferably 25±5)
Reagent (fold molar excess, M:R)	1:1-1:50	1:8-1:22 (preferably 1:10)
Linear range ($mg.L^{-1}$)	0.001-100	0.01-60
Molar absorptivity ($L.mol^{-1}cm^{-1}$)	4.06×10^5-4.23×10^5	4.32×10^5
Limit of quantization ($mg.L^{-1}$)	0.1-10	10
Detection limit ($mg.L^{-1}$)	0-100	1.00
Sandell's sensitivity ($ng.cm^{-2}$)	0-100	5
Reproducibility (% RSD)	0- 5	0-2

Table 2. Tolerance limits of foreign ions [a], tolerance ratio [Species(x)/Mo^{VI}(w/w)].

Species x	Tolerance ratio x/Mo (w/w)	Species x	Tolerance ratio x/Mo (w/w)
Aluminum	100	Lead(II)	50[e]
Arsenic(III)	50	Magnesium	100
Arsenic(V)	100	Molybdenum(V)	50[b]
Antimony	100	Mercury(II)	100
Azide	100	Manganese(II)	100
Bismuth(III)	100	Manganese (VII)	100
Bromide	100	Nickel(II)	80
Barium	100	Nitrate	100
Beryllium	100	Oxalate	100
Cadmium	100	Phosphorous	100
Cobalt(II)	100	Phosphate	100
Cobalt(III)	100	Potassium	100
Calcium	100	Selenium(IV)	50
Chloride	100	Selenium(VI)	50
Citrate	100	Strontium	80
Chromium(VI)	20[b]	Sulphate	100
Chromium(III)	80	Sodium	100
Cesium	100	Tartrate	1000
Copper(II)	20[b]	Tin(II)	100
Cerium(III)	100	Tin(IV)	100
EDTA	1000	Titanium(IV)	100
Fluoride	100	Tellurium(IV)	50
Iron(II)	100	Thiocyanate	100
Iron(III)	20[c]	Tungsten(VI)	50
Iodide	100	Vanadium(V)	10[d]
Lithium	80	Uranium(VI)	100
Lead(II)	100	Zinc	100

[a] Tolerance limit was defined as ratio that causes less than ±5 percent interference.
[b] With10 mg/L EDTA.
[c] With 10 mg/L 1,10-phenonthroline.
[d] With 10 mg/L tartrate.

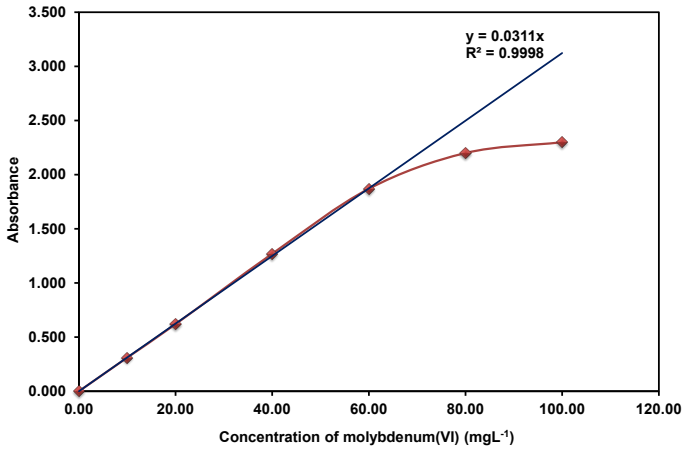

Figure 9. Calibration graph of D: 10-60 mg/L of molybdenum (VI).

analyzed at least five times). The relative standard deviation (n = 5) was 0-2.0 % for 0.1-600 µg of molybdenum in 10 mL, indicating that this method is highly precise and reproducible.

The detection limit (3s of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for molybdenum were found to be 1.0 µg/L and 5 ng/cm^2, respectively. The method was also tested by analyzing several synthetic mixtures containing molybdenum and diverse ions (Table 3). The results for total molybdenum were in good agreement with certified values (Table 4). The reliability of our Mo-chelate procedure was tested by recovery studies. The average percentage recovery obtained for addition of molybdenum spike to some environmental water samples was quantitative as shown in Table 5.

Table 3. Determination of molybdenum in some synthetic mixtures.

