

Research Article

Selective Extraction and Determination of Chromium Concentration Using *Luffa cylindrica* Fibers as Sorbent and Detection by FAAS

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In this approach, a nonchromatographic method was developed for selective extraction and determination of Cr(III) concentration in isotonic and energy drinks by FAAS. This new method uses *Luffa cylindrica* fibers as the solid phase extraction and an off-line flow injection system. Cr(III) and Cr(VI) adsorption behavior onto *Luffa* fibers allowed the selective separation of Cr(III) in the pH range of 4 to 5. The system variables were optimized through full factorial and Doehlert designs. Under optimal conditions, the detection and quantification limit for Cr(III) was $19.2 \mu\text{g}\cdot\text{L}^{-1}$ and $63.9 \mu\text{g}\cdot\text{L}^{-1}$, respectively, with precision below 0.19%. A high tolerance toward interfering ions was observed for the proposed method. Recovery test results obtained for different isotonic and energy drinks samples were higher than 87.6%. The method's accuracy was confirmed through analysis of certified reference materials, water and sediment river samples (APS-1071 and APS-1066).

1. Introduction

Among the several oxidation states of chromium, trivalent and hexavalent states are the ones mainly present in the nature. Cr(VI) is toxic and abundant in contaminated waters and soils, while Cr(III) is naturally present in animal cells, exerting potentiating effect of insulin action, resulting in an improved uptake of glucose in the blood [1]. For this reason, research on the evaluation of chromium content in food has gained more importance.

Many food supplements manufacturers have started to enrich their products with chromium, and they are promising to their costumers benefits such as weight loss, muscle gain, and better physical performance [2], even in the absence of studies confirming these effects. Since the toxicity of Cr(VI) to humans is well established, studies concerning the determination of safety levels of Cr in food are usually directed to Cr(III).

Inductively coupled plasma spectrometry is the standard method for chromium determination in food analysis [3]; however, this is a high-cost technique, making the flame atomic absorption spectrometry (FAAS) an advantageous alternative.

Considering the toxicity of Cr(VI) to humans, a new analytical method for food analysis must be capable of quantifying the two states of chromium. Even for highly sensitive techniques, the redox speciation of chromium is possible by implementing a prior sample extraction procedure. Separation techniques based on the selective retention of chromium using adsorbents, such as solid phase extraction (SPE) are processes widely used to study chromium speciation [4, 5].

Alves et al. [6] developed a method for selective extraction of chromium in water using *Moringa oleifera* husks in solid-phase extraction with a flow injection system and detection by FAAS. It was concluded that Cr(III) and Cr(VI)

adsorption behavior onto *Moringa* husks allows the selective separation of Cr(III) in the pH range of 7 to 9 and Cr(VI) in the pH range of 1 to 2.

Luffa cylindrica is a herbaceous plant belonging to the order of Cucurbitales and the Cucurbitaceae family. Although its fibers have been used for removal of congo red [7] and cationic surfactant [8], for adsorption of phenol [9] and metallic ions, they have never been used in the development of nonchromatographic methods for metallic ion speciation.

Currently, it is produced in large scale in Brazil, being mainly used as natural bath sponges and as raw material in the manufacturing of insoles for shoes. Other properties and advantages, such as renewability, nonpollutant, high porosity, presence of polysaccharides and lignin in its composition, easy and low cost of production, make these fibers a promising material to be used as a natural adsorbent.

Thus, the purpose of this study was to use *Luffa cylindrica* fibers in the development of an off-line method for selective extraction of Cr(III) from isotonic and energy drinks and its concentration evaluation by FAAS.

2. Experimental

2.1. Instrumentation. A Varian flame atomic absorption spectrometer, model SpectrAA 220 (Victoria, Australia), equipped with a chromium hollow-cathode lamp and a deuterium lamp for background correction was used for chromium detection. The instrument was operated under the manufacturer's conditions: 7 mA lamp current, 357.9 nm wavelength, 0.1 nm slit width, 17 mm burner height, acetylene flow rate of $2.0 \text{ L}\cdot\text{min}^{-1}$, and air flow rate of $13.5 \text{ L}\cdot\text{min}^{-1}$. A Gehaka PG1800 pH meter was used to adjust the pH of the samples and working solutions.

2.2. Reagents, Solutions, and Samples. Plastic bottles used to store the solutions and glassware were previously cleaned in a 10% v/v HNO_3 bath for 24 h. Subsequently, the material was washed with deionized water and then dried at room temperature.

A $1000 \text{ mg}\cdot\text{L}^{-1}$ stock standard solution Cr(III) or Cr(VI) (Carlo Erba, Val de Reuil, France) was used to prepare the working solutions. Suprapur® nitric acid (65% v/v) from Merck (Darmstadt, Germany) was used to prepare the eluent solutions. All dilutions were carried out by adding ultrapure water obtained from a Milli-Q system.

Water and sediment river reference materials APS-1071 and APS-1066 from Alpha Resources (Stevensville, USA) were used for accuracy test. This certified material contains As, Ba, Cd, Cr, Pb, Hg, Se, and Cr in the concentrations 100, 50, 50, 100, 100, 20, 50, and $100 \mu\text{g}\cdot\text{mL}^{-1}$, respectively.

Isotonic and energy drinks samples were purchased in local stores and used for recovery tests.

2.3. Sorbent Preparation. The *Luffa cylindrica* fibers used to construct the minicolumn were obtained in local stores in the city of Catalão (state of Goiás, Brazil). They were previously washed with deionized water, dried at 25°C , then

crushed in a Black and Decker blender, and finally passed through a 2.0 mm nominal opening sieve.

Polyethylene tubes with 2.0 mm internal diameter and 3.2 mm external diameter were used to prepare the minicolumns, which were then sealed at their ends with glass wool to prevent loss of adsorbent through the flow system.

2.4. Preconcentration System. A Minipuls™ 3 peristaltic pump from Gilson (Villiers Le Bel, France) equipped with eight channels, Tygon®, and polyethylene tubes were used to pump the solutions through the minicolumn during the elution and extraction steps. The flow system was the same used by Araújo et al. [10], and it is briefly described below.

During the extraction step, the sample solutions are pumped through the minicolumn, and the effluent is discharged; in this step, the metallic ion is adsorbed in the *Luffa* fibers. In the elution step, the eluent percolates the column, generating the eluate (analyte and acid solution). In order to avoid progressive tightening of the packed column, the elution was performed in the opposite direction to the sample loading. Finally, the eluate is collected for further analysis by FAAS.

2.5. Optimization Strategy for Cr(III) Separation. The effect of pH solution on the Cr(III) and Cr(VI) adsorption was investigated by varying the pH from 1 to 10. The pH was adjusted by adding $0.1 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 or NH_4OH .

Fifty milliliters of two solutions (one for each species) were placed under stirring with 0.25 g of sorbent for 30 min, separately. After filtration, chromium species concentration was measured in the supernatant. The retained amount of chromium in the sorbent was calculated by the difference between the initial and final concentrations.

By knowing the pH where the Cr(III) selective extraction was possible, a 2^4 factorial design was used to evaluate the influence of the following factors: adsorbent mass, sample flow rate, concentration, and eluent volume, as their interactions in the system. In all performed experiments, the concentration of Cr(III) was maintained at $500 \mu\text{g}\cdot\text{L}^{-1}$, at pH equal to 4.0, and the volume of chromium solution that percolates in the column at 15.0 mL.

Adsorbent mass and eluent volume were significant variables in relation to flow system, and later a Doehlert design was used to optimize these variables.

2.6. Studies of Interfering Ions. The influence of other ions, which could be adsorbed on the minicolumn, was also investigated. The selection of concomitant ions and their proportions evaluation was based on the isotonic and energy drinks samples composition. These drinks are mainly composed of minerals such as Ca, Cu, Fe, K, Mg, Na, and Zn in concentrations around $1 \text{ mg}\cdot\text{L}^{-1}$, in addition to sugars and dyes.

The selectivity test was carried out through the preparation of binary solutions containing the possible interference ion and the analyte ($500 \mu\text{g}\cdot\text{L}^{-1}$); these solutions were further submitted to the flow system. The effect of each

interference ion was evaluated from the calculation of interference factor (IF) [11].

A specific test to evaluate the influence of Cr(VI) in the adsorption of Cr(III) in *Luffa cylindrica* fibers was made. Binary solutions containing a 1:1 Cr(III) and Cr(VI) ratio were prepared and subject to the extraction flow system.

3. Results and Discussion

3.1. Optimization of Chromium Separation. The effect of pH solution on the Cr(III) and Cr(VI) adsorption was studied using univariate analysis. It can be seen from Figure 1 that inorganic species of chromium are adsorbed differently by *Luffa cylindrica* fibers, evidencing its potential as a bio-adsorbent for selective extraction and determination of these species.

The maximum adsorption for Cr(VI) ions occurs at pH 1.0. This behavior may be due the fact that, under this condition, the sorbent is positively charged, while the HCrO_4^- is the predominant specie among all different species of Cr(VI) present in the aqueous solution [6]. No adsorption was observed at pH values higher than 2.0.

On the contrary, Cr(III)'s higher adsorption was observed in the pH range of 3 to 8. In this case, the formation of a double layer between the charged surface of sorbent and the polar medium might be the explanation for the higher adsorption [12]. At higher pH values, *Luffa*'s surface has negative charge, predominant forms of chromium in this pH range are also negative, and there was a decrease of Cr(III) ions adsorption. Thus, the occurrence of selective adsorption of *Luffa* by chromium inorganic species at pH 4.0 is evident.

After pH solution optimization, the significance of each operational parameter selected in the flow system (sample flow rate, adsorbent mass, volume, and eluent concentration) and their interactions in the extraction system were determined using 2^4 full factorial design. The minimum and maximum levels selected for each variable are shown in Table 1. Analysis of variance (ANOVA) was performed to determine whether the experimental factors studied were significant (at a p value of 0.05) in the performance of the system. The main effects and their interactions are presented in the Pareto chart shown in Figure 2.

It may be observed that no significant effect of interactions was observed in the Pareto chart. Neither the eluent concentration (3) nor the sample flow rate (2) was considered significant. Thus, since the eluent concentration has a positive effect (2.0302), higher analytical signals are obtained when this variable is maintained at its highest level ($1.0 \text{ mol}\cdot\text{L}^{-1}$). The sample flow rate has a negative effect (-0.3123), indicating that higher analytical signals are obtained if this variable is maintained at its lowest level ($2.0 \text{ mL}\cdot\text{min}^{-1}$).

Both the adsorbent mass (1) and the eluent volume (4) were considered significant at 95% confidence interval and both had a positive effect, indicating that better analytical signals are obtained when they are maintained at higher levels. A Doehlert design was applied to the values of these variables, making it possible to construct a response surface

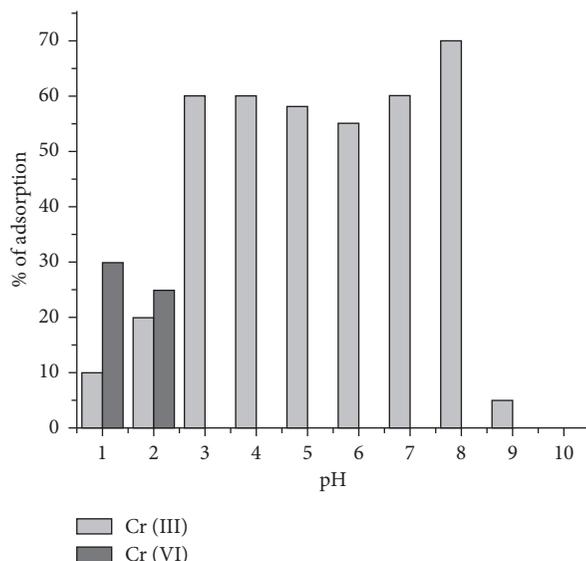


FIGURE 1: Evaluation of Cr species adsorption at different pH values.

TABLE 1: Tested conditions for Cr(III) adsorption in the study of multivariate optimization using SPE with a *Luffa cylindrica* fibers column and detection by FAAS.

Adsorbent mass (mg)	Sample flow rate ($\text{mL}\cdot\text{min}^{-1}$)	Eluent concentration ($\text{mol}\cdot\text{L}^{-1}$)	Eluent volume (μL)	Integrated absorbance
50	2	0.5	100	0.013
100	2	0.5	100	0.024
50	4	0.5	100	0.012
100	4	0.5	100	0.016
50	2	1.0	100	0.018
100	2	1.0	100	0.023
50	4	1.0	100	0.015
100	4	1.0	100	0.025
50	2	0.5	1000	0.015
100	2	0.5	1000	0.020
50	4	0.5	1000	0.024
100	4	0.5	1000	0.026
0	2	1.0	1000	0.022
100	2	1.0	1000	0.030
50	4	1.0	1000	0.025
100	4	1.0	1000	0.026

(Figure 3). The equation that describes the model is given as follows:

$$\begin{aligned} \text{absorbance} = & 0.003570 + 0.00007082 * (\text{eluent volume}) \\ & - 0.0000001 * (\text{eluent volume})^2 + 0.00002889 \\ & * (\text{adsorbent mass}) - 0.000000014896 \\ & * (\text{adsorbent mass})^2 + 0.00000006620 \\ & * (\text{eluent volume}) * (\text{adsorbent mass}). \end{aligned} \quad (1)$$

The Lagrange criterion was applied to confirm whether the critical point of the response surface corresponds to a

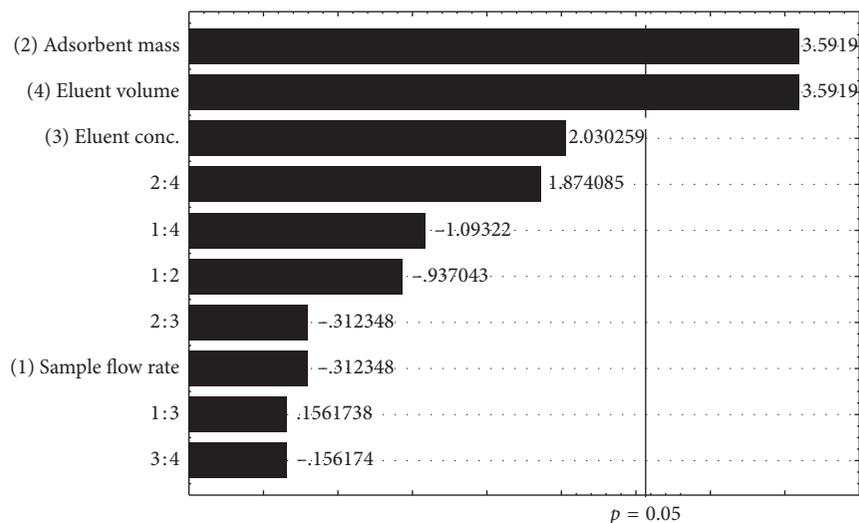


FIGURE 2: Matrix of full factorial design and the analytical response for each experiment for Cr(III) adsorption.

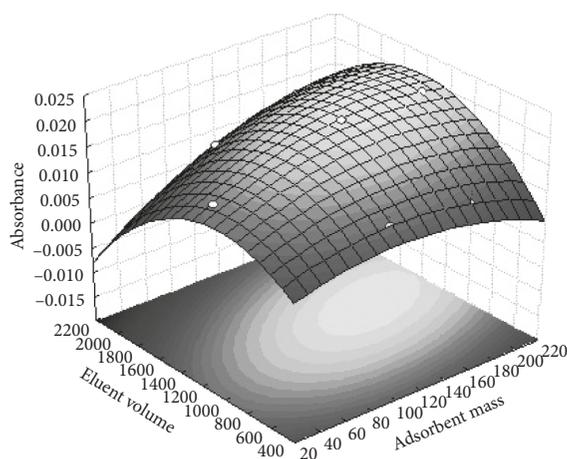


FIGURE 3: Response surface for optimization of adsorbent mass and eluent volume.

maximum. The critical point obtained was 170.0 mg and 1348 μL for adsorbent mass and eluent volume, respectively.

3.2. Studies of Interfering Ions. The effect of Cu^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ ions was assessed to identify their potential for interference on Cr(III) adsorption in the separation system under optimized conditions. The level of interference was obtained from the interference factor (IF), and the results are shown in Table 2. Thus, the interference factor, IF, is defined by the following equation: $\text{IF} = A'/A$, where A' and A are the values of the analytical signals for solutions of Cr(III) in the presence and absence of potential interferents, respectively.

According to the data, the tested ions did not present interference in the Cr(III) adsorption once all IF values obtained were below 1.10 or above 0.90. As understood from the results, the proposed method has strong selectivity, and the common ions have no interference effect on Cr(III) adsorption.

TABLE 2: Interference factor obtained to evaluate the influence of possible interfering ions.

Interferent ion	Concentration ($\text{mg}\cdot\text{L}^{-1}$)	I.F
Cu^{2+}	1.0	1.03
Fe^{3+}	0.5	0.92
Mn^{2+}	0.2	1.07
Zn^{2+}	1.0	1.00
Ca^{2+}	1.0	1.04
Mg^{2+}	1.0	1.07
Na^+	0.5	1.00
K^+	0.5	1.00

The concentration of Cr(III) in the presence of Cr(VI) was evaluated by constructing calibration curves after both species were subjected to the extraction flow system (Figure 4). After statistical analysis, no significant difference between the curves was found, showing that the separation of chromium inorganic species was efficient.

3.3. Analytical Features for Cr(III) Determination. After the system conditions were optimized, the main analytical features (detection limit and method repeatability) of the method were evaluated.

The detection limit was calculated as being three times the standard deviation of 15 independent measurements of a blank sample divided by the slope of the calibration curve [13]. For Cr(III), the obtained detection limit was $19.2 \mu\text{g}\cdot\text{L}^{-1}$. A satisfactory correlation coefficient was obtained (0.9977) for analytical signals observed experimentally until $2000 \mu\text{g}\cdot\text{L}^{-1}$ ($\text{Abs} = 4.36 \times 10^{-5} [\text{Cr(III)}] + 0.00175$).

The repeatability of the proposed method was assessed by performing ten consecutive preconcentration steps at $500 \mu\text{g}\cdot\text{L}^{-1}$ of chromium and expressing the result in terms of its relative standard deviation, the obtained value being 0.19.

3.4. Application of the Method and Recovery Tests. The proposed method was applied to isotonic and energy drinks purchased in local stores. To assess the analyte recovery, all

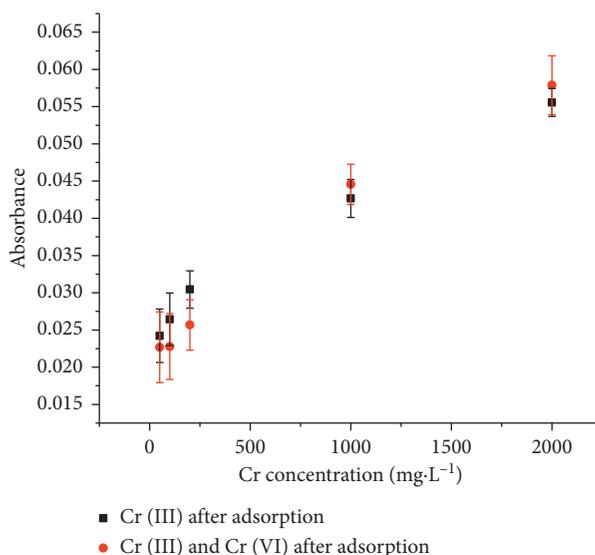


FIGURE 4: Evaluation of Cr(III) in the presence of Cr(VI).

TABLE 3: Relative recovery for the six samples of isotonic and energy drinks submitted to the proposed method.

Sample	Cr(III) mg·L ⁻¹		Recovery (%)
	Added	Found	
Isotonic drink 1	0.50	0.53 ± 0.0069	107.35
Isotonic drink 2	0.50	0.50 ± 0.0012	100.61
Isotonic drink 2	0.50	0.51 ± 0.0006	102.55
Energy drink 1	0.50	0.48 ± 0.0056	96.400
Energy drink 2	0.50	0.520 ± 0.0007	104.01
Energy drink 3	0.50	0.438 ± 0.0045	87.60

samples were spiked with Cr(III) solution at concentrations \pm mg·L⁻¹, and analytical curves were constructed to compare the slopes. The obtained results are shown in Table 3, where it can be seen that no difference between the recovery values for the samples was found, indicating that the analyte was quantitatively retained and eluted for all the evaluated samples.

Moreover, the accuracy was also checked by testing certified water sample (APS-1071) and river sediment certified sample (APS-1066), the results being summarized in Table 4. Once again, a good consistency between the results obtained in all instance can be observed, since the experimental values are consistent with the reference values, confirming the proposed method reliability.

3.5. Sorbent Stability. The results for sorbent stability indicate that the sorbent used to construct the column exhibits good stability in successive preconcentration/elution cycles using HNO₃ 1.0 mol·L⁻¹. The adsorbent presented stability for about 94 preconcentration/elution steps. These stabilities can be considered excellent when compared with other adsorbents [6].

4. Conclusion

The 2⁴ factorial design employed was very important because it allowed to establish the optimal eluent concentration and

TABLE 4: Analysis of reference materials.

Sample	Proposed method Cr(III) (mg·L ⁻¹)	Certified value Cr(III) (mg·L ⁻¹)
River water-1071	100.38 ± 0.014	100.00 ± 0.5
River sediment-1066	299.57 ± 0.006	300.00 ± 0.5

sample flow rate with greater separation efficiency by performing a smaller number of experiments, using less reagents and generating less residues, reducing the analysis cost and the environmental impact, confirming the concept of “Clean Chemistry”.

The procedure developed using SPE with detection by FAAS allowed the separation and direct determination of Cr(III) at the level of μ g·L⁻¹ in isotonic and energy drinks samples.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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