

Speciation, liquid–liquid extraction, sequential separation, preconcentration, transport and ICP-AES determination of Cr(III), Mo(VI) and W(VI) with calix-crown hydroxamic acid in high purity grade materials and environmental samples

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Abstract

A new functionalized calix[6]crown hydroxamic acid is reported for the speciation, liquid–liquid extraction, sequential separation and trace determination of Cr(III), Mo(VI) and W(VI). Chromium(III), molybdenum(VI) and tungsten(VI) are extracted at pH 4.5, 1.5 M HCl and 6.0 M HCl, respectively with calixcrown hydroxamic acid (37,38,39,40,41,42-hexahydroxy-7,25,31-calix[6]crown hydroxamic acid) in chloroform in presence of large number of cations and anions. The extraction mechanism is investigated. The various extraction parameters, appropriate pH/M HCl, choice of solvent, effect of the reagent concentration, temperature and distribution constant have been studied. The speciation, preconcentration and kinetic of transport has been investigated. The maximum transport is observed 35, 45 and 30 min for chromium(III), molybdenum(VI) and tungsten(IV), respectively. For trace determination the extracts were directly inserted into the plasma for inductively coupled plasma atomic emission spectrometry, ICP-AES, measurements of chromium, molybdenum and tungsten which increase the sensitivity by 30-fold, with detection limits of 3 ng ml^{-1} . The method is applied for the determination of chromium, molybdenum and tungsten in high purity grade ores, biological and environmental samples. The chromium was recovered from the effluent of electroplating industries.

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1. Introduction

Chromium, molybdenum and tungsten are important constituents of modern alloys and these elements are quite abundant in untreated waste waters of iron, steel, leather tanning, metal plating, battery, electro wiring, metal finishing, aerospace and electronic industries. The heavy metal emissions are of increasing importance is assessment of risks associated with a combustion system. Metal contributes about 7–9% of a typical waste by weight, a significant fraction of incombustible matter in hazardous waste. Atmo-

spheric emission of Cr, Mo, As, Cu, Ni etc. and their salts are regulated under the clean act. Many of these, like Cr, Mo emitted into the atmosphere pose serious health hazards. The bioinorganic chemistry of chromium, molybdenum and tungsten plays an important role in biological systems [1]. Since these are the essential elements contributing to the function of 11 known enzymes, their accurate determination in blood plasma is important to obtain an insight into their metabolism. It passes continuation risk to natural environment concern because of its toxicity [2]. In contrast, Cr(VI) is carcinogenic and can diffuse through cell membrane and oxidize molecules with toxic results [3,4].

In recent year, it has become recognized that trace metal analysis must involve the metal speciation in addition to total metal analysis. Biomedical, biological and toxicological

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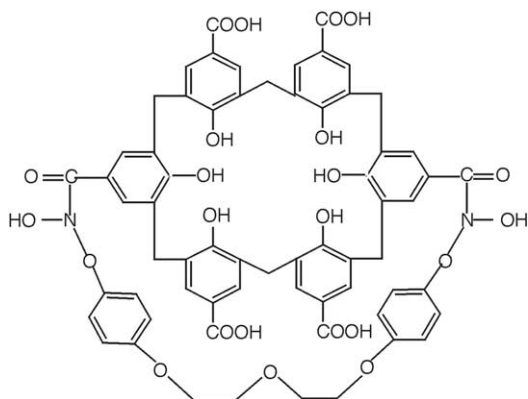


Fig. 1. 37,38,39,40,41,42-hexahydroxy-7.

properties depend upon the specific form in which, the metal is present and combinations of metals have different effects on the environment depending on the nature of the mixture. Hard chrome and molybdenum alloys plating of gun barrels release these metals on firing rounds and transport of these aerosol particles to different environmental conditions causes a health hazard. Number of papers on chromium speciation analysis has significantly increased in recent years because of the wide spread contamination of environment due to industrial, fungicides, magnetic tapes and metallurgy.

Various reagents have been used for the extraction, separation and determination of chromium [5–15], molybdenum [16–20] and tungsten [21–25]; however, these methods are tedious, time consuming, non specific and difficult to separate sequentially chromium, molybdenum and tungsten from each other. Recently, macrocyclic compounds like crown ethers and calixarenes are reported for the chromatographic separation of chromium [26].

On the other hand, atomic spectroscopic method (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-Mass spectrometry do not distinguish Cr(III) and Cr(VI) but gives the total concentration. Dicyclo 18-crown-6 is reported for the extraction of molybdenum and tungsten as thiocyanates [27–29]. However, no systematic studies for their separation are reported.

Calix-crown ethers [30] are the new class of ligands having the binding properties towards alkali and alkaline metals, which can be tuned by the subtle conformation changes around the binding region. Hydroxamic acids are the versatile analytical reagents for the estimation and separation of metals [31–38]. The introduction of the hydroxamic acid group in to the macrocycles may enhance the complexing ability towards the metal ions. With this in a view, in the present investigation, new functionalized calix-crown ether with hydroxamic acid group (Fig. 1) is synthesized and used for the complexation, liquid–liquid extraction, speciation and sequential separation of Cr(III), Mo(VI) and W(VI) from solid wastes. The present extraction method removes the bulk of the major elements and at the same time, concentrates the desired metal species into a small volume of the solution. The chloroform extract

is directly inserted into plasma, which produces a 30-fold increase in sensitivity and detection limit.

2. Experimental

2.1. Chemicals

All the chemicals and solvents used were of analytical grade and from E. Merck unless otherwise specified.

2.2. Reagents

Stock solution (1.68×10^{-3} M, 0.2%) of calix-crown hydroxamic acid was prepared in CHCl_3 .

2.3. Apparatus

The CIBA corning glass vessels were used. Electronic spectra were recorded on a CIBA-Corning 2800 UV–visible spectrophotometer with matching 10 mm quartz cells, pH measurements were performed with Systronic pH meter Model 335, equipped with a combined glass and calomel electrode.

Plasma Scan Model 710 Sequential plasma, Inductively Coupled Atomic Emission Spectrophotometer with plasma Scan multitasking computer and peristaltic pump was used. The following conditions were set for ICP-AES, Ref 27.12 M HZ, incidental power 2000 W, GMK nebulizer, Sample concentration 1.0 ng mL^{-1} , RF power 5 W, observation height 14 mm, argon coolant flow 13 L min^{-1} , wavelength set for chromium 262.72 nm, for molybdenum 202.30 nm and for tungsten 207.91 nm.

2.4. Metal solutions

Standard solutions of Cr(III), Mo(VI) and W(VI) were prepared by dissolving 3.83 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in 250 mL of water, 1.79 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 100 mL of water and 1.84 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 250 mL of water. Final concentrations were determined spectrophotometrically [9,14,15,17,36].

2.5. Extraction procedure

An aliquot of sample solution containing 98.2–196.2 μg of Cr(III), 99–198 μg of Mo(VI) or 99–199 μg of W(VI) was transferred in to 25 mL separator funnel and pH or molarity of the HCl solution was adjusted [for Cr(III) pH 4.5, Mo(VI) 1.5 M HCl and for W(VI) 6.0 M HCl] with buffer or conc. HCl. The mixture was then shaken with 5.0 mL (0.2%) chloroform solution of calix-crown hydroxamic acid for 5 min. The organic layer was separated, dried over anhydrous sodium sulfate and transferred to 10.0 mL volumetric flask. The organic layer was made up to 10.0 mL with

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