Sample	Composition of mixtures (mg/L)	Molybdenum (mg/L)		
		Added	Found (n = 5) [a]	Recovery±SD (%) [b]
A	Mo^{VI}	0.5	0.49	98±0.5
		1.00	1.00	100±0.00
B	As in A +Sn^{2+} + Se^{VI}+ Ag+ Sb^{3+}	0.5	0.50	102±1.0
		1.00	1.02	102±0.6
C	As in B + Cr^{VI} + Cr^{3+}+ Mn^{VII}+ Ce^{3+} + Cu^{2+} +EDTA(50)	0.5	0.49	98±0.8
		1.00	0.99	99±0.5
D	As in C+ Al + V(V) + Hg^{2+} + Fe^{2+} +EDTA(50)	0.5	0.52	104±1.2
		1.00	1.03	103±1.3
E	As in D + Cu^{2+} +Ni^{2}+ W^{VI} Na^{+}+EDTA(50)	0.5	0.53	106±1.5
		1.00	1.05	105±1.3
F	As in E + Zn^{2+} + Se^{IV} +Mg + Cd	0.5	0.54	108±1.8
		1.00	1.08	108±1.6

[a] Average of five analysis of each sample.
[b] The measure of precision is the Standard Deviation (SD).

Table 4. Determination of molybdenum in some certified reference materials.

Sample No	Certified reference materials composition (%)	Molybdenum (%)		
		In C.R.M sample	Found (n=5) [a]	RSD (%) [b]
1	BCS-CRM 200/2: High-speed tool steel(Mo, W, Mn, C ,Si, S, O, V, Cr, and Ni)	4.92	4.92±0.05	1.5
2	BAS-CRM 64b: High-speed steels (Cr, Mo, V, and Tc)	4.95	4.93±0.03	1.6
3	BAS-10 gi High Speed brass (Cu, Fe, Pb, Ni, Sn, Al, Mo, Zn, and Mn)	0.15	0.17±0.10	2.5
4	GSBH 40101- 96 : Cr_{12}MoV-Dies steel (Cr, Ni, Mo, V, Cu, Co)	1.00	0.98±0.08	1.9
5	YSBC 1013-1-95 ; Cr_{17}MoVCo : High tensile steels (C, Cr, Mo, V, Si, Mn and Co)	0.52	0.50±0.15	2.0
6	NASS-1: Sea Water [c]	11.5[d]±1.9	11.7[b]±1.0	1.5
7	SWRS-1: River Water [c]	0.78[d]±0.04	0.82[b]±0.08	1.8
8	NIST®SRM®1577c : Bovine liver [c]	3.3[e]	3.2[c]± 0.5	1.5
9	ERM-BB001(EVISA) : Human hair [c]	3.24[e]±0.24	3.21[c]±0.5	1.8

[a] Average of five analysis of each samples.
[b] The measure of precision is the relative standard deviation (RSD).
[c] These CRMs were from the National Research Council of Canada.
[d] Values in µg/L.
[e] Values mg/kg.

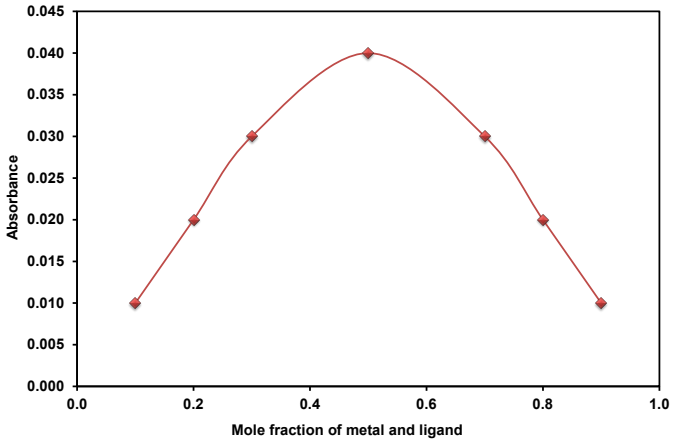

Figure 10. Job's method for determining the composition of Mo: Sal-BH(1:1)complex.

The results of biological analyses by the spectrophotometric method were in excellent agreement with those obtained by ICP-OES (Table 6). Hence, the precision and accuracy of the method were excellent. With suitable masking, the reaction can be made highly selective.

