



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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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.

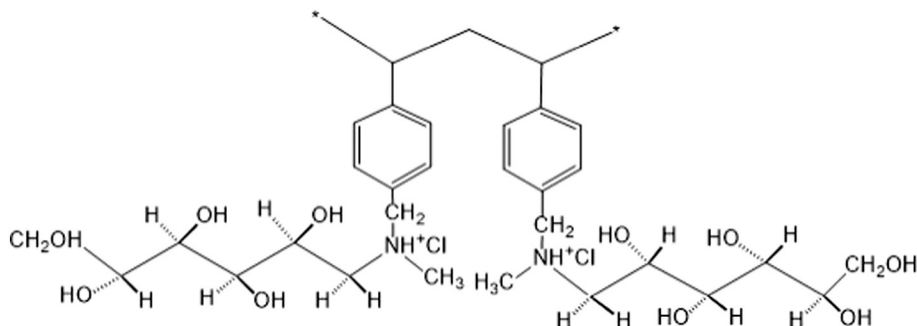


Fig. 1. Structural backbone of the ion-exchanger resin.

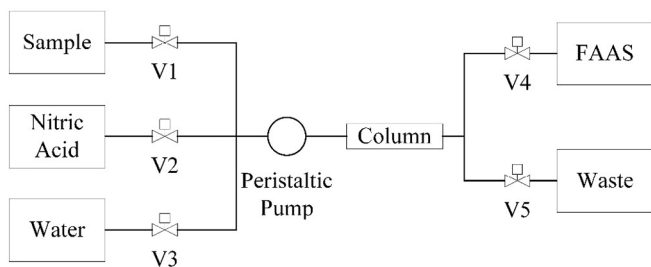


Fig. 2. Schematic diagram of the on-line flow injection preconcentration system.

2.3.3. Data collection and processing strategy

The spectrometer software was provided by Thermo Scientific (SOLAAR Data Station 11.00). In our hands, it was reconfigured in order to register the analytical signal once per second during the elution process. Registered values were exported to a data analysis and graphing software (Origin Pro 9.0.0). Plots of absorbance vs time were obtained and the curves were further integrated to obtain their corresponding areas (Fig. 3).

3. Results and discussion

3.1. Batch experiment

3.1.1. Effect of the pH on the adsorption of Cr (VI)

Fig. 4 shows that the efficiency of NMDG to adsorb Cr (VI) was maximum ($77.3 \text{ mg} \cdot \text{g}^{-1} \text{ resin}$) at pH 3. The decrease in the efficiency of the resin to retain Cr (VI) when pH was lower than 3, was attributed to the presence of oxidizable groups in the anion exchanger (hydroxyl and amino groups). The oxidation potential of Cr (VI) increases with the decrease of the pH, therefore, it turns very high at low values of pH. When chromium (VI) oxidizes organic matter, it is reduced to chromium (III) and desorbed from the exchanger. This effect was especially noticeable at pH 1.

Above pH 5, the retention efficiency of Cr (VI) decreases as pH increases. This result was expected considering that the ratio of protonated amino groups decreases with increasing pH [30].

3.2. On-line preconcentration experiments

3.2.1. Selection of FIA parameters

The effect of loading flow rate on the retention of chromium was studied in the range of $30\text{--}60 \text{ mL} \cdot \text{min}^{-1}$. A volumetric flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$ was chosen as the most advantageous since when it was higher than $50 \text{ mL} \cdot \text{min}^{-1}$, retention of chromium on the solid phase was not satisfactory.

Elution of Cr (VI) from the column was carried out with a nitric acid solution (2 M). Elution flow rate was fixed in $7.5 \text{ mL} \cdot \text{min}^{-1}$, according to the flow rate of the FAAS nebulizer.

