

# Cloud-point preconcentration and spectrophotometric determination of trace amounts of molybdenum(VI) in steels and water samples

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## Abstract

A cloud-point extraction process using micelle of the cationic surfactant CTAB to extract Mo(VI) from aqueous solutions was investigated. The method is based on the color reaction of molybdenum with bromopyrogallol red in the presence of potassium iodide at pH 1.0 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 0.3–320.0 ng mL<sup>-1</sup> of molybdenum(VI) ion and the detection limit of the method was 0.1 ng mL<sup>-1</sup>. The relative standard deviation (R.S.D.) and relative error for five replicate measurements of 65.0 ng mL<sup>-1</sup> Mo(VI) were 1.1% and 1.9%, respectively. The interference effect of some anions and cations was also tested. The method was applied to the determination of molybdenum(VI) in steels and tap water and well water samples.

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**Keywords:** Cloud-point extraction; Spectrophotometric determination; Molybdenum(VI); Water samples; Alloy steels

## 1. Introduction

Molybdenum is an essential trace element for both animals and plants. Molybdenum has also found wide usage in a variety of industrial processes, e.g., alloying agent in steels and cast iron; high-temperature alloys; tool steels; pigments for printing inks, paints and ceramics; catalyst; solid lubricants; missile and aircraft parts; reactor vessels; cermets; die-casting copper base alloys and special batteries [1]. This diversity of biological functioning and sources makes it a prime necessity for an accurate determination of molybdenum at trace levels in various matrices.

There are many analytical techniques available for the determination of molybdenum such as neutron activation analysis (NAA) [2], inductively coupled plasma-mass spectrometry (ICP-MS) [3], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [4], flame atomic absorption spectrometry (FAAS) [5] voltammetry [6], spectrofluorimetry [7] and

spectrophotometry [8–12]. Most of these techniques such as NAA and ICP-MS necessitate the use of rather sophisticated and high cost instruments.

Spectrophotometric methods are most commonly used for the determination of molybdenum, especially in developing countries. A number of reagents [13–18] including xylenol orange, thiocyanate, chlorsulfophenol S, toluene-3,4-dithiol, 2-amino-4-chlorobenzenethiol, phenylfluorone, catechol violet, morin, 8-hydroxyquinoline, thiazolylazo compounds, 7,8-dihydroxy-4-methylcoumarin and bromopyrogallol red have been proposed for the determination of molybdenum.

However, due to the presence of molybdenum in environmental and biological samples at low levels, its separation from other elements presents and also the use of a preconcentration is usually necessary.

Cloud-point extraction (CPE), based on the clouding phenomena of surfactants, has become more and more attractive. CPE offers many advantages over traditional liquid–liquid extraction [19]. For charged micelles, the phenomenon rarely occurs, presumably because electrostatic repulsion prevents phase separation in most cases. In the presence of salt,

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long-tailed cationic surfactants can self-assemble in aqueous solution into long, flexible wormlike micelles, thus rendering the solution viscoelastic [20,21]. High concentrations of salt cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases [22]. 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) [23,24]. 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 [25–28]. Recently, we used the cloud-point extraction for preconcentration of trace quantities of some cations and determination by spectrophotometry [29–32].

Cloud-point extraction of molybdenum(VI) was obtained using bromopyrogallol red/cetyltrimethylammonium/nonylphenoxypolyethoxy-ethanol mixed medium [33] as well as 8-hydroxyquinoline in the presence of the surfactant Triton X-100 [34]. The last system was applied for analysis of plant material extracts by ICP-MS with the limit of detection of  $0.8 \text{ ng g}^{-1}$ . This paper proposes a method to preconcentration and determination of molybdenum by spectrophotometry based on cloud-point extraction (CPE) of the complex of molybdenum(VI) with bromopyrogallol red complex in surfactant media.

## 2. Experimental

### 2.1. Apparatus

A Perkin-Elmer Lambda 45 UV/Vis spectrometer was used for recording absorbance spectra. Absorption measurements at fixed wavelength were performed using a Shimadzu UV-mini-1240V spectrophotometer with 1-cm quartz cell (0.5 mL). A Metrohm pH meter (model 713) with a combined glass electrode was used for pH measurements. A water bath with good temperature control and a centrifuge with 10-mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process.