4. Applications

The proposed method was successfully applied to the determination of molybdenum in a series of synthetic mixtures of various compositions (Table 3) and also in a number of real samples e.g. several Certified Reference Materials (CRMs) (Table 4). The method was also extended to the determination of molybdenum in a number of environmental, biological, food and soil samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each such sample were analyzed for molybdenum content; the recoveries in both the "spiked" (added to the samples before the mineralization or dissolution) and the "unspiked" samples are in good agreement (Table 5). The results of biological analyses by spectrophotometric method were found to be in excellent agreement with those obtained by ICE-OES (Table 6). The results of soil samples analyses by the spectrophotometric method were found to be excellent agreement with those of obtained by AAS (Table 7). The results of some vegetable and food samples by the spectrophotometric method were found to be excellent agreement with those obtained by ICP-OES (Table 8). The precision and accuracy of the method were excellent.

4.1. Determination of molybdenum in some synthetic mixtures

Several synthetic mixtures of varying compositions containing molybdenum and diverse ions of known concentrations were determined by the present method using tartrate or EDTA as masking agent and the results were found to be highly reproducible.

Table 5. Determination of molybdenum in some environmental water samples.

Sample		Molybdenum (µg/L)		Recovery±s (%)	s_r (%) [b]
		Added	Found [a]		
Tap water		0	7.5	-	-
(Chattogram city)		100	105.0	98±0.5	0.21
		500	500.0	100±0.0	0.00
Rain water		0	4.5	-	-
(Chattogram city)		100	103.5	99±0.6	0.10
		500	504.0	99.9±0.1	0.35
Well water		0	8.5	-	-
(Chattogram city)		100	108.0	99.5±0.8	0.23
		500	507.5	99.8±1.0	0.18
	Karnaphully	0	15.0	-	-
	(Upper)	100	108.0	100.8±0.5	0.17
River water		500	507.5	100.4±0.6	0.31
	Karnaphully	0	17.0	-	-
	(Lower)	100	118.0	99.1±0.8	0.16
		500	517.0	100.0±0.00	0.00
	Bay of Bengal	0	10.0	-	-
	(Upper)	100	110.0	100.0±0.00	0.00
		500	512.5	99.5±0.6	0.10
Sea water	Bay of Bangle	0	12.5	-	-
	(Lower)	100	113.0	99.5±1.0	0.18
		500	515.5	99.5±1.1	0.26
	T.S.P complex [c]	0	130.0	-	-
		100	238.0	96.63±1.2	0.52
		500	636.0	99.00±0.8	0.36
	BSRM [d]	0	175.0	-	-
Drain water		100	275.0	100.0±0.0	0.00
		500	680.0	99.2±0.5	0.45
	Berger paint [e]	0	95.0	-	-
		100	198.0	98.4±1.0	0.29
		500	599.0	99.33±1.5	0.37

[a] Average of five replicate determinations of each sample.
[b] The measure of precision is the relative standard deviation.
[c] Triple Super PhosphateComplex Ltd., Patenga, Chattogram.
[d] Bangladesh steels Re-rolling Mills, Nasirabad, Chattogram.
[e] Berger Paints Bangladesh Ltd., Kalurghat, Chattogram.

Table 6. Determination of molybdenum in some human fluids, hair and nail samples.

Sample no	Sample source[a]	Sample	Molybdenum (µg/L)			
			ICP-OES (n = 5)		Proposed method (n = 5)	
			Found	RSD (%) [b]	Found	RSD (%) [b]
1	Normal adult (Male) (Nonsmoker)	Blood	12.00	1.5	11.5	1.3
		Urine	3.50	1.0	3.25	1.0
2	Cardiovascular patient (Male)	Blood	110.5	1.6	112.6	1.8
		Urine	28.8	1.3	29.9	1.5
3	Liver cirrhosis patient (Female)	Blood	90.5	1.5	91.8	1.7
		Urine	23.6	1.2	24.5	1.3
4	Gastrointestinal disturbance (Male)	Blood	165.8	1.8	168.0	2.0
		Urine	42.5	1.5	43.5	1.5
5	Hypertension patient (Female)	Blood	75.0	1.6	78.5	1.2
		Urine	20.0	1.3	20.5	1.0
6	Lactating mother	Human milk	8.0	1.5	7.9	1.8
7	Normal (Man)	Human hair	0.25 [c]	1.5	0.28	1.0
8	Normal (Man)	Human nail	1.9 [c]	1.8	1.8	1.5

[a] Samples were collected from Chittagong Medical College and Hospitals.
[b] The measure of precision is the relative standard deviation (RSD).
[c] Values in mg/g.

