

## One-Pot Separation and Preconcentration for the Determination of Chromium Species Using an Aqueous Biphasic System

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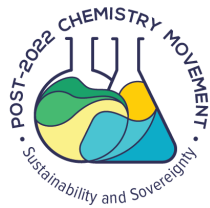
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The widespread use of the trace metal chromium in industrial processes and the known toxicity of Cr<sup>VI</sup> species have stimulated interest in chromium speciation analysis. However, some analytical detection systems are not suitable for the quantification of Cr<sup>III</sup> and Cr<sup>VI</sup> species. In the present study, an aqueous biphasic system (ABS) was employed as an environmentally safe, simple, and economical alternative. The ABS allows the implementation of an efficient separation step before quantifying of the species of interest by flame atomic absorption spectrometry. A robust speciation and preconcentration method was developed, which can be applied to samples with a wide concentration range, without the use of any extractants and interconversion of the species during the procedure. The proposed method was successfully used to determine the chromium species present in tap, treatment plant, river, and electroplating wastewater samples. Recovery percentages of 87.9-107% were achieved, suggesting minor water matrix interference. The proposed method had acceptable limits of detection and quantification of 5.38 and 16.3 µg kg<sup>-1</sup>, respectively.

**Keywords:** speciation, aqueous biphasic system, flame atomic absorption spectrometry, biphasic system, Cr<sup>III</sup>, Cr<sup>VI</sup>



### Introduction

Water is an essential natural resource for life on Earth. Water, when contaminated, can expose living organisms to various harmful pollutants and pathogens.<sup>1,2</sup> Several classes of water pollutants pose concerns, but heavy metals are particularly concerning as they are continuously being released as contaminants, have high solubility in aquatic environments, and can be gradually absorbed by living organisms, which may lead to their incorporation into the food chain.<sup>2,3</sup> These pollutants can bioaccumulate in organisms and may reach high toxic levels that can eventually endanger human health.<sup>2,3</sup> Global water pollution remains a pressing issue and therefore, must be addressed immediately.<sup>2</sup>

Chromium metal contamination has become a severe environmental problem.<sup>4,5</sup> Chromium mainly exists in two forms, Cr<sup>III</sup> and Cr<sup>VI</sup>, and the toxicity of each species depends on their specific oxidation states.<sup>3,4,6</sup> Cr<sup>III</sup> is relatively non-toxic and is an essential nutrient for humans, while Cr<sup>VI</sup> species are potentially mutagenic and carcinogenic agents.<sup>3,4,6</sup> They are widely used in industrial processes, such as metallurgy, electroplating, refractories, pigments, and leather tanning, making it easier to reach larger bodies of water and cause widespread harm to the environment.<sup>3,7,8</sup>

To mitigate this environmental problem, the Brazilian National Environmental Council (CONAMA) established maximum allowable concentrations for Cr<sup>III</sup> and Cr<sup>VI</sup> of 1.0 and 0.1 mg L<sup>-1</sup>, respectively, for effluent discharges in aquatic bodies.<sup>9</sup> For drinking water, the Brazil Ministry of Health and the World Health Organization (WHO) set the maximum allowable concentration for total

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chromium as  $0.05 \text{ mg L}^{-1}$ .<sup>10,11</sup> Meanwhile, the United States Environmental Protection Agency (EPA) established a total chromium concentration of  $0.1 \text{ mg L}^{-1}$ .<sup>12</sup> However, due to the carcinogenicity of  $\text{Cr}^{\text{VI}}$ , the current guideline value of  $0.05 \text{ mg L}^{-1}$  for this species is under debate. Hence, there is a need to accurately measure the impact of chromium on human health, other biological organisms, and ecological systems, and it is necessary to perform the speciation of  $\text{Cr}^{\text{VI}}$  and  $\text{Cr}^{\text{III}}$  species, i.e., the analytical and quantitative identification of the different chemical forms of chromium present in a sample. However, under typical conditions, traditional instrumentation techniques to determine metal ions, such as flame atomic absorption spectrometry (FAAS),<sup>13,14</sup> electrothermal atomic absorption spectrometry (ETAAS),<sup>15,16</sup> inductively coupled plasma optical emission spectrometry (ICP OES),<sup>17,18</sup> and inductively coupled plasma-mass spectrometry (ICP-MS),<sup>19</sup> have no selectivity for different valence states.<sup>20</sup>

