Canadian Chemical Transactions Year 2015 | Volume 3 | Issue 4 | Page 486-496

Research Article

DOI:10.13179/canchemtrans.2015.03.04.0251

Utilization of Cloud-Point Preconcentration for Spectrophotometric Determination of Trace Amounts of Molybdenum(VI) in Plants and Water Samples

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Received: *November 10, 2015* ***Revised:*** *January 5, 2015* ***Accepted:*** *January 5, 2015* *Published: January 10, 2016*

Abstract: A cloud-point preconcentration process using micelle of the non-ionic surfactant Triton X-114 to extract Mo(VI) from aqueous solutions was investigated. The method is based on the color reaction of molybdenum with 5-(2-benzothiazolyl-azo)8-hydroxy-quinoline (BTAHQ) in the presence of potassium bromide at pH 1.75 glycine/HCl buffer media and micelle-mediated extraction of complex. The optimal extraction and reaction conditions (e.g., surfactant concentration, reagent concentration and effect of time) were studied and the analytical characteristics of the method (e.g., limit of detection, linear range, preconcentration and improvement factors) were obtained. Linearity was obeyed in the range of 0.2–180 ng/mL of molybdenum(VI) ion and the detection limit of the method was 0.06 ng/mL. The relative standard deviation (RSD) and relative error for six replicate measurements of 100 ng/mL Mo(VI) were 0.88 % and 1.5 %, respectively. Preconcentration and improvement factors were found to be 250 and 5.0, respectively. The interference effect of some anions and cations was also tested. The method was applied to the determination of molybdenum(VI) in plants and water samples.

Keywords: Cloud-point preconcentration; molybdenum(VI) determination; spectrophotometry; plant and water analysis.

1. INTRODUCTION

Molybdenum is an important essential element for plants and animals since it play a significant role in a wide variety of plants and animals [1,2]. This element is also essential for bacteria in the fixation of atmospheric nitrogen and in the reduction of nitrate to nitrite. However, its deficiency or excess can cause damage to organisms. Thus rapid, selective and sensitive methods for the molybdenum determination in plants samples are required in order to clarify its behavior in the organism and/or environment.

A number of spectrophotometric methods based on complex formation are used for the determination of molybdenum [3–22]. Owing to their low sensitivity and selectivity, preconcentration and/or separation steps are usually necessary. There have been reported highly sensitive analytical techniques for the molybdenum determination such as spectrofluorimetry [23], voltammetry [24,25], atomic absorption spectrometry (AAS) [26], inductively coupled plasma-atomic emission spectrometry

(ICP-AES) [27], and ICP-mass spectrometry (ICP-MS) [28]. ICP techniques necessitate the use of rather high cost instruments.

Cloud-point preconcentration (CPP), based on the clouding phenomena of surfactants, has become more and more attractive. CPE offers many advantages over traditional liquid–liquid extraction [29]. For charged micelles, the phenomenon rarely occurs, presumably because electrostatic repulsion prevents phase separation in most cases. In the presence of salt, long-tailed cationic surfactants can self-assemble in aqueous solution into long, flexible wormlike micelles, thus rendering the solution viscoelastic [30,31]. High concentrations of salt cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases [32]. This phenomenon, originally termed coacervation, has been investigated since the 1940s and was first observed for mixtures of the cationic surfactant Hyamine 1622 with salts such as potassium thiocyanate (KSCN) and potassium chloride (KCl) [33,34]. The phase separation is typically of the upper consolute type, i.e., it occurs on cooling below a characteristic temperature *T*c, which, in turn, increases with salt content. Some separation and preconcentration cloud-point extraction procedures have been developed for various chemical species prior to their determination by different methods [35–42].

Cloud-point extraction of molybdenum(VI) was obtained using bromopyrogallol red / cetyltrimethylammonium / nonylphenoxypolyethoxy ethanol mixed medium [43] or cloud-point extraction (CPE) of the complex of Mo(VI) with bromopyrogallol red complex in surfactant media [44], as well as 8-hydroxyquinoline in the presence of the surfactant Triton X-100 [29]. The last system was applied for analysis of plant material extracts by ICP-MS with the limit of detection of 0.8 ng/g. The goal of the present work is to develop a method to preconcentration and determination of molybdenum by spectrophotometry based on cloud-point extraction (CPE) of the complex of molybdenum(VI) with 5-(2-benzothiazolylazo)8-hydroxy-quinoline (BTAHQ) complex in surfactant media.