Table 7. Determination of molybdenum level in some surface soil samples.

No	Sample source	Molybdenum (mg/kg) (n=5)			
		AAS (n=5)		Proposed method (n=5)	
		Found [a]	RSD [b]	Found	RSD [b]
1	Agricultural soil (Chittagong University)	1.70	1.0	1.72	1.0
2	Glass industrial soil (PHP glass)	1.96	1.4	1.98	1.5
3	Steel industrial soil (Bangladesh Steel Re-rolling Mills Ltd., Chottrogram, Bangladesh)	2.33	2.5	2.31	2.1
4	Paint industrial soil (Berger paint)	2.38	2.5	2.35	2.0
5	Paint industrial soil (Elite paints)	2.28	2.2	2.25	1.8
6	Industrial soil (Eastern Cables Ltd)	1.98	2.0	1.96	1.9
7	Fertilizer industrial soil (Triple Super PhosphateComplex Ltd. Chottrogram)	2.08	1.5	2.05	1.6
8	Marine soil (sediments)	1.18	1.0	1.15	0.8
9	Traffic soil (Kadamtoli Bus Terminal Chottrogram)	1.36	1.6	1.35	1.5
10	Pharmaceutical soil (Glaxo Smith Kline)	1.85	2.0	1.88	1.8

[a] Average of five replicate analysis of each sample.
[b] The measure of precision is the relative standard deviation(RSD).
[c] Composition of the soil samples: C, N, P, K, Na, Ca, Mg, Fe, Pb, Cu, Zn, Mn, Mo, Co, NO_3, NO_2 and SO_4, etc.

Table 8. Determination of molybdenum in some food, fruits and vegetable samples.

Serial no	Sample	Molybdenum (µg/kg) Found [a] ± S (n=5)				Sample source
		ICP-OES (n=5)		Proposed method (n=5)		
		Found	RSD [b]	Found	RSD [b]	
1	Carrot *(Daucuscarota)*	65.5	1.0	68.8	1.1	Local Market, Chottrogram
2	Rice *(Oryza sativa)*	400.0	1.5	405.0	1.5	Local Market, Chottrogram
3	Wheat *(Trictiumaestivum)*	377.5	1.8	378.0	1.9	Local Market, Chottrogram
4	Corn *(Zea mays)*	147.0	1.5	150.0	1.6	Local Market, Chottrogram
5	Mango *(Mangiferaindica)*	175.0	1.8	180.0	2.0	Local Market, Chottrogram
6	Arum *(Arum discorides)*	260.0	1.6	265.0	2.1	Local Market, Chottrogram
7	Radish *(Raphanussativas)*	40.0	1.2	43.5	1.3	Local Market, Chottrogram
8	Potato (*Solanum tuberosum)*	125.0	1.6	130.0	1.5	Local Market, Chottrogram

[a] Average of five replicate analyses of each sample.
[b] The measure of precision is the relative standard deviation (RSD).
[c] Values in µg/L.

The results are shown in Table 3. Accurate recoveries were achieved in all solutions in the range 98±0.5 to 100±0.01%. The reliability of our molybdenum-Sal-BH procedure was approved by quantitative recovery of molybdenum(VI) spiked in several synthetic mixture containing molybdenum(VI) and diverse ions. The method has high precision and accuracy (s = ±0.01 for 0.5 µg/L).

