



Selective determination of Cr (VI) by on-line solid phase extraction FI-SPE-FAAS using an ion exchanger resin as sorbent: An improvement treatment of the analytical signal



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ARTICLE INFO

Article history:

Received 14 June 2016

Received in revised form 20 July 2016

Accepted 13 August 2016

Available online 15 August 2016

Keywords:

Cr (VI) selective analysis

Flow injection

Flame atomic absorption spectrometry

Analytical signal processing

ABSTRACT

A flow injection (FI) technique based on an on-line solid phase extraction (SPE) coupled with flame atomic absorption spectroscopy (FAAS) to selectively quantify chromium (VI) in the presence of chromium (III) was developed. An anion exchanger was used as solid sorbent and the detection limit found was two order of magnitude lower than that expected quantifying by FAAS.

Until now, quantitative determinations in FAAS were carried out by measuring the height of the peaks rather than their area. In our hands, the software was reconfigured and the area under the peaks could be measured. Considering area instead of height, the enhancement factor increases from 6.7 to 360 (approx. 54 times) giving a detection limit of $0.034 \mu\text{g} \cdot \text{L}^{-1}$, lower than that obtained using much more expensive instruments such as electrothermal atomic absorption spectrometry (ETAAS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES), greatly enhancing the potential of this methodology for future use in speciation studies. The operation conditions were: pH 3, sample loading $50 \text{ mL} \cdot \text{min}^{-1}$, elution flow rate $7.5 \text{ mL} \cdot \text{min}^{-1}$. The anion exchanger lifetime was over 100 adsorption/desorption cycles. Anions commonly present in natural aqueous systems did not interfere in the chromium retention.

The accuracy was validated using a certified reference material (Fluka Analytical, QC3453).

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1. Introduction

Metals are common contaminants in water and accumulate in living tissues throughout the food chain. Due to biomagnifications, humans receive the maximum impact since they are at the top of the food chain [1]. Particularly, chromium is one of the major trace heavy metal pollutants in the environment [2]. It is well known that while Cr (III) is an essential nutrient required for sugar and fat metabolism, Cr (VI) is an extremely carcinogenic agent [3]. Therefore, it is essential to accurately define the individual quantity of Cr (VI).

Many modern instrumental techniques, such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) can only measure total amount of chromium. As a result, preliminary species separation is required before detection.

On the other hand, taking into account that a maximum chromium limit of $50 \mu\text{g} \cdot \text{L}^{-1}$ has been established by the World Health

Organization (WHO) for drinking water, to ensure reliability of results, an analytical technique with the detection limit at least one order $< 50 \mu\text{g} \cdot \text{L}^{-1}$ must be chosen.

The last three techniques mentioned above meet this objective but are very costly and require highly trained personnel for their use. On the contrary, FAAS is a much cheaper and simpler technique to operate. However, in this case, it is necessary to introduce a preliminary step of preconcentration to achieve the limits of detection required.

Flow injection analysis (FIA) [4] appeared as a powerful tool to perform these operations. Advantages of the method are the possibility of automation and the elimination of the usual drawbacks of the off-line work at the sub-ppb level.

Several systems involving different strategies have been described in the literature. Among these strategies, solid phase extraction (SPE) in packed micro-columns [5–17] and the precipitation, co-precipitation or complexation of the analyte followed by its collection on adsorbent resins [18–20], knotted reactors [21–23] and microextraction with ionic liquids [24,25] are the most popular.

Taking into account that in acidic aqueous medium, at low concentration, Cr (VI) exists as anion (HCrO_4^-), while at the same conditions Cr (III) exists as a positive ion, the use of an anion exchanger as solid

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sorbent for a FIA-SPE-FAAS experiment could be a good alternative for chromium speciation.

Until now, quantitative measurement in FAAS were carried out by measuring the height of the peaks rather than their area. This is because the configuration of the software does not allow collection of area. This limitation does not affect the analysis in the case of sharp peaks, but in the case of broad peaks, as those obtained in the elution profile of an ion exchanger, consider height rather than area for quantitation analysis results in low sensitivity essays [26–28].

This is probably the reason why ion exchangers, despite being the most obvious choice for speciation studies, have not commonly been selected for this purpose by the scientific community.

In our hands, the software of the FAAS was reconfigured in order to quantify considering the area of the peaks instead of their heights and drastic improvements in the figures of merit was achieved.

The main objective of this work is to present a novel strategy of analyses for a FIA-SPE-FAAS system which led us to quantify selectively Cr (VI) in presence of Cr (III) with a detection limit lower than that obtained using more expensive instrumental as electrothermal atomic absorption spectrometry (ETAAS) or inductively coupled plasma-atomic emission spectrometry (IPC-AES). The sorbent used was an anion exchanger synthesized in our lab from a commercial chloromethylated styrene-divinylbenzene resin.

The operation conditions as well as the influence of other anions in the efficiency of the process are discussed. The accuracy of the proposed method is demonstrated by the analysis of water certified reference material.