2. EXPERIMENTAL

2.1. Apparatus

A Perkin-Elmer Lambda 12 UV/Vis spectrometer was used for recording absorbance spectra with 1.0-mm quartz cell. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A water bath with good temperature control and a centrifuge with 25-mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process. Tabletop Low Speed Large Capacity Centrifuge model L-550 was used

2.2. Reagents

The surfactants, Triton X-100, Triton X 114, Triton X-45, Tween 60, and Tween 80, emulgent-OP, (obtained from Sigma company) was used without further purification. Stock solution of molybdenum at a concentration of 1000 μg mL^{-1} was prepared by dissolving appropriate amount of Na_2MoO_4 salt (obtained from Merck) in bidistilled water. Working standard solutions were obtained by appropriate dilution of the stock solution.

BTAHQ was synthesized according to the method described previously [45-50]. Stock solutions of 5.0×10^{-4} M BTAHQ was prepared by dissolving an appropriate weight of pure reagent in least amount of ethanol (15 mL) and then diluted to the mark in a 100-mL calibrated flask with ethanol. The solution pH 1.75 was adjusted with glycine/hydrochloric acid buffer. *N*,*N*-Dimethylformamide (DMF) solvent and

potassium bromide salt were purchased from Merck.

2.3. General procedure

An aliquot of a molybdenum(VI) standard solution was transferred to a 25 mL centrifuge tube, 1.5 mL of the 5.0×10^{-4} M BTAHA solution and 6.0 mL buffer solution of pH 1.75 were added. This was followed by the addition of 2.0 mL of 5.0 % Triton X-114 solution and 2.5 mL of 0.3 M of KBr solution. The solution was taken up to the mark with bidistilled water and allowed to stand for 5.0 min in room temperature. Separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 10 min at 4000 rpm. Then, the aqueous phase could be separated by inverting the tube. The surfactant-rich phase of this procedure was dissolved and diluted to 0.1 mL with the DMF and transferred into a 1.0-mm quartz cell. The absorbance of the solution was measured at 686 nm. The blank solution was submitted to the same procedure with Mo(VI).

2.4. Plant samples preparation

Leaves were picked during the flowering period. The sample comprised the third or fourth leaves from the apix [51]. It was immediately dried in a forced draft oven for 24 h at 65 ^{o}C to prevent the decomposition or weight loss. After the sample has been divided into pieces and ground with a small mill, a suitable portion was weight (5.0 g dry material) in porcelain crucible and it was ashed using a muffle at 550-600 ^{o}C for 3.0 h. After cooling to 25 ^{o}C, 5.0 mL of a 6.0 M HCl solution was added to the crucible and warmed up to dry in a hot plate. The residue was dissolved using 5.0 mL of 1.4 M HCl solution. It was filtered through a paper (Whatman no. 41) and the volume was made up to 25 mL with the 1.4 M HCl solution.

3. RESULTS AND DISCUSSION

Molybdenum occurs principally in the VI oxidation state as molybdate (MoO_4^{2-}) ions, which form condensed species in an acid media. In strongly acidic solutions, molybdenyl cations (MoO_2^{2+}) are present [52].

BTAHQ is often used as a chromgenic reagent for the determination of a number of metals, particularly molybdenum(VI) [45-50]. The addition of surfactant-active substances improves the selectivity and sensitivity of the metal determinations due to the batho- and hyperchromic effects that can be observed.

However, in the presence of a non-ionic surfactant Mo(VI) complex was formed instantaneously. Anionic and cationic surfactants have no effect, an amphoteric surfactant has some effect, but a non-ionic surfactant is most effective. Among those non-ionic surfactants used are Tween-60, Tween-80, emulgent-OP, Triton X-100, Triton X-114, Triton X-45, etc.; Triton X-114 was used in subsequent experiments, since they are highly concordant. Complex of molybdenum with BTAHQ in the presence of Triton X-114 in aqueous media has a maximum absorbance at 675 nm. The solution was turbid by addition of the bromide ion. Therefore, the ternary complex of Mo(VI)–BTAHQ–Triton X-114 can be extracted by CPP method. The absorption spectrum of the ternary complex in surfactant-rich phase shows a maximum absorbance at 686 nm (Fig. 1). After separation of surfactant-rich phase, the absorbance was measured at 686 nm against a reagent blank as the reference.