### 2.2. Reagents

The surfactants, cetyltrimethylammonium bromide (CTAB) (obtained from Sigma company) was used without further purification. Stock solution of molybdenum at a concentration of  $1000 \mu\text{g mL}^{-1}$  was prepared by dissolving appropriate amount of  $\text{Na}_2\text{MoO}_4$  salt (obtained from Merck) in triply distilled water. Working standard solutions were obtained by appropriate dilution of the stock solution. A solution of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  of bromopyrogallol red (BPR), (obtained from Merck) was prepared by dissolving appropriate amounts of this reagent in triply distilled water. The solution pH  $1.0 \pm 0.1$  was adjusted with glycine/ hydrochloric acid buffer. *N,N*-Dimethyl formamide

(DMF) solvent and potassium iodide salt were purchased from Merck.

### 2.3. Procedure

An aliquot of a molybdenum(VI) standard solution was transferred to a 10 mL centrifuge tube, 1.0 mL of the  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  BPR solution and 3.0 mL buffer solution were added. This was followed by the addition of 3.0 mL of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  surfactant CTAB solution and 1.5 mL of  $0.2 \text{ mol L}^{-1}$  of KI solution. The solution was taken up to the mark with triply distilled water and allowed to stand for 10 min in room temperature. Separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 15 min at 3800 rpm. Then, the aqueous phase could be separated by inverting the tube. The surfactant-rich phase of this procedure was dissolved and diluted to 0.5 mL with the DMF and transferred into a 0.5-mL quartz cell. The absorbance of the solution was measured at 576 nm. The blank solution was submitted to the same procedure and its absorbance was measured at 576 nm.

### 2.4. Determination of molybdenum in alloy steels

An accurately weighed amount of steel sample (0.5 g) was dissolved completely in minimum amount of aqua regia by slow heating on a sand bath. To this, 5 mL of 1:1  $\text{H}_2\text{O}:\text{H}_2\text{SO}_4$  mixture was added and evaporated to dryness. The residue was dissolved in 20 mL of distilled water and filtered through Whatman filter paper no. 40. The filtrate was collected in a 250 mL volumetric flask and made up to the mark with distilled water. The sample solution was appropriately diluted to obtain the concentration in the required range. Suitable aliquots were taken and analysed for molybdenum using the proposed procedure. Ascorbic acid solution was added to mask iron wherever necessary. The amount of molybdenum in the sample solution was deduced from the calibration curve.

## 3. Results and discussion

Molybdenum occurs principally in the VI oxidation state as molybdate ( $\text{MoO}_4^{2-}$ ) ions, which form condensed species in an acid media. In strongly acidic solutions, molybdenyl cations ( $\text{MoO}_2^{2+}$ ) are present [35].

Bromopyrogallol red is often used as a chromogenic reagent for the determination of a large number of metals, particularly molybdenum(VI) [36,37]. 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 [38]. The complexation of molybdenum(VI) with bromopyrogallol red in the presence of the nonionic surfactant Triton X-114 has been studied spectrophotometrically. A mixed-ligand complex is reported with the component ratio 1:1:1 and a stability constant of  $\log \beta = 8.2$  [39].

The literature results for the complexation of molybdenum with BPR in the presence of CTAB showed the component ratio of 1:2:2 (Mo:BPR:CTAB) [40].

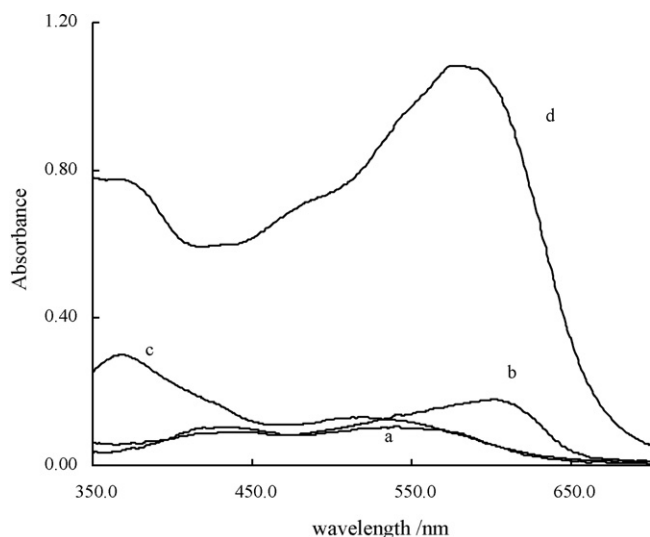


Fig. 1. Absorption spectra for BPR in the presence of CTAB (a) and its complex with molybdenum(VI) in aqueous media (b); BPR (c) and its complex after extraction in surfactant-rich phase (d); conditions: BPR,  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ; molybdenum,  $0.2 \mu\text{g mL}^{-1}$ ; KI,  $0.03 \text{ mol L}^{-1}$ ; CTAB concentration,  $3.0 \times 10^{-4} \text{ mol L}^{-1}$ ; pH, 1.0.