4.2. Determination of molybdenum in some certified reference materials

Certified Reference Materials: alloys, brass and some CRMs were analyzed to evaluate the validation of the method. A 0.1 g amount of an alloy or steel or brass containing 0.15-4.95% of molybdenum was accurately weighed and placed in a 50 mL Erlenmeyer flask following a method recommended by Parker [46]. To it, 10 mL of concentrated HNO_3 and 2 mL of concentrated H_2SO_4 were carefully added. The solution was heated and simmered gently after the addition of another 10mL of concentrated HNO_3 until all carbides were decomposed. Then a further 2 mL of 1+1 H_2SO_4 and 2 mL 2% (*w*:*v*) freshly prepared ammonium persulfate were added. The solution was carefully evaporated to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature (25±5 °C). After suitable dilution with deionized water, the contents of the Erlenmeyer flask were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute NH_4OH solution in the presence of 1-2 mL of 0.01% (*w*:*v*) tartrate solution. The resulting solution filtered, if necessary, through Whatman no. 40 filter paper into a 100mL calibrated flask. The residue (silica and tungstic acid) was washed with a small volume of hot (1+99) H_2SO_4, followed by water; the volume was made up to the mark with deionized water.

A suitable aliquot (1-2 mL) of the above-mentioned solution was taken into a 10mL calibrated flask and the molybdenum(VI) content was determined; as described under general procedure using EDTA or tartrate as masking agent. The proposed procedure for spectrophotometric determination of molybdenum was applied to the analysis of sea water (NASS-1), river water (SWRS-1), bovine liver (NIST-SRM-1577c), and human hair (ERM-BB001(EVISA), CRMs obtained from the National Research Council, Government of Canada using tartrate or EDTA as a masking agent, following a method recommended by Sun *et al.* [47]. Based on five replicate analyses, the average molybdenum concentrations determined by spectrophotometric method were found to be in good agreement with the certified values. The results are shown in Table 4.

4.3. Determination of molybdenum in some environmental water samples

Each filtered (with Whatman No. 40) environmental water sample (1000 mL) was evaporated nearly to dryness with a mixture of 2 mL concentrated H_2SO_4 and 10 mL of concentrated HNO_3 in presence freshly prepared 2 mL of 2% (*w*:*v*) persulfate in a fume cupboard, to oxidize molybdenum(V) to molybdenum(VI) following a method recommended by Greenberg *et al.* [48] and was cooled to room temperature. The residue was heated with 10mL of deionized water in order to dissolves the salts. The solution was then cooled and neutralized with dilute NH_4OH solution in the presence of a 1-2 mL of 0.01 % (*w*:*v*) tartrate or EDTA solution. The resulting solution was then filtered (if necessary) and quantitatively transferred into a 25 mL calibrated flask and made up to the mark with deionized water.

An aliquot (1-2 mL) of this pre-concentrated water sample was pipette into a 10 mL calibrated flask and the molybdenum content was determined as described under the Procedure, using tartrate or EDTA as a masking agent. To test the validity of our method, we have analyzed different types of portable and polluted water samples in spiked and un-spiked condition. The reliability of our molybdenum-chelate procedure was tested by recovery studies. The average percentage obtained for the addition of molybdenum(VI) spiked to same environment water samples was quantitative. The analyses water samples formolybdenum from various sources are shown in Table 5. Most spectrophotometric methods for the determination of molybdenum in natural and sea-water require preconcentration of molybdenum [46]. The concentration of molybdenum in natural and sea-water is a few µg/Lin Taiwan [49]. The mean concentration of molybdenum found in US drinking waters is <10 µg/L [48].

4.4. Determination of molybdenum in some biological samples

Human blood (2-5 mL) or Urine (10-20 mL) or milk (5-10 mL) samples were taken in a 100 mL micro-Kjeldal flask. The biological samples were digested accordingly following a particular method [47] was initially dried in an oven at 120 °C for 24 h. Blood serum samples were further dried in an oven at 200 °C for an additional 24 h. Then, the biological samples were dry-ashed in a muffle furnace at 300 °C for 24 h, then at 450 °C for 4 h. After dry-ashing, samples were wet-ashed with 5mL concentrated nitric acid and 2mL of 30% hydrogen peroxide. The mixture was heated to just below boiling until complete oxidation of molybdenum(V) to molybdenum(VI). The samples were cooled and wet-ashed three more times in the same manner. At completion, the white residue was dissolved with 10 mL of 1 M HNO_3 by heating of an excess Human hair or nail (1-2 g) was digested in presence of an excess oxidizing agent according to the method recommended by Stahr [50]and diluted to 20.0mL for analysis. After neutralizing pH by addition of dilute NH_4OH in the presence of 1-2 mL of a 0.01 % (*w*:*v*) tartrate or EDTA solution. The resultant solution was then filtered and transferred quantitatively into a 25 mL calibrated flask and made up to the mark with de-ionized water.