Table 1
Times events of preconcentration procedure.

| Time (min) | Process | Description |
|------------|---------|---|
| 0–2 | Loading | The pump starts and the sample is sent into the column at a flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$. V1 and V5 valves are opened while the others are closed. |
| 2–7 | Elution | V1, V2, V4 and V5 valves are switched. Nitric acid elutes the chromium from the column into the FAAS at a flow rate of $7.5 \text{ mL} \cdot \text{min}^{-1}$. |
| 7–10 | Washing | V2, V3, V4 and V5 valves are switched. The column is rinsed with water at a flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$. |

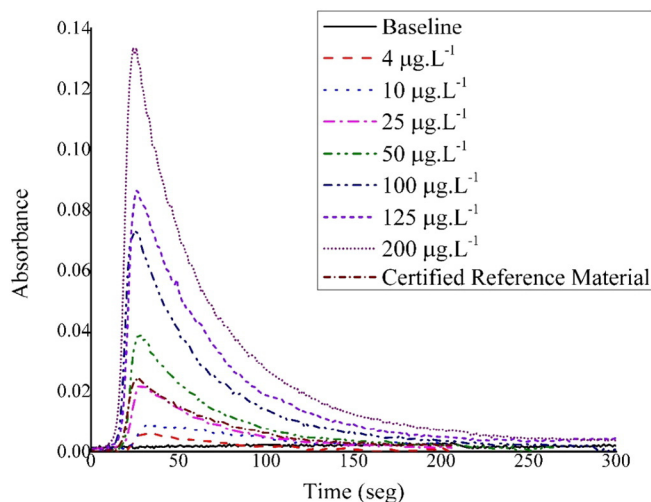


Fig. 3. Elution profile.

3.2.2. Analytical performance and method accuracy

As was discussed above, to quantify considering the area of the peaks, the spectrometer's software was reconfigured (see Experimental section).

The improvements in the figures of merit obtained by quantifying considering the area of the peaks instead of their height were dramatic (Table 2). The enhancement factor increases from 6.7 to 360 (approx. 5370% or 54 times), giving a detection limit of $0.034 \text{ } \mu\text{g} \cdot \text{L}^{-1}$, below those expected using more expensive instruments such as ETAAS or IPC-AES. Besides, significant improvements of the precision were also observed.

Under the conditions detailed in the experimental section, the analytical performance of the FI-SPE-FAAS method for selective Cr(VI) determination resulted as follows: the repeatability expressed as relative standard deviation (RSD) was 4.2% for ten replicate measurements of a $10 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ Cr(VI) solution. The limit of detection (LOD) calculated as the concentration associated with three times the standard deviation of 10 independent measurements of the procedural blank (3σ criterion) was $0.034 \text{ } \mu\text{g} \cdot \text{L}^{-1}$. The limit of quantification (LOQ) resulted to be $0.11 \text{ } \mu\text{g} \cdot \text{L}^{-1}$.

The calibration curve was linear from levels to the LOQ up to $500 \text{ } \mu\text{g} \cdot \text{L}^{-1}$. A good correlation coefficient has been obtained with $R^2 = 0.99895$ (Table 3).

Analysis of variance (ANOVA) was applied to fitted function, showing that lack of fit was significant ($p = 1.22 \times 10^{-8} < 0.05$).

The sample throughput depends on the mode operation and on the sample volume used for the analyte determination. Under the selected variables operations a sample throughput of 6 samples per hour was achieved.

To study the accuracy of the method, a certified reference material with chromium (VI) content of $32.0 \pm 1.62 \text{ } \mu\text{g} \cdot \text{L}^{-1}$, was analyzed. The result obtained ((mean \pm RSD, $n = 5$) $31.4 \text{ } \mu\text{g} \cdot \text{L}^{-1} \pm 6.2\%$) was in good agreement with the certified value. Additionally, the result was compared with the certified value using the Student's test. The calculated t was 0.69, which is lower than the t critical value (2.776), considering 95% of confidence level.

3.2.3. Selective quantification of Cr (VI) in the presence of Cr (III)

A solution of $25 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ of Cr (III) was investigated and, as expected, non-retention of chromium was observed. At acidic pH Cr (VI) at low concentration exists mainly as HCrO_4^- and this anionic form can strongly interact with the ammonium groups of the resin through electrostatic forces. On the contrary, ammonium ions will exert a repulsive force upon the positive species of Cr (III).