Complex of molybdenum with BPR in the presence of CTAB in aqueous media has a maximum absorbance at 605 nm. The solution was turbid by addition of the iodide ion. Therefore, the ternary complex of Mo(VI)–BPR–CTAB can be extracted by CPE method. The absorption spectrum of the ternary complex in surfactant-rich phase shows a maximum absorbance at 576 nm (Fig. 1). After separation of surfactant-rich phase, the absorbance was measured at 576 nm against a reagent blank as the reference.

### 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 optimized system. 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 0.4–3.0. The absorbance of the Mo(VI)–BPR–CTAB system at 576 nm in surfactant-rich phase was studied against the reagent blank. The absorbance was nearly constant in the pH range of 0.6–1.2, and developed at higher pHs. Therefore, pH 1.0 was selected as optimal.

Effect of BPR concentration on the extraction and determination of molybdenum was investigated in the range of  $0.2\text{--}2.0 \times 10^{-5} \text{ mol L}^{-1}$ . The sensitivity of the method increased by increasing BPR concentration up to  $1.0 \times 10^{-5} \text{ mol L}^{-1}$  and decreased at higher concentrations. It was expected that increasing BPR causes an increase in the absorbance of complex, because increasing in BPR concentration caused an increase in concentration of the complex. At concentrations higher than  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ , the concentration of uncomplexed BPR in surfactant-rich phase increases

significantly. Therefore, much probably decrease of absorbance change at concentrations higher than  $1.0 \times 10^{-5} \text{ mol L}^{-1}$  is due to this fact that the free BPR competes with the complexes in extraction to surfactant-rich phase. A concentration of  $1.0 \times 10^{-5} \text{ mol L}^{-1}$  of BPR was selected as the optimum.

Effect of CTAB concentration on the extraction and determination of molybdenum was investigated in the range of  $1.5\text{--}4.0 \times 10^{-4} \text{ mol L}^{-1}$ . The amount of the absorbance for sample increased by increasing CTAB concentration up to  $3.0 \times 10^{-4} \text{ mol L}^{-1}$  and decreased at higher concentrations. The blank signal also increased by increasing CTAB concentration. This is due to more extraction of BPR by increasing CTAB concentration, but the difference between the sample and blank signals ( $\Delta A$ ) increased by increasing CTAB concentration up to  $3.0 \times 10^{-4} \text{ mol L}^{-1}$  and decreased at higher concentrations. Therefore,  $3.0 \times 10^{-4} \text{ mol L}^{-1}$  CTAB was chosen as the optimum.

Addition of salt can cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases. Several inorganic salts including NaCl, NaF,  $\text{KNO}_3$ , KBr and KI, were tested and KI was found as the best. Therefore, iodide was added to induce micelle growth and extraction of complex. The effect of iodide concentration was studied in the range of  $0.015\text{--}0.05 \text{ mol L}^{-1}$ . Addition of  $0.03 \text{ mol L}^{-1}$  iodide sufficed for maximum extraction of the complex and the signal decreased at higher concentrations. A concentration of  $0.03 \text{ mol L}^{-1}$  iodide was selected for further works.

Effect of time on the reaction and also on the CPE procedure was investigated. The results showed that complexation reaction was completed in 10 min. Also a 15 min centrifugation at 3800 rpm was found to be enough for successful CPE.

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 20 was archived using the proposed method.

### 3.2. Analytical characteristics

Table 1 summarizes the analytical characteristics of the optimized method, including regression equation, linear range

Table 1  
Analytical features of the proposed method

Regression equation ( $n = 16$ )	$\Delta A = 0.0057C + 0.0059$ , $r^2 = 0.999$
Regression equation ( $n = 10$ ) before preconcentration	$\Delta A = 0.79C - 0.037$ , $r^2 = 0.998$
Linear range ( $\text{ng mL}^{-1}$ )	0.3–320.0, (50.0–700) <sup>a</sup>
Limit of detection ( $3S_B/m$ blank, $\text{ng mL}^{-1}$ ) ( $n = 5$ )	0.1
Preconcentration factor	20
Improvement factor	7.2

<sup>a</sup> Linear range before preconcentration.