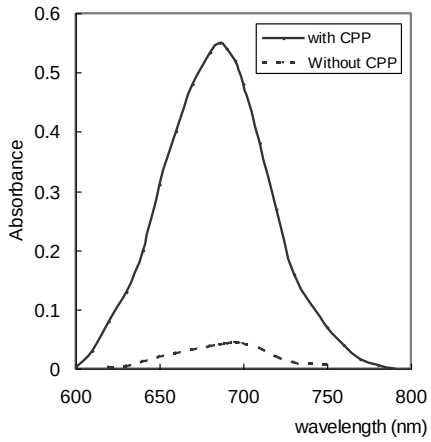

Fig. 1. Absorbtion spectra for 100 ng/mL complexed with 3×10^{-5} M BTAHQ with our without CPP at pH

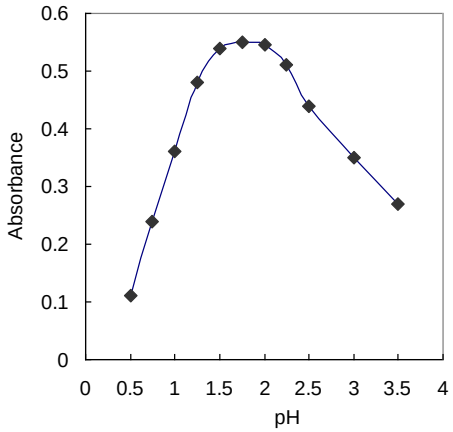

Fig. 2. Effect of pH value on the complexation of 100 ng/mL Mo(VI) with 3×10^{-5} M BTAHQ at the optimum conditions

3.1. Optimization of the system

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to obtain optimum conditions. These parameters were optimized by setting all parameters to be constant and optimizing one each time.

The effect of pH on the absorbance at a constant concentration of complex in surfactant-rich phase was investigated in the range of 0.5–3.5. The absorbance of the Mo(VI)–BTAHQ–Triton X-114, system at 686 nm in surfactant-rich phase was studied against the reagent blank. The absorbance was nearly constant in the pH range of 1.5–2.0, and developed at higher pHs. Therefore, pH 1.75 was selected as optimal [Fig. 2]. Moreover the amount of pH 1.75 was studied to select the optimum volume. A 5.0–7.0 mL of pH 1.75 gave the highest absorbance value. Therefore 6.0 mL of pH 1.75 per 25 mL was selected for all further studies.

Effect of BTAHQ concentration on the extraction and determination of molybdenum was investigated in the range of 0.5–6.0 × 10^{-5} M. The sensitivity of the method increased by increasing BTAHQ concentration up to 3.0 × 10^{-5} M [Fig. 3] and decreased at higher concentrations. It was expected that increasing BTAHQ causes an increase in the absorbance of complex, because increasing in BTAHQ concentration caused an increase in concentration of the complex. At concentrations higher than 3.5 × 10^{-5} M, the concentration of uncomplexed BTAHQ in surfactant-rich phase increases significantly. Therefore, much probably decrease of absorbance change at concentrations higher than 3.5 × 10^{-5} M is due to this fact that the free BTAHQ competes with the complexes in extraction to surfactant-rich phase. A concentration of 3.0 × 10^{-5} M of BTAHQ was selected as the optimum.

Effect of Triton X-114, concentration on the extraction and determination of molybdenum was investigated in the range of 0.5–4.0 mL of 5.0 % Triton X-114. The amount of the absorbance for sample increased by increasing Triton X-114 concentration up to 2.0 mL and decreased at higher concentrations. The blank signal also increased by increasing Triton X-114 concentration. This is due to more extraction of BTAHQ by increasing Triton X-114 concentration, but the difference between the sample and blank signals (ΔA) increased by increasing Triton X-114 concentration up to 2.0 mL of 5.0 % Triton X-114 and decreased at higher concentrations. Therefore, 2.0 mL of 5.0 % Triton X-114 was chosen as the optimum.

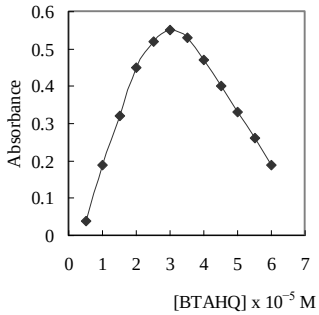

Fig. 3. Effect of [BTAHQ] on the complexation of 100 ng/mL of Mo(VI) at the optimum conditions

Addition of salt can cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases. Several inorganic salts including NaCl, NaF, KNO_3, KBr and KI, were tested and KBr was found as the best. Therefore, bromide was added to induce micelle growth and extraction of complex. The effect of bromide concentration was studied in the range of 0.01–0.08 M. Addition of 0.03 M bromide sufficed for maximum extraction of the complex and the asorbance decreased at higher concentrations. A concentration of 0.03 M bromide was selected for further works.