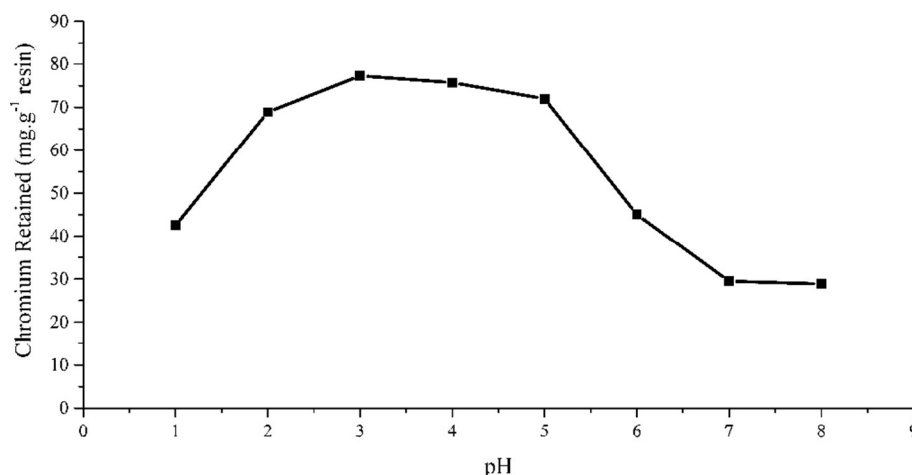


Fig. 4. Influence of the pH on the adsorption of Cr (VI).

When a solution composed of equal quantities of Cr (III) and Cr (VI) ($25 \mu\text{g}\cdot\text{L}^{-1}$ each) was evaluated, unsurprisingly, only $25 \mu\text{g}\cdot\text{L}^{-1}$ of chromium was measured, confirming the results of the previous study.

3.2.4. Interference studies

In order to evaluate the selectivity of the proposed system, the interference of H_2AsO_4^- and H_2PO_4^- was evaluated. Various amounts of ions were added to a $25 \mu\text{g}\cdot\text{L}^{-1}$ Cr (VI) standard solution and no obvious interference was observed at concentration up to $1000 \mu\text{g}\cdot\text{L}^{-1}$.

3.2.5. Analyses of real samples and recovery experiments

Synthetic river water [31], as well as tap water, were spiked with Cr (VI) solutions, in order to investigate the influence of the anions presents in these natural matrices in the efficiency of the adsorption process. As in the case of ultrapure water, retention of Cr (VI) was quantitative.

3.2.6. Regeneration cycles

In order to know the economic feasibility of this methodology, the maximum number of regeneration cycles of the resin before exhibited a decrease in its retention efficiency was studied. The anion exchanger lifetime was over 100 adsorption/desorption cycles.

Table 2

Comparison of the figures of merit obtained considering peak height or peak area.

| | Peak area | Peak height |
|--|------------------------|-------------------------|
| Regression equation (C in $\text{mg}\cdot\text{L}^{-1}$) | $A = 34.677 C - 0.018$ | $A = 0.6486 C + 0.0053$ |
| Correlation coefficient | 0.99895 | 0.99798 |
| Enhancement factor | 360 | 6.7 |
| Detection limit (3σ), $\mu\text{g}\cdot\text{L}^{-1}$ | 0.034 | 1.83 |
| Precision (RSD, n = 10), $10 \mu\text{g}\cdot\text{L}^{-1}$ | 4.2% | 9.15% |
| Upper linear range ($\mu\text{g}\cdot\text{L}^{-1}$) | 500 | 500 |

Table 3

Estimated parameters of the linear regression.

| Coefficient | Mean | Standard error | Confidence intervals ($\alpha = 0.05$) |
|-------------|--------|----------------|--|
| Intercept | -0.018 | 0.050 | -0.147 – 0.110 |
| Slope | 34.677 | 0.503 | 33.384 – 35.970 |

4. Conclusions

The methodology described in this article allowed us to quantify selectively chromium (VI) in presence of chromium (III) by FAAS with a detection limit two order of magnitude lower than that traditionally expected using this analytical technique. Even more, the detection limit was lower than that obtained using much more expensive instruments such as electrothermal atomic absorption spectrometry or inductively coupled plasma atomic emission spectroscopy. The key to achieve the goal was the reconfiguration of the software, what that enabled us to quantify on the basis of the peak area.

The anions commonly present in the water did not diminish the ability of the anion-exchanger to retain chromium (VI) which suggests that it is feasible the use of this material in complex aqueous matrices. The accuracy of the methodology was established analyzing certified water, with excellent results.

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