



A new chelating resin: Synthesis, characterization and application for speciation of chromium (III)/(VI) species

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ARTICLE INFO

Article history:

Received 28 July 2011

Received in revised form

14 November 2011

Accepted 16 November 2011

Keywords:

Chelating resin

Separation

Preconcentration

Chromium speciation

FAAS

ABSTRACT

A new method for speciation, preconcentration and separation of Cr(III) and Cr(VI) in different matrices was developed using solid phase extraction and flame atomic absorption spectrometry (FAAS). Poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene (MAD), was synthesized and characterized as a new chelating resin for the speciation of Cr(III)/Cr(VI) species. Cr(III) was quantitatively recovered on chelating resin at pH range of 1.5–4.5, while Cr(VI) was not quantitatively recovered in all the pH's. The optimum conditions for the speciation of Cr(III)/Cr(VI) species were investigated on several commonly tested experimental parameters such as pH of the solution, amount of the resin, sample volume, and interfering ions. The preconcentration factor was found to be 200. The limit of detection for Cr(III) corresponding to three times the standard deviation of the blank (3 s) was found $0.01 \mu\text{g L}^{-1}$. Adsorption capacity and binding equilibrium constant were calculated to be 34.3 mg g^{-1} and 1.5 L mg^{-1} , respectively. The method was validated by analysing certified reference materials. The proposed method was applied to the determination and speciation of chromium species in various water and food samples with satisfactory results.

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1. Introduction

Chromium is extensively used either as alloy or as trivalent or hexavalent salt in a variety of industrial processes such as metallurgical, chemical industries, electroplating, refractories, pigments, tanning industries, oxidative dyeing and cooling water towers [1]. The importance of chromium speciation is governed by the fact that the toxicity and reactivity depend on the chemical form or oxidation state of chromium. Cr(III) is relatively non-toxic and an essential nutrient for humans, and trace amounts of Cr(III) are considered as essential to mammals for their maintenance of normal glucose tolerance factor, lipid and protein metabolism, and are therefore essential for human health [2].

On the contrary, Cr(VI) species are highly toxic as a potential carcinogenic agent due to their high oxidation potential and their relatively small size, which enables them to penetrate through biological cell membranes [3]. Cr(VI) inhibits the enzymatic sulfur uptake of the cell and is also harmful to lungs, liver and kidney. The oxidation of sulfur dioxide and formation of acidic aerosols involved in global acid rain are observed in air due to chromium particulates [4]. Also, Cr(VI) diffuses as CrO_4^{2-} or HCrO_4^- through cell membranes and oxidize biological molecules, causing toxic results,

such as chronic ulcers and corrosive action in nasal septum, in the body [5,6]. Also, it has been known that the two species, Cr(III) and Cr(VI), were stable and that interconversion was limited by the high potential necessary to oxidize Cr(III) to Cr(VI). Besides, the relative kinetic of the transformation was thought to be slow. However, experimental evidences clearly show that this is not true. In fact, as the pH is raised the potential of chromate dramatically decreases and even mild oxidants can produce considerable amounts of Cr(VI) with rapid enough reaction rates [7].

Chromium species in water, mainly exist as chromate (CrO_4^{2-}) and cationic hydroxo complexes ($\text{Cr}(\text{OH})_2^{2+}$ and $\text{Cr}(\text{OH})_2^+$) and organically bound or colloiddally sorbed Cr(III) [8]. So it is noteworthy to estimate the individual species of chromium in natural water, waste water or drinking water. Therefore, it is necessary to control the level of Cr(VI) in natural and drinking water, where typical concentrations of total chromium are in the range $0.1\text{--}0.5 \mu\text{g L}^{-1}$ [9–12]. These facts show that speciation analysis of Cr, as well as its determination, is very important for its biological and environmental evaluations.

Chromium at trace level can be determined after separation and preconcentration followed by instrumental analysis. Low chromium levels are usually determined by separation of one specific form by sorption [8,13], liquid–liquid extraction [14,15] or coprecipitation [5,16]. In some cases, preconcentration of selective chromium species (not all chromium species) followed by detection has been carried out using electroanalytical techniques [17–19].

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Nevertheless, the report on the use of solid phase resin for pH dependent speciation following selective elution of different forms of chromium, viz. Cr(III) and Cr(VI) is scarce [20–27].

Considering all separation techniques for preconcentration and separation of analytes from different matrices, solid phase extraction using chelating resins is the method of choice for separation of trace constituents from the environmental and natural water systems and different sources due to its high separation efficiency, good reproducibility of retention parameters and high sensitivity [23,28,29].

Moreover, the use of chelating sorbents can provide a better separation of interferent ions, high efficiency and higher rate of process, and the possibility of combining with different determination methods [30]. Therefore, a variety of chelating resins have been studied from the viewpoint of the effective and/or selective adsorption of elements [31]. Chelating resins are typically characterized by functional groups containing O, N, S and P donor atoms which coordinate to different metal ions [32–34]. Chelating resins containing heterocyclic functional groups receive a great deal of attention since they display high affinity towards heavy and noble metal ions [35]. Much attention has been drawn to the synthesis of chelating resins and to the investigation of their adsorption behavior for the selective and quantitative separation of specific metal ions from various matrices, because both their adsorption ability and adsorption selectivity are superior to those of ion exchangers in a trace and/or ultra trace concentration range. On the other hand, metal separation in aqueous solutions by using membranes and synthesis of selective adsorbents are also very important [36,37].