Effect of time on the reaction and also on the CPP procedure was investigated. The results showed that complexation reaction was completed in 5.0 min. Also a 10 min centrifugation at 4000 rpm was found to be enough for successful CPP.

Because the surfactant-rich phase was precipitate, different solvents were tried so as to select the one producing the optimal results regarding sensitivity. Among methanol, ethanol, DMF, acetone and acetonitrile, DMF gave the best results due to high sensitivity and low overlapping of spectra of components. Therefore, DMF was chosen in order to have appropriate amount of sample for transferring and measurement of the absorbance of the sample and also a suitable preconcentration factor. Therefore, a preconcentration factor of 250 was archived using the proposed method.

3.2. Stoichiometric ratio

The nature of the complex was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of BTAHQ to Mo(VI), obtained by varying the BTAHQ concentration, showed inflection at molar ratio 2.0, indicating presence of two BTAHQ molecules in the formed complex. Moreover, the Job method showed a ratio of BTAHQ to Mo(VI) = 2.0. Consequently, the results indicated that the stoichiometric ratio was (2 : 1) [BTAHQ : Mo(VI)]. The conditional formation constant (log K), calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 7.57, whereas the true constant was 7.75.

For ternary complexes of Mo–BTAHN–Triton X-114, the stoichiometric ratio as obtained from molar ratio indicated the formation of 1:1 for $[(BTAHN)_2$ Mo] : Triton X-114; so we conjectured that the ternary complex $[(BTAHN)_2Mo]$ [Triton X-114] is formed in the system. The structure of which is probably as follows:

$$2\ BTAHN + Mo(VI) \rightleftharpoons [(BTAHN)_2Mo]$$

$$[(BTAHN)_2Mo] + [\text{Triton X-114}] \rightleftharpoons \{[(BTAHN)_2Mo][\text{Triton X-114}]\}$$

3.3. Selectivity

The effect of different cations and anions on the determination of 100 ng/ mL molybdenum by the proposed method was studied. An ion was considered to be an interferent when it caused a variation greater than ± 3.0 % in the absorbance of the sample. For the determination of 100 ng/mL Mo(VI) by this method, the foreign ions can be tolerated at the levels given in Table 1. BTAHQ forms stable complexes with various metal ions, including transition metal ions. Most of the cations and anions examined do not interfere with the extraction and determination of molybdenum. Fe^{3+} interfered at 1.0 µg/mL. The interfering effects of Fe^{3+} up to 5.0 µg/mL, were completely removed by the addition of 5.0×10^{-4} M ascorbic acid to the solution. The ions Cu^{2+} and Pb^{2+} interfered at 2.0 µg/mL.

Table 1. Tolerance ratios of diverse ions on the determination of 100 ng/mL of Mo(VI)

Ion	Tolerance limit, foreign/Mo (w/w)
K^+, Na^+	18000
Ca^{2+}, Mg^{2+}	12000
Br^-	8000
F^-, Cl^-, I^-	4000
SO_4^{2-}, PO_4^{2-}	2250
Co^{2+}, NO_3^-	1500
Sr^{2+}, Cr^{3+},	1000
Ni^{2+}, Citrate,	800
EDTA, Tartarate	600
Fe^{3+}	500[a]
Cu^{2+}, Pb^{2+}	200

[a]: after addition of ascorbic acid

Table 2. Analytical features of the proposed method

Parameters	CPP method	Before CPP
Amount of DMF	0.1	---
pH	1.75	1.75
Optimum [BTAHQ] M	3×10^{-5}	3×10^{-5}
Reaction time (min)	5.0	5.0
Stirring time (min)	10	----
Beer's range (ng/L)	0.2 - 180	150 -10000
Ringbom range (ng/L)	0.5 - 174	300 - 9850
Molar absorptivity (L/mol cm)	5.28×10^6	1.05×10^5
Sandell sensitivity (ng/cm^2)	0.0182	0.894
Intercept		
Slope (µg/L)	5.5	0.11
intercept	- 0.003	0.009
Correlation coefficient (*r*)	0.9996	0.9992
RSD [a] (%)	0.55	1.65
Detection limits (ng/L)	0.06	45
Quantification limits (ng/L)	0.19	148
Preconcentration factor	250	
Improvement factor	50	