Analytical methods have often been employed to allow the separation of the species of interest before quantification.<sup>4,5</sup> A common strategy to separate the more-toxic species from the less-toxic ones is the traditional liquid-liquid extraction (LLE).<sup>21-24</sup> LLE is simple and adaptable to different experimental conditions (e.g., analyte concentration, pH, and temperature), uses several extractants, and provides a method to separate and preconcentrate analytes. However, this technique has several drawbacks, such as a slow phase separation step when emulsions are formed and the use of large quantities of organic solvents that can be toxic, flammable, and volatile.<sup>25-28</sup>

Techniques such as LLE that use or generate hazardous substances are now being discouraged since these do not follow the concept of green chemistry. Green chemistry-or chemistry for sustainable development-is an emerging field whose ultimate goal is to develop correct scientific actions and/or safe industrial processes to protect the environment.<sup>29</sup> A promising alternative to the traditional LLE based on the principles of green chemistry is the aqueous biphasic system (ABS).<sup>26,30,31</sup> This system contains two immiscible aqueous-rich phases, which can be a mixture of polymer-polymer,<sup>32</sup> polymer-electrolyte,<sup>33</sup> or electrolyte-electrolyte<sup>34</sup> components that quickly form under specific conditions (e.g., temperature, pressure, and concentration). The ABS is currently at the forefront of safer extraction alternatives, consisting mainly of water and another component of polymers and/or electrolytes, all of which are non-toxic, non-flammable, and biodegradable.<sup>27,31,35</sup>

Studies have already demonstrated the efficiency of the ABS to speciate  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$ .<sup>35-38</sup> Some showed that the ABS could speciate chromium species without the use of any extractant, which is an economic and environmental

gain.<sup>35,37,38</sup> However, there are currently no studies on the potential of these systems for the preconcentration of analytes and determination of low chromium contents using a low-cost and robust instrumentation technique, such as FAAS.<sup>39</sup> In the current work, which is based on our previous paper,<sup>35</sup> we have developed a chromium speciation and preconcentration analytical method using the ABS-consisting of poly(ethylene oxide) (PEO) polymer, sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and water-without any organic solvent or auxiliary extractant, followed by FAAS for chromium determination. Factors affecting chromium speciation, such as the interconversion of the chemical species, analyte concentration, water matrices, and interfering ions, were investigated. The proposed green and facile method was successfully applied to the speciation of  $\text{Cr}^{\text{III}}$  and  $\text{Cr}^{\text{VI}}$  species in different types of water samples with significant results.

## Experimental

### Chemicals

All reagents were of analytical grade and were used as received without further purification. All experiments were performed using deionized water (Millipore Corp., Massachusetts, USA). The PEO polymer with an average molar mass of  $1500 \text{ g mol}^{-1}$ , denoted as PEO1500, was acquired from Synth (São Paulo, Brazil).  $\text{Na}_2\text{SO}_4$  and chromium chloride ( $\text{CrCl}_3$ ) were obtained from Vetec (Rio de Janeiro, Brazil). Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and 1,5-diphenylcarbazine extractant were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrochloric acid (HCl) was acquired from Merck (Darmstadt, Germany) and acetone was purchased from Alphatec (Rio de Janeiro, Brazil).

