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# Development of a new on-line system for the sequential speciation and determination of chromium species in various samples using a combination of chelating and ion exchange resins



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## ABSTRACT

A new on-line flow injection (FI) procedure for the sequential separation, preconcentration and speciation of Cr(III)/Cr(VI) species in different matrices is described based on the combining of solid phase extraction and flame atomic absorption spectrometry (FAAS). Poly 2-(5-methylisoxazol)methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinyl-benzene and Dowex 21K resins were used as chelating and ion-exchange materials for the separation/preconcentration of Cr(III) and Cr(VI) ions, respectively. Trace amounts of chromium retained on the resins were eluted sequentially with HNO<sub>3</sub> and then introduced directly to the nebulizer-burner system of FAAS. The optimum conditions such as pH of the sample solution, amount of the resin, volume of the sample and interfering ions, which are effective on the quantitative recovery of the analytes, were investigated for sequential determination of Cr(III) and Cr(VI) ions. The preconcentration factors were found to be 48 and 30 for Cr(III) and Cr(VI), and the detection limits corresponding to three times the standard deviation of the blank (3s/b) were 0.05 and 0.3 µg L<sup>-1</sup>, respectively. The method was verified by analyzing a certified reference material. The proposed method was applied to the determination based on the speciation of chromium in various real samples with satisfactory results.

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## 1. Introduction

Toxic metal ions are major sources of pollution in environmental and water resources. Chromium is ubiquitous in nature, occurring in various chemically, physically and morphologically different forms. The metal ions may also enter tap water supply systems from the corrosion inhibitors used in water pipes and containers [1]. Chromium is one of the most abundant elements with the potential to contaminate groundwater, and so can be a major source of drinking water contamination [2,3]. Chromium is considered to be necessary for the production of electroplating and metal finishing processes, tanning of leather, and for the pigment and chemical industries [4]. Research purposes, industrial applications and ecotoxicological concerns are some of the fields in which the determination of chromium at trace levels has attracted considerable interest [1].

Toxicological studies have indicated that the degree of toxicity of metal ions depends on its chemical form. Chromium is mainly found

in solution form in two oxidation states, III and VI, both showing well differentiated chemical properties and environmental consequences [5,6]. Such difference in toxicity is one of the main reasons for the recent enormous development of analytical methods for differentiating the various forms of Cr existing in the medium of interest [7]. Chromium species can enter into the environment from their discharge [8]. 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 [9]. Chromium deficiency is associated with cardiovascular diseases and diabetes, while excessive amounts of this element, particularly in the more toxic Cr(VI) valence state, are detrimental to health as it may be involved in the pathogenesis of some diseases such as lung and gastrointestinal cancer [10]. The toxic nature of Cr(VI) is attributed to its higher oxidation potential and relatively smaller size, which enables it to penetrate through biological cell membranes. Moreover, in air, chromium particulates play an important role in the oxidation of sulfur dioxide, leading to the formation of acidic aerosols responsible for global acid rain [7]. Cr(VI) has an adverse impact on the liver, lungs, kidneys [2] and causes cancer by oxidizing biological species such as DNA and some proteins [3].

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Owing to these two contrasting effects, the precise and accurate determination of Cr(VI); especially at ultratrace levels; in environmental samples is urgently required for environmental protection, food and agricultural chemistry. However, the direct determination of Cr(III) and Cr(VI) at ultratrace levels is limited due to their low concentrations. Therefore, in ultratrace analysis, a preconcentration/separation is necessary to improve sensitivity and selectivity of determination [11]. Various preconcentration techniques such as solvent extraction [9,10], ion-exchange [12], cloud point extraction [13], hollow fiber microextraction [14], and solid phase extraction [5,15] have been applied for the extraction of trace levels of chromium ions from environmental samples. Flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma–mass spectrometry (ICP-MS) can only yield the total amount of chromium. As a result, preliminary species separation and preconcentration are required before the determination of analytes by any of the techniques mentioned above [6].

Flow injection analysis (FIA) has appeared as a powerful tool for on-line operations such as separation/preconcentration [16,17]. On-line solid phase extraction (SPE) may be used in order to improve the sensitivity and selectivity of FAAS. In addition it has some extra advantages: large availability, easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation using various flow injection systems [18–21].

Chelating sorbents can provide a better separation of interfering ions, high efficiency and higher rate of process, and the possibility of combining with on-line SPE–FAAS [22]. Chelating resins are typically characterized by functional groups containing O, N, S and P donor atoms which coordinate to different metal ions [23,24]. Ion exchange resins are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers) [25]. Metal separation in aqueous solutions by using adsorbents is also very important.