Details about handling the spectrometer's software are also described.

2. Experimental

2.1. Instrumentation and reagents

Total chromium concentration was determined on a nitrous oxide-acetylene flame type atomic absorption spectrometer (Model iCE 3000, Thermo Scientific).

Chloromethylated styrene-divinylbenzene resin (1% cross-linked, 50–100 Mesh, MW 10245, 2.5–4 mmol Cl·g⁻¹) and *N*-methyl-*D*-glucamine were purchased from Aldrich Chemical Company. Hydrochloric acid and nitric acid were purchased from Merck Company. Cr (III) solutions were prepared from 1000 mg·L⁻¹ Cr standard solution (Merck). Aqueous solutions of Cr (VI) were prepared from solid K₂Cr₂O₇ (Aldrich). Single element stock solution of H₂PO₄⁻ was prepared from solid KH₂PO₄ (Aldrich) and As (V) solutions were prepared from 1000 mg·L⁻¹ As standard solution (Merck).

Stock solution of synthetic river water was prepared from NaCl (Aldrich), NaF (Aldrich), NaHCO₃ (Aldrich) and Na₂SO₄ (Aldrich).

Unless otherwise specified, solutions were prepared with ultrapure water (18 MΩ quality). Dioxane was reagent grade (Aldrich) and used without further purification.

The standard reference materials (Fluka Analytical, QC3453), containing trace of Cr (VI) in water was used for the validation of the proposed method.

2.2. Synthesis and characterization of the anion exchanger

2.2.1. Synthesis

The anion exchanger (NMDG) (Fig. 1) was synthesized as described by Dambies [29], with modifications to the amine:polymer ratio and the reaction time. In this case, chloromethylated styrene-divinylbenzene resin (1.6 g) was placed in a 100 mL round-bottom flask, *N*-methyl-*D*-glucamine (3.8 g), dioxane (30 mL) and water (3 mL) were added and the mixture was refluxed for 30 h. After washing with water, resin was conditioned with HCl (1 M) and vacuum dried for 17 h at 60 °C.

2.2.2. Characterization

Nitrogen content was determined by elemental analysis performed on an Exeter CE-440 elemental analyzer (Coventry, UK). The result (2.56%; 1.83 mmol N·g⁻¹ of resin) was similar to that previously reported [29].

The total capacity was measured in a batch experiment. Resin (200 mg) was suspended in 50 mL of NaOH (aqueous solution, 25 mM) and the mixture was stirred at 400 rpm for 24 h. After that, the mixture was filtered off and the supernatant was titrated with HCl (aqueous 25 mM) using phenolphthalein as indicator.

2.3. Adsorption studies

2.3.1. Batch experiments

2.3.1.1. Maximum Cr (VI) adsorption. The resin (50 mg) was suspended in 100 mL of aqueous solution of Cr (VI) (50 mg·L⁻¹) and the mixture was stirred at 400 rpm for 24 h. After that, the mixture was filtered off and chromium concentration in the supernatant was determined by FAAS.

2.3.1.2. Effect of pH on the adsorption of Cr (VI). The effect of pH on the adsorption of Cr (VI) was studied in a pH range of 1.0–8.0 at 25 °C. 100 mL of an aqueous solution of Cr (VI) (50 mg·L⁻¹) was shaken with 50 mg of dry resin at 400 rpm for 24 h. The pH was adjusted using HCl (0.1 M) or NaOH (0.1 M). After filtration, total chromium was determined by FAAS.

2.3.2. Online preconcentration experiments

Preconcentration of Cr (VI) was performed by online flow-injection on a glass micro-column (i.d. 0.9 cm) (Sigma-Aldrich) filled with NMDG (250 mg). The system consisted in a peristaltic pump connected by tygon tubes to the micro-column and solenoid valves that are switched to lead the flow (Fig. 2). Time events during the preconcentration procedures are shown in Table 1.

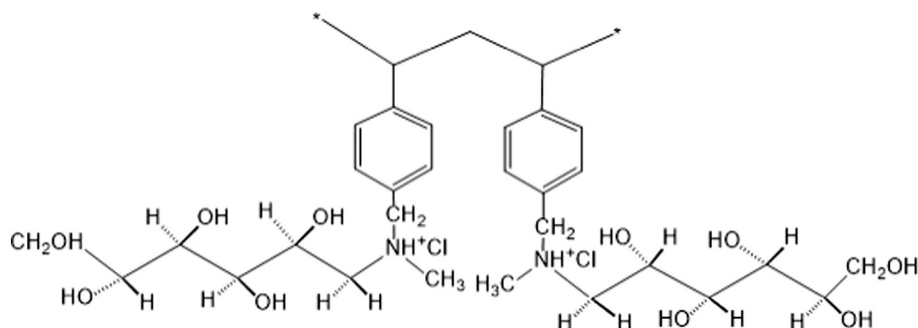


Fig. 1. Structural backbone of the ion-exchanger resin.

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