A suitable aliquot (1-2 mL) of the final solution was pipette into a 10 mL calibrated flask and the molybdenum content was

determined as described under the procedure using tartrate or EDTA as masking agent. The results of biological analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by ICP-OES. The results are shown in Table 6.

The abnormally high value for the gastrointestinal disturbance and cardiovascular patient are probably due to the involvement of high molybdenum concentrations with As and Zn. The occurrence of such high molybdenum contents is also reported in gastrointestinal disturbance and cardio-vascular patients from some developed countries [48].

4.5. Determination of molybdenum in some surface soil samples

An air dried homogenized soil sample (100 g) was weighed accurately and placed in a 100 mL micro-Kjeldahl flask. The sample was digested in presence of oxidizing agent (2 mL of 2% freshly prepared ammonium persulfate solution) following the method recommended by Hesse [51]. The solution was then neutralized with dilute NH_4OH in the presence of a 1-2 mL of 0.01% (*w*:*v*) EDTA or tartrate solution. The resulting solution was then filtrated and quantitatively transferred to a 25 mL calibrated flask and madeto the mark with de-ionized water.

Suitable aliquots (1-2 mL) were transferred into a 10mL calibrated flask and a calculated amount of 0.025 M H_2SO_4 needed to give a final acidity of 0.0025-0.0075 M H_2SO_4 was added followed by 1 mL of 0.01% (*w*:*v*) EDTA or Chloride solution as masking agent. The molybdenum content was then determined by the above procedure and quantified from a calibration graph prepared concurrently. The results of soil analyses by spectrophotometric method were found to be excellent agreement with those obtained by AAS. The results are shown in Table 7. The average value of molybdenum in Bangladesh surface soil analysis was found to be 1.9 mg/kg.

4.6. Determination of molybdenum in some vegetable and food samples

The vegetable and food samples collected prior to the determination were pretreated in the following way. Edible portion of samples was first washed clean with tap water followed by rewashing with de-ionized water. After removing de-ionized water from the surface of vegetables and fruits, the samples were cut into small pieces and dried at 65 °C in oven. An air dried vegetables and fruits samples (10 g) were taken in a 100 mL micro-Kjeldahl flask in presence of oxidizing agent (2 mL of 2% freshly prepared ammonium persulfate solution) and digested following a method recommended by Stahr [50]. A glass bead and 10mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was revved and cooled at room temperature. 1 mL volume of concentrated sulfuric acid was added carefully, followed by the addition of 2 mL of concentrated HF, and heating was continued for at least ½ h and then cooled. The solution of flask then neutralized with dilute NH_4OH in the presence of 1-2 mL of a 0.01 % (*w*:*v*) tartrate or EDTA solution. The resultant solution was then filtered and transferred quantitatively into a 25 mL calibrated flask and made up to the mark with de-ionized water.

A suitable aliquot (1-2 mL) of the final solution was pipette into a 10 mL calibrated flask and the molybdenum content was determined as described under the procedure using tartrate as masking agent. Highly values of molybdenum for rice are probably due to the involvement of high molybdenum concentration in soil [52]. The results of vegetable and food analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by ICP-OES. The results are shown in Table 8.