In this study, the synthesized chelating resin, poly 2-(5-methylisoxazol) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene [MIAAm/AMPS/DVB] [5] and Dowex 21K as ion-exchange resin were used for the separation, preconcentration and speciation of Cr(III) and Cr(VI), respectively. Using the new flow injection (FI) system which combined a solid phase extraction procedure and FAAS technique, the analyte ions in aqueous solutions were sequentially determined. The accuracy of the method was verified by analysis of a certified reference material (CWW-TMD wastewater) and recovery measurements made with spiked natural water samples. The results showed good agreement with the certified value and the recoveries were sufficiently high.

## 2. Experimental

### 2.1. Instrument

A Perkin-Elmer (Norwalk, CT, USA) model AAnalyst 800 flame atomic absorption spectrometer equipped with a deuterium background correction system and an air-acetylene burner was used for the determination of chromium. The wavelength used for chromium was 357.9 nm. A spectral bandwidth of 0.7 nm, acetylene flow rate of 1.4 L min<sup>-1</sup>, and nebulizer flow rate of 10.0 mL min<sup>-1</sup> were the conventional working parameters. For measuring pH values in the

aqueous phase, a Consort model C533 pH meter combined with a glass-electrode and a magnetic stirrer (Chiltern) were used.

The flow injection system comprises a peristaltic pump with variable speed (Watson-Marlow Inc., Wilmington, MA, USA), a multichannel peristaltic pump (Ismatec SA, Glattbrugg, Switzerland) furnished with silicone tubes to deliver all solutions, and two three-way valves (Cole-Parmer Inc. Co., IL, USA) to select solution ways. The peristaltic pumps (PP) and valves (V) are controlled by a five channel timer and each channel has 36 different timing periods adjustable with thumble switches. This unit was of home-made construction. The flow injection system was constructed using fittings, unions and tees made of plastic and high density polyethylene (HDPE) materials. The chelating resin and anion exchange resin (Dowex 21K) packed into the minicolumns (glass, 2.0 cm length and 0.2 cm i.d.) were used for the on-line separation/preconcentration and sequential speciation of the chromium ions.

### 2.2. Reagents and standard solutions

All reagents used were of the highest available purity and of at least analytical reagent grade (Merck, Darmstadt, Germany). Deionized pure water was used for the preparation of the stock solutions. Cr(III) and Cr(VI) stock solutions (1000 mg L<sup>-1</sup>) were prepared from Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and K<sub>2</sub>CrO<sub>4</sub>, respectively [5]. Test solutions were prepared from these stock solutions on a daily basis at pH 3.0 by adjusting with respect to the buffer solution. The following buffer solutions were used for the presented separation/preconcentration procedure: HCl/KCl buffer for pH 1.0–2.0; CH<sub>3</sub>COONa/CH<sub>3</sub>COOH buffer for pH 3.0–5.0; CH<sub>3</sub>COONH<sub>4</sub>/CH<sub>3</sub>COOH buffer for pH 6.0–7.0. A 3.0 mol L<sup>-1</sup> HNO<sub>3</sub> was used as eluent throughout the experiments.

Poly-2-(5-methylisoxazole) methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene, the chelating resin was synthesized according to the literature [5]. The adsorption capacity of the chelating resin for Cr(III) was 34.3 mg g<sup>-1</sup> and the binding equilibrium constant was 1.5 L mg<sup>-1</sup> [5]. Dowex 21K was purchased from Sigma-Aldrich. It is a strong base anion exchange resin (in Cl<sup>-</sup> form) and has quaternary amine functional groups. Its total exchange capacity is 1.2 eq L<sup>-1</sup> min<sup>-1</sup> and has excellent kinetics, excellent regeneration efficiency and outstanding physical stability [26].

The reusability of the resins (life-time) was also investigated using proposed minicolumn procedures. It was found that the life-time is quantitative without any loss in the recovery throughout the study. The both of the resins can be used for quantitative recovery of chromium ions even after 550 cycles. Therefore, the resins show better reusability and stability towards chromium ions.

### 2.3. Column preparation

The chelating and anion exchange resins were washed successively with 1 mol L<sup>-1</sup> HNO<sub>3</sub>, 1 mol L<sup>-1</sup> NaOH, acetone, ethyl alcohol and deionized water and were then dried in an oven at about 60 °C. The minicolumns made of glass were 2 cm in length and 0.2 cm in diameter contained 0.1 g of each resin in water suspension. The resin bed heights in the column were approximately 0.3 cm. The minicolumns were washed thoroughly with deionized water and then conditioned at the working pH 3.0 using the buffer solution.

### 2.4. Procedure for Cr(III) and Cr(VI)

First, the proposed method was tested by using model solutions before the application of the speciation procedure for Cr(III) and Cr(VI) ions to real samples. For that purpose, the pH of the test solutions including 0.1 mg L<sup>-1</sup> of Cr(III) and 0.6 mg L<sup>-1</sup> of Cr(VI) was adjusted to pH 3.0 using acetic acid/sodium acetate buffer. The minicolumn was conditioned by passing the buffer solution

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