Table 2  
Tolerance ratios of diverse ions on the determination of  $0.2 \mu\text{g mL}^{-1}$  of molybdenum

Ion	Tolerance limit, foreign/Mo (w/w)
$\text{K}^+$ , $\text{Ca}^{2+}$	10000
$\text{Ni}^{2+}$ , $\text{Cl}^-$	2500
$\text{Co}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Cr}^{3+}$ , $\text{NO}_3^-$	1000
$\text{Mn}^{2+}$	4300
$\text{SO}_4^{2-}$	5000
Citrate, EDTA	300
$\text{Cd}^{2+}$	40.0
Tartarate	30.0
$\text{Fe}^{3+}$	80 <sup>a</sup>
$\text{Cu}^{2+}$ , $\text{Pb}^{2+}$	8.0

<sup>a</sup> After removal as described in text.

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  $0.1 \text{ ng mL}^{-1}$ . Because the amount of molybdenum in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of 0.5 mL DMF, the solution is concentrated by a factor of 20. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that of the calibration graph in micellar media without preconcentration, was 7.2.

The relative standard deviation (R.S.D.) and relative error for five replicate measurements of  $30.0 \text{ ng mL}^{-1}$  of molybdenum was 3.8% and 1.1% and for  $65.0 \text{ ng mL}^{-1}$  of molybdenum was 1.9% and 2.5%, respectively.

### 3.3. Selectivity

The effect of different cations and anions on the determination of  $0.2 \mu\text{g mL}^{-1}$  molybdenum by the proposed method was studied. An ion was considered to be an interferent when it caused a variation greater than  $\pm 5\%$  in the absorbance of the sample. For the determination of  $0.2 \mu\text{g mL}^{-1}$  Mo(VI) by this method, the foreign ions can be tolerated at the levels given in Table 2. BPR forms stable complexes with various metal ions, including transition metal ions. Most of the

Table 3  
Determination of molybdenum in the water samples by the proposed method

Sample	Molybdenum added ( $\text{ng mL}^{-1}$ )	Molybdenum found <sup>a</sup> ( $\text{ng mL}^{-1}$ )	Recovery (%)
Tap water	0.0	n.d <sup>b</sup>	–
	8.0	$8.2 \pm 0.1$	102.1
	50.0	$50.2 \pm 0.4$	100.3
	150.0	$155.3 \pm 0.3$	103.5
Mineral water	0.0	n.d	–
	8.00	$8.5 \pm 0.1$	106.5
	70.0	$68.1 \pm 0.3$	97.3
	250.0	$248.9 \pm 0.4$	99.5

<sup>a</sup> Mean  $\pm$  S.D. ( $n = 4$ ).

<sup>b</sup> Not detected.

Table 4  
Determination of molybdenum(VI) in standard steel samples by the proposed method

Steel samples <sup>a</sup>	Present	Found <sup>b</sup>	Recovery (%)
Steel-1	100	98.80	97.8
Steel-2	200	200.01	100.01

<sup>a</sup> Composition of samples (%): Ni, 41.9; Fe, 36; Cr, 12.46; Ti, 2.95; Mo, 5.83; Si, 0.28; Al, 0.24; Co, 0.21; Mn, 0.08; Cu, 0.032 and C, 0.03 [45].

<sup>b</sup> Mean value of three determination.

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

Sorbent or reagent	Analytical method	Detection limits ( $\text{ng mL}^{-1}$ )	Ref.
Activated carbon/calmagite	ICP-OES	0.75	41
Polyurethane foam/thiocyanate	ICP-OES	1.5	42
Muromac A-1	ETAAS	0.25	43
Amberlite XAD-8	Spectrophotometry	–	44
Amberlite IRA 743	LC-ETAAS	2	45

cations and anions examined do not interfere with the extraction and determination of molybdenum.  $\text{Fe}^{3+}$  interfered at  $20 \mu\text{g mL}^{-1}$ . The interfering effects of  $\text{Fe}^{3+}$  up to  $80 \mu\text{g mL}^{-1}$ , were completely removed by the addition of  $5.0 \times 10^{-4} \text{ mol L}^{-1}$  ascorbic acid to the solution. The ions  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  interfered at  $1.6 \mu\text{g mL}^{-1}$ .

### 3.4. Determination of Mo(VI) in water samples

The proposed method was successfully applied to the determination of molybdenum ion in water samples. The results are shown in Table 3. The recoveries are close to 100% and indicate the proposed method was helpful for the determination of molybdenum in the real samples.

### 3.5. Determination of Mo(VI) in standard alloy steels

The validity of the proposed method was determined in standard steel samples containing Mo(VI). Satisfactory results were obtained for the recovery of the metal ion indicating that the proposed method is effective for its determination. The results are given in Table 4.

## 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 [4,41–44] and cloud-point extraction [33,34] indicates that this method has a lower detection limit, wider linear range and is a con-

venient, safe, simple, rapid and inexpensive method for the determination of trace quantities of molybdenum to real samples.

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