### Apparatus

Chromium determination were carried out using an ultraviolet-visible (UV-Vis) molecular absorption spectrometer (Shimadzu, 2550, Kyoto, Japan) at 540 nm and FAAS equipment (Varian, AA240, Melbourne, Australia). The following FAAS conditions were used: deuterium as the background correction, a wavelength of 357.9 nm, lamp current of 7.0 mA, and a slit width of 0.2 nm. The pH of the aqueous solutions was controlled using a pH meter (Metrohm, 827, Herisau, Switzerland) equipped with a combined glass electrode. An analytical balance (Shimadzu, AY 220, São Paulo, Brazil), centrifuge (Thermo Scientific, Heraeus Megafuge 11R, Osterode,

Germany), and thermostatic bath (Marconi, MA 184, São Paulo, Brazil) were used to prepare the ABS.

#### Composition of aqueous biphasic system

PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS with a tie-line length (TLL) of 46.97% (m/m) was used for chromium speciation and preconcentration. The system consisted of a top phase (TP) with 43.41% (m/m) PEO1500 and 1.46% (m/m) Na<sub>2</sub>SO<sub>4</sub> and a bottom phase (BP) with 1.03% (m/m) PEO1500 and 21.71% (m/m) Na<sub>2</sub>SO<sub>4</sub>.<sup>40</sup>

#### Influence of the concentration of chromium species on the extraction percentage

An aqueous HCl solution (0.0100 mol L<sup>-1</sup>, pH 2.00) was prepared using deionized water acidified with concentrated HCl. Appropriate quantities of PEO1500 (0.889 g), Na<sub>2</sub>SO<sub>4</sub> (0.463 g), and aqueous solutions of Cr<sup>III</sup> and Cr<sup>VI</sup> (2.65 g) at pH 2.00 were added to centrifuge tubes. The overall composition of the system was 22.2% (m/m) PEO1500, 11.6% (m/m) Na<sub>2</sub>SO<sub>4</sub>, and Cr<sup>III</sup> or Cr<sup>VI</sup> within the range of 4.00 to 600 mg kg<sup>-1</sup>. Blank assays were performed using an aqueous HCl solution (pH 2.00), without any chromium species. Each centrifuge tube was manually stirred for 3 min, centrifuged at 9503 g for 5 min, and placed in a thermostatic bath at 25.0 °C for 20 min. An ABS containing two phases with an equal mass of 2.00 g was obtained: a TP rich in PEO and a BP rich in Na<sub>2</sub>SO<sub>4</sub>. An aliquot of the TP was collected and diluted. Subsequently, FAAS measurements were performed to determine the concentration of the unknown chromium species extracted from the TP and BP after obtaining standard calibration curves (with a determination coefficient (R<sup>2</sup>) ≥ 0.999). To calculate the extraction percentage (%E), the following equations 1 and 2, were used:

$$E_{TP} (\%) = \frac{(n_{M^{x+}})_{TP}}{(n_{M^{x+}})_{Total}} \times 100 \quad (1)$$

$$E_{BP} (\%) = \frac{(n_{M^{x+}})_{BP}}{(n_{M^{x+}})_{Total}} \times 100 \quad (2)$$

where  $(n_{M^{x+}})_{TP}$  is the quantity of metal ions in the TP,  $(n_{M^{x+}})_{BP}$  is the quantity of metal ions in the BP, and  $(n_{M^{x+}})_{Total}$  is the total quantity of metal ions in the ABS. All experiments were performed in triplicate.

