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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^{-1} of molybdenum(VI) ion and the detection limit of the method was 0.1 ng mL^{-1}. The relative standard deviation (R.S.D.) and relative error for five replicate measurements of 65.0 ng mL^{-1} 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.

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-dithol, 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 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, cetyltrimethylammounium bromide (CTAB) (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 triply distilled water. Working standard solutions were obtained by appropriate dilution of the stock solution. A solution of 1.0×10^{-4} 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 ± 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 1.0×10^{-4} mol L^{-1} BPR solution and 3.0 mL buffer solution were added. This was followed by the addition of 3.0 mL of 1.0×10^{-3} mol L^{-1} surfactant CTAB solution and 1.5 mL of 0.2 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 H_2O:H_2SO_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 (MoO_4^{2-}) ions, which form condensed species in an acid media. In strongly acidic solutions, molybdenyl cations (MoO_2^{2+}) are present [35].

Bromopyrogallol red is often used as a chromgenic 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].