Table 3. Results comparison

Samples	Proposed method (µg/kg) Mo	ICP–AES (µg/kg) Mo
Rice leaves	135 ± 14	133 ± 14
Jack fruit leaves	82 ± 6.0	83 ± 10
Banana leaves	275 ± 5.0	274 ± 10
Sleeve leaves	65 ± 6.0	66 ± 8.0
Cane leaves	98 ± 12	98 ± 8.0
Corn leaves	92 ± 11	95 ± 10
Pepper black root	613 ± 20	616 ± 11
Pepper black stalk	522 ± 4.0	521 ± 22
Pepper black leaves	1433 ± 20	1440 ± 30
Fruit salad	185 ± 7.0	186 ± 6.0
Soya bean	1025 ± 30	1030 ± 50
Pinus leaves	294 ± 16	295 ± 22

Results average of six consecutive measurements. Paired *t*-test found value = 0.97; table value = 2.56 for 95% confidence level.

Table 4. Determination of molybdenum in the water samples by the proposed method

Sample	Molybdenum added (ng/mL)	Molybdenum found[a] (ng/mL)	Recovery (%)
Tap water (100 mL)	0.0	n.d[b]	---
	20	20.15 ± 0.2	100.75
	40	40.25 ±0.15	100.63
	80	80.40 ±0.3	100.50
Ground water (100 mL)	0.0	---	
	30	30.45	101.50
	60	60.60	101.00
	120	120.65	100.54
Seawater (100 mL)	0.0	---	
	40	39.5	98.75
	80	79.6	99.50
	160	159.7	99.81

[a]: Mean ± SD (n = 6). [b]: Not detected.

3.4. Analytical characteristics

Table 2 summarizes the analytical characteristics of the optimized method, including regression equation, linear range and limit of detection, reproducibility, and preconcentration and improvement factors. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L, S_B, and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.06 ng/mL.

Because the amount of molybdenum in 25 mL of sample solution is measured after preconcentration by CPP in a final volume of 0.1 mL DMF, the solution is concentrated by a factor of 250. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPP method to that of the calibration graph in micellar media without preconcentration, was 50.

The relative standard deviation (RSD) and relative error for six replicate measurements of 100 ng/mL of molybdenum was 0.88% and 1.5% and for 150 ng/ mL of molybdenum was 1.5% and 1.25%, respectively.

3.5. Analytical applications

Aiming to demonstrate the usefulness of the proposed system a set of samples comprising several plant materials was analyzed. The system was run using the optimized parameters summarized in Table 2. The results of sample are shown in Table 3. Accuracy was assessed by comparing results with these obtained using inductive coupled plasma optical emission spectrometry (ICP–AES). Applying the paired t-test no significant difference at 95% confidence level was observed.

The proposed method was successfully applied to the determination of molybdenum in water samples. The results are shown in Table 4. The recoveries are close to 100% and indicate the proposed method was helpful for the determination of molybdenum in the real samples.

Table 5. Preconcentration procedures for determination of molybdenum(VI) using sorbent extraction

Sorbent or reagent	Analytical method	Detection limits (ng/mL)	Ref.
Activated carbon/calmagite	ICP-OES	0.75	44
Polyuretane foam/ thiocyanate	CP-OES	1.5	53
Amberlite XAD-8	spectrophotometry	---	54
Amberlite IRA 743	LC-ETAAS	2	55
Bromopyrogallol red	spectrophotometry	0.1	56
Muromac A-1	ETAAS	0.25	57
Potassium thiocyanate and stannous chloride	LLE-S	4.6	58
Thiocyanate and methyl trioctyl ammonium chloride	LLE-spectrophotometry	5.0	59

4. CONCLUSION

The proposed procedure gives a simple, very sensitive and low-cost spectrophotometric procedure for determination of molybdenum ion that can be applied to real samples. The surfactant has been used for preconcentration of molybdenum in water, and thus toxic solvent extraction, has been avoided. A comparison between the proposed method with the previously reported methods for preconcentration and determination of molybdenum (Table 5) by solid phase extraction [54–57] and cloud-point extraction [43, 52] indicates that this method has a lower detection limit, wider linear range and is a convenient, safe, simple, rapid and inexpensive method for the determination of trace quantities of molybdenum to real samples.

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The authors declare no conflict of interest

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