#### Aqueous biphasic extraction of Cr<sup>VI</sup> in the presence of Cr<sup>III</sup>

The ABS was prepared by mixing appropriate quantities

of PEO1500 (2.00 g), Na<sub>2</sub>SO<sub>4</sub> (1.04 g), aqueous HCl solution (0.0100 mol L<sup>-1</sup>, pH 2.0), and Cr<sup>III</sup> and Cr<sup>VI</sup> species (5.96 g) in a centrifuge tube, in triplicate. The overall composition of the system was 22.2% (m/m) PEO1500, 11.6% (m/m) Na<sub>2</sub>SO<sub>4</sub>, and 8.00 mg kg<sup>-1</sup> chromium species. Blank assays were also performed. Each centrifuge tube was manually stirred for 3 min, centrifuged at 9503 g for 5 min, and placed in a thermostatic bath at 25.0 °C for 20 min. Subsequently, two separate clear phases with the same mass of 4.50 g each were obtained. For the total chromium determination, TP and BP aliquots were collected, diluted, and the total chromium concentrations in the TP ( $C_{TP}^{Total}$ ) and BP ( $C_{BP}^{Total}$ ) were measured using FAAS. The Cr<sup>VI</sup> in the BP was determined using a UV-Vis spectrometer by reaction with 1,5-diphenylcarbazide in an acidic medium, as recommended by the Standard Methods for the Examination of Water and Wastewater.<sup>41</sup> The quantity of each chemical species in the TP and BP was calculated by subtracting the amount of Cr<sup>VI</sup>. Equations 1 and 2 were used to determine the %E of Cr<sup>III</sup> for TP and BP ( $\%E_{TP}^{Cr^{III}}$  and  $\%E_{BP}^{Cr^{III}}$ , respectively) and the %E of Cr<sup>VI</sup> for TP and BP ( $\%E_{TP}^{Cr^{VI}}$  and  $\%E_{BP}^{Cr^{VI}}$ , respectively).

#### Sample collection and metal quantification

Clean polyethylene bottles were used to collect water samples from our laboratory tap (Viçosa, Minas Gerais, Brazil), local wastewater treatment plants (WTP) (Viçosa, Minas Gerais, Brazil), and the Piracicaba River located near an industrial disposal site (Ipatinga, Minas Gerais, Brazil). The samples were filtered and acidified with concentrated HCl to pH 2.00. All samples were stored at 4 °C, and separate portions were allocated for chromium determination using FAAS. Wastewater samples from the electroplating industry (Ubá, Minas Gerais, Brazil) were also collected in clean polyethylene bottles, and the pH was measured. These samples were also stored at 4 °C and had separate portions allocated for the determination of Cr<sup>III</sup>, Cr<sup>VI</sup>, Cu<sup>II</sup>, Fe<sup>II</sup>/Fe<sup>III</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup> ions using FAAS.

#### Speciation and preconcentration of chromium species at low concentrations in water samples

First, measurements were performed to determine chromium species in the collected acidified water samples. Subsequently, the water samples were simultaneously spiked with Cr<sup>III</sup> and Cr<sup>VI</sup> species at different concentrations (Cr<sup>III</sup> = 0.500 and 1.00 mg kg<sup>-1</sup>, Cr<sup>VI</sup> = 0.0500 and 0.100 mg kg<sup>-1</sup>). The same process was performed using acidified deionized water as the blank. In separate vessels, PEO1500 (0.682 g), Na<sub>2</sub>SO<sub>4</sub> (13.1 g), and the spiked water

sample (46.2 g) were added. This procedure was performed and blank samples were prepared, both in triplicate, for the water samples from our laboratory tap, local wastewater treatment plants, and Piracicaba River. The vessels were manually stirred for 3 min and then placed in a thermostatic bath at 25.0 °C for 20 min. The obtained systems contained 1.40 g of TP and 58.6 g of BP. Aliquots from the TP and BP were collected, diluted, and subjected to FAAS to determine  $C_{TP}^{Total}$  and  $C_{BP}^{Total}$ . A similar ABS was prepared by adding only one chromium species, Cr<sup>III</sup> or Cr<sup>VI</sup>, and the concentrations of Cr<sup>III</sup> or Cr<sup>VI</sup> in the TP and BP were obtained using FAAS. The values of  $\%E_{TP}^{Cr^{III}}$ ,  $\%E_{BP}^{Cr^{III}}$ ,  $\%E_{TP}^{Cr^{VI}}$ , and  $\%E_{BP}^{Cr^{VI}}$ , were determined using equations 1 and 2.