4.7. Determination of molybdenum (V) and molybdenum (VI) in mixtures

Suitable aliquots (1-2 mL) of molybdenum (V + VI) mixtures (preferably 1:1, 1:5, 1:10) were taken in a 25 mL conical flask. A few drops of 0.5 M sulfuric acid and 1-3 mL of 1% (*w*:*v*) potassium permanganate solution were added to oxidize the pentavalent molybdenum. A 5mL volume of water was added to the mixtures, which were then heated on a steam bath for 10-15 min, with occasional gentle shaking, and then cooled to room temperature. Then, 3-4 drops of a freshly prepared sodium azide solution (2.5%,*w*:*v*) was added and heated gently with the further addition of 2-3 mL of water, if necessary, for 5 min to drive off the azide cooled to room temperature. The reaction mixtures were transferred quantitatively into a 10 mL volumetric flask; 1 mL of a 3.95×10^{-3} M Sal-BH reagent solution was added, followed by the addition of 1 mL of 0.5 M H_2SO_4. It was made up to the mark with deionized water. The absorbance was measured after 1 min at 440 nm against a reagent blank. The total molybdenum content was calculated with the help of a calibration graph. An equal aliquot of the above molybdenum (V + VI) mixture was taken into a 25 mL beaker (1 mL) of 0.01% (*w*:*v*); tartrate was added to mask molybdenum (V) and neutralize with dilute NH_4OH. After, the content of the beaker was transferred into a 10 mL volumetric flask, 1 mL of a 0.5 M sulfuric solution was added, followed by the addition of 1 mL of 3.95×10^{-3} M Sal-BH reagent, and made up to the volume with deionized water. After 1 min the absorbance was measured against a reagent blank, as before. The molybdenum concentration was calculated in µg/L or µg/mL with the aid of a calibration graph. This gave a measure of molybdenum (VI) originally present in the mixture. This value was subtracted from that of the total molybdenum to determine the molybdenum (V) present in the mixture. The results were found to be highly reproducible. The occurrence of such reproducible results is also reported for different oxidation states of molybdenum [54]. The results of a set of determinations are given in Table 9.

5. Conclusions

A new sensitive and inexpensive method with the molybdenum-Sal-BH complex was developed for the determination of molybdenum in biological, soil, food and vegetable samples, for continuous monitoring to establish the trace levels of molybdenum in various samples matrices. Compared with other methods in the literature [7-35,53,54], the proposed method has several remarkable analytical characteristics: (i) The proposed method is highly sensitive with molar absorptivity of the complex of 4.32×10^5 L/mol.cm. Thus, amount of ng/g of molybdenum can be determined without pre-concentration, (ii) The proposed method is very simple, rapid and stable. The reaction of molybdenum (VI) with Sal-BH is completed rapidly in 1 min at room temperature so it does not involve any stringent reaction conditions and offer the advantage of high complex stability (24 h) and (iii) The method has added the advantage of simultaneous determining individual amounts of Mo(V) and Mo(VI). With suitable masking agents, the reaction can be made highly selective. The proposed method using Sal-BH in aqueous solutions not only is one of the most sensitive methods for determination of molybdenum but also is excellent in terms of selectivity and simplicity. Therefore, this method will be successfully applied to the routine monitoring of trace amounts of molybdenum in real, environmental, biological, soil, food and vegetable samples.

Table 9. Determination of molybdenum (V) and molybdenum (VI) speciation in mixtures.

Serial no	Mo(IV): Mo(VI)	Mo, taken (mg/L)		Mo, found (mg/L)		Error (mg/L)	
		Mo(VI)	Mo(V)	Mo(VI)	Mo(V)	Mo(VI)	Mo(V)
1	1:1	1.00	1.00	0.99	0.98	0.01	0.02
1	1:1	1.00	1.00	1.00	0.98	0.00	0.02
1	1:1	1.00	1.00	0.99	0.99	1.00	0.00
Mean error: Mo(VI) = ±0.0067 Mo(V) = ± 0.014							
Standard deviation: Mo(VI) = ±0.006 Mo(V) = ± 0.01							
1	1:5	1.00	5.00	0.99	4.98	0.01	0.02
1	1:5	1.00	5.00	0.98	4.99	0.02	0.01
1	1:5	1.00	5.00	0.99	4.98	0.01	0.02
Mean error: Mo(VI) = ±0.013 Mo(V) = ±0.017							
Standard deviation: Mo(VI) =±0.0058 Mo(V) = ±0.0058							
1	1:10	1.00	10.00	0.98	9.99	0.02	0.01
1	1:10	1.00	10.00	0,98	9.98	0.02	0.02
1	1:10	1.00	10.00	0.99	9.98	0.01	0.02
Mean error: Mo(VI) = ±0.016 Mo(V) = ±0.016							
Standard deviation: Mo(VI) =± 0.0058 Mo(V) =± 0.0058							

It is a new method needs neither heating nor extraction to organic phase, works satisfactorily and could be an alternative method for the rapid determination of molybdenum in a wide variety of sample solutions and found superior to spectrophotometric methods described in different literature [7-35,53,54].

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