In this study, a newly synthesized chelating resin, poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene (MAD), was used for the separation, preconcentration and speciation of Cr(III) and Cr(VI) species. The Cr(III) was quantitatively separated from Cr(VI) and preconcentrated. Cr(VI) concentrations were obtained as the respective differences between total chromium and Cr(III). The synthesized chelating resin was characterized by spectral studies (FT-IR, ^1H - and ^{13}C -NMR spectra). The analytical characteristics of the resin were established and optimum recovery conditions were determined for Cr(III). The adsorption capacity of the sorbent for Cr(III) was also studied. The proposed method was applied in the determination and speciation of inorganic chromium species in various water and food samples.

2. Experimental

2.1. Instrument

A PerkinElmer model AAnalyst 800 flame atomic absorption spectrometer (Norwalk, CT, USA) equipped with a deuterium background correction system and an air-acetylene burner was used for the determination of chromium. The wavelength used was 357.9 nm. Spectral bandwidth of 0.7 nm, acetylene flow rate of 1.4 L min^{-1} , and nebulizer flow rate of 10.0 mL min^{-1} were conventional working parameters. For measuring pH values in the aqueous phase, a Consort model C533 pH meter combined with a

glass-electrode and also a magnetic stirrer (Chiltern) were used. A Shimadzu FT-IR model 8400 spectrophotometer was used by applying the attenuated total reflectance (ATR) technique. ^1H - and ^{13}C -NMR spectra of the monomer and the polymer were recorded on a Bruker 400 MHz NMR spectrometer using CDCl_3 and DMSO-d_6 as solvents and tetramethylsilane as the internal standart. The specific surface area (in $\text{m}^2\text{ g}^{-1}$) of the chelating resin beads was determined by mercury porosimetry and BET method from low-temperature nitrogen adsorption isotherms which were obtained at 77 K using a high-vacuum volumetric apparatus. The samples were degassed at $100^\circ\text{C}/698\text{ mm Hg}$ for 5 h. The average granule dimension of the chelating resin beads was determined by Mastersizer 2000 equipment and laser light scattering technique. The apparent density of the chelating resin was determined by the cylinder method, a modification of the ASTM D 792 standard [38].

2.2. Reagents and standard solutions

All reagents used were of the highest available purity and at least analytical reagent grade (Merck, Darmstadt, Germany). Deionized water was used for the preparation of the solutions. Cr(III) and Cr(VI) stock solutions (1000 mg L^{-1}) were prepared from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and K_2CrO_4 [15]. From these solutions, dilute working solutions were prepared on a daily basis. The reduction of Cr(VI) to Cr(III) was carried out using hydroxylamine hydrochloride as the reducing agent. The following buffer solutions were used for the presented preconcentration procedure: HCl/KCl buffer for pH 1.0–2.0; $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer for pH 3.0–5.0; $\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$ buffer for pH 6.0–7.0. 2.0 mol L^{-1} hydrochloric acid solution was used as eluent throughout the experiments.

2,2'-Azobisisobutyronitrile (AIBN) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (Merck, Darmstadt, Germany) were used without further purification. Divinylbenzene (DVB), *N,N*-dimethylformamide, diethylether, and benzene (Merck) were commercial products of analytical grade and used as received unless otherwise noted.

2.3. Synthesis of monomer and chelating resin

2.3.1. 5-Methyl isoxazolyl methacrylamide (MIM) monomer

To a well-stirred solution of 3-amino-5-methyl isoxazole (0.294 g, 3.0 mmol) and triethylamine (9.0 mmol) in 30 mL acetonitrile, was added methacryloyl chloride (0.313 g, 3.0 mmol) with dropwise under cooling conditions in an ice bath ($0\text{--}5^\circ\text{C}$). After the complete addition of methacryloyl chloride, the reaction mixture was stirred for 24 h at room temperature, then filtered and evaporated with a rotavapor. A dark-yellow product was obtained and recrystallized from methanol as a yellow powder (yield: 70%). The reaction scheme of the monomer is shown in Fig. 1.

2.3.2. Synthesis of chelating resin

The preparation of poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propane sulfonic acid-co-divinylbenzene (MAD) chelating resin was carried out

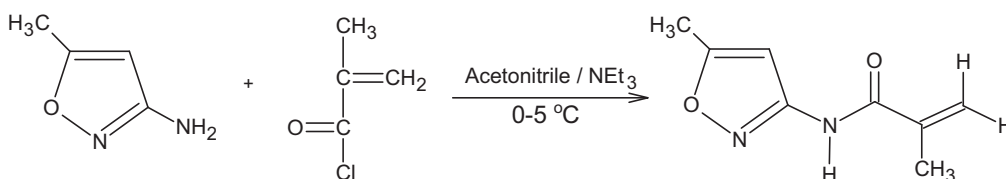


Fig. 1. Reaction scheme of 5-methyl isoxazolyl methacrylamide (MIM).

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