### Speciation of chromium species at high concentrations in the electroplating wastewater samples

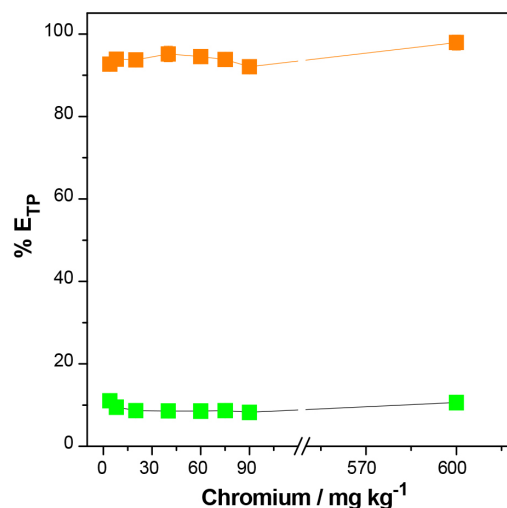
For the speciation of Cr<sup>III</sup> and Cr<sup>VI</sup>, PEO1500 (1.48 g), Na<sub>2</sub>SO<sub>4</sub> (2.12 g), and electroplating industry wastewater (4.40 g) were added to a centrifuge tube. The tube was manually stirred for 3 min, centrifuged at 9503 g for 5 min, and placed in a thermostatic bath at 25.0 °C for 20 min. An ABS was formed with equal mass phases of 4.00 g. TP and BP aliquots were collected and diluted. The total chromium, Cu<sup>II</sup>, Fe<sup>III</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup> concentrations in the TP and BP were then determined using FAAS. To validate the obtained results, the Cr<sup>VI</sup> concentration was measured using the standard method of Cr<sup>VI</sup> water analysis,<sup>41</sup> and the Cr<sup>III</sup> concentration was calculated by subtracting the Cr<sup>VI</sup> concentration from the total chromium concentration.

## Results and Discussion

### Influence of the concentration of chromium species on the extraction percentage

Based on our previous research,<sup>35</sup> we have demonstrated that ABS consisting of macromolecule (PEO 1500 or the triblock copolymer L64), electrolyte (Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>, or C<sub>4</sub>H<sub>4</sub>Na<sub>2</sub>O<sub>6</sub>) and water have potential to separated Cr<sup>III</sup> and Cr<sup>VI</sup> without the use of any organic solvent or extractant. Cr<sup>III</sup> favorably concentrated in the electrolyte-rich phase (BP) in these systems, while Cr<sup>VI</sup> preferred the polymer-rich phase (TP).<sup>35</sup> The separation process of the chromium species was affected by electrolyte nature, pH, polymer hydrophobicity and TLL.<sup>35</sup> Expressive results were obtained in PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS with a TLL of 46.97% (m/m).<sup>35</sup> This study aimed to determine the driving force of the extraction behavior of Cr<sup>III</sup> and Cr<sup>VI</sup> species and therefore it was not applied in real samples.<sup>35</sup> Fluorescence spectroscopy showed that the extraction

behavior of Cr<sup>III</sup> and Cr<sup>VI</sup> is governed by specific interactions that occur between the Cr<sup>VI</sup> species and the ethylene oxide (EO) groups of macromolecule, which are not observed for Cr<sup>III</sup>.<sup>35</sup> UV-Vis molecular absorption spectroscopy revealed that the high  $\%E_{TP}^{Cr^{VI}}$  is due to the presence of HCrO<sub>4</sub><sup>-</sup> species, predominant at pH 2.00.<sup>35</sup> It is well known that in addition to pH, the chromium concentration also affects the chromium species present in a solution.<sup>42,43</sup> Therefore, the effect on the aqueous biphasic extraction of Cr<sup>III</sup> and Cr<sup>VI</sup> species at different chromium concentrations using PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS was investigated (Figure 1).



**Figure 1.** Effect of chromium concentration on the extraction percentage (%E) of Cr<sup>III</sup> and Cr<sup>VI</sup> using PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS, pH = 2.00, TLL = 46.97% (m/m), T = 25.0 °C. (■) Cr<sup>III</sup> and (■) Cr<sup>VI</sup>.

When the concentration of Cr<sup>III</sup> and Cr<sup>VI</sup> increased from 4.00 to 600 mg L<sup>-1</sup>, the  $\%E_{TP}^{Cr^{III}}$  and  $\%E_{TP}^{Cr^{VI}}$  remained almost constant. This extraction behavior may be associated with the minimal changes in the form of the chromium species within the investigated concentration range. Therefore, the current method can also be applied to samples with a wider chromium concentration range.

Based on the study of da Silva and Loh,<sup>44</sup> Patrício *et al.*<sup>35</sup> suggested that the Cr<sup>VI</sup> extraction behavior is related to the formation of a pseudopolycation during phase separation. According to da Silva and Loh,<sup>44</sup> when polymer and electrolyte solutions are mixed, solvation waters of ions and macromolecules are released due to intermolecular interactions between the cations and the EO groups of the polymer. This enthalpic and entropic process ends when the polymer surface becomes saturated, preventing a further gain in the entropy arising from the release of water molecules. At this time, to decrease the Gibbs free energy of the system, phase separation occurs, producing a top phase enriched with macromolecules adsorbed by cations, and resulting in a positively charged polymer

surface called a pseudopolycation. Pseudopolycations can interact with negatively charged species through electrostatic interactions. Although almost all Cr<sup>VI</sup> species exist as anions, Patricio *et al.*<sup>35</sup> confirmed the preferential extraction of HCrO<sub>4</sub><sup>-</sup> ions. Therefore, the low %E<sub>TP</sub><sup>Cr<sup>III</sup></sup> can be attributed to the predominant formation of cationic complexes, which interact with the species present in the salt-rich phase (BP) and are electrostatically repulsed when in contact with pseudopolycations in the TP.<sup>35</sup> These results agree with other studies reporting that cationic species do not extract to the macromolecule-rich phase (TP) of the ABS.<sup>30,45-47</sup>

#### Aqueous biphasic extraction of Cr<sup>VI</sup> in the presence of Cr<sup>III</sup>

The chromium speciation procedure aimed to quantify and identify each species. However, a recurrent problem in the determination of chromium species is the interconversion between the Cr<sup>III</sup> and Cr<sup>VI</sup> forms.<sup>48,49</sup> Therefore, to perform the speciation of Cr<sup>III</sup> and Cr<sup>VI</sup> using the ABS, the stability of the species within the system was first examined. The %E of Cr<sup>III</sup> and Cr<sup>VI</sup> for the TP and BP when they were individually added to the ABS were compared to the %E of the chromium species when they were simultaneously added (Table 1).

The %E obtained when the chromium species were individually added in the ABS were similar to those obtained when chromium species were simultaneously added to the system. The comparable %E values when the chromium species were added using the two mechanisms and the calculated mass balance of each chromium species, which is close to 100%, show that the procedure does not cause interconversion between Cr<sup>III</sup> and Cr<sup>VI</sup>.

#### Speciation and preconcentration of chromium species at low concentrations in the water samples

For one-pot aqueous biphasic speciation, the first step was the addition of only Cr<sup>III</sup> or Cr<sup>VI</sup> to the preconcentration and speciation systems formed by PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS at pH 2.00. The ABS contained 1.40 g of TP and 58.6 g of BP. The analytes were determined using the non-selective, sensitive, and low-cost FAAS technique. The

FAAS performance was improved by the enrichment of Cr<sup>VI</sup> in the TP to achieve the allowable limits recommended by the Ministry of Health and WHO.<sup>10,12</sup>

The %E of each chromium species in the TP and BP was determined using equations 1 and 2: E<sub>TP</sub><sup>Cr<sup>III</sup></sup> = 0.0866%, E<sub>BP</sub><sup>Cr<sup>III</sup></sup> = 102%, E<sub>TP</sub><sup>Cr<sup>VI</sup></sup> = 20.4%, and E<sub>BP</sub><sup>Cr<sup>VI</sup></sup> = 73.2%. The %E values were then substituted into equations 3 and 4:

$$\%E_{TP}^{Cr^{III}} \times C_{Cr^{III}}^{ABS} + \%E_{TP}^{Cr^{VI}} \times C_{Cr^{VI}}^{ABS} = \frac{m_{TP} \times C_{TP}^{Total}}{m_{ABS}} \quad (3)$$

$$\%E_{BP}^{Cr^{III}} \times C_{Cr^{III}}^{ABS} + \%E_{BP}^{Cr^{VI}} \times C_{Cr^{VI}}^{ABS} = \frac{m_{BP} \times C_{BP}^{Total}}{m_{ABS}} \quad (4)$$

where C<sub>Cr<sup>III</sup></sub><sup>ABS</sup> and C<sub>Cr<sup>VI</sup></sub><sup>ABS</sup> are the Cr<sup>III</sup> and Cr<sup>VI</sup> concentrations in the ABS, respectively. m<sub>TP</sub>, m<sub>BP</sub>, and m<sub>ABS</sub> are the masses of the TP (1.40 g), BP (58.6 g), and ABS (60.0 g), respectively. C<sub>TP</sub><sup>Total</sup> and C<sub>BP</sub><sup>Total</sup> are the total chromium concentrations obtained using FAAS in the TP and BP, respectively. The resulting equations are expressed by equations 5 and 6:

$$0.000866 \times C_{Cr^{III}}^{ABS} + 0.204 \times C_{Cr^{VI}}^{ABS} = \frac{1.40 \times C_{TP}^{Total}}{60.0} \quad (5)$$

$$1.02 \times C_{Cr^{III}}^{ABS} + 0.732 \times C_{Cr^{VI}}^{ABS} = \frac{58.6 \times C_{BP}^{Total}}{60.0} \quad (6)$$

The known concentrations of Cr<sup>III</sup> and Cr<sup>VI</sup> in the spiked water samples are denoted as C<sub>Cr<sup>III</sup></sub><sup>Spiked</sup> and C<sub>Cr<sup>VI</sup></sub><sup>Spiked</sup>, respectively. To estimate the precision and accuracy of the proposed method, deionized water samples were spiked with the following chromium concentrations: C<sub>Cr<sup>III</sup></sub><sup>Spiked</sup> = 0.500 mg kg<sup>-1</sup> and C<sub>Cr<sup>VI</sup></sub><sup>Spiked</sup> = 0.0500 mg kg<sup>-1</sup>; C<sub>Cr<sup>III</sup></sub><sup>Spiked</sup> = 0.518 mg kg<sup>-1</sup> and C<sub>Cr<sup>VI</sup></sub><sup>Spiked</sup> = 0.100 mg kg<sup>-1</sup>; and C<sub>Cr<sup>III</sup></sub><sup>Spiked</sup> = 0.996 mg kg<sup>-1</sup> and C<sub>Cr<sup>VI</sup></sub><sup>Spiked</sup> = 0.100 mg kg<sup>-1</sup>. The PEO1500 + Na<sub>2</sub>SO<sub>4</sub> system with the spiked water samples at pH 2.00 was used to efficiently separate the more-toxic species from the less-toxic ones. The total chromium concentrations obtained using FAAS in the TP (C<sub>TP</sub><sup>Total</sup>) and BP (C<sub>BP</sub><sup>Total</sup>) were substituted in equations 5 and 6. Subsequently, the ABS concentrations, C<sub>Cr<sup>III</sup></sub><sup>ABS</sup> and C<sub>Cr<sup>VI</sup></sub><sup>ABS</sup> were obtained. Finally, the C<sub>Cr<sup>III</sup></sub><sup>ABS</sup> and C<sub>Cr<sup>VI</sup></sub><sup>ABS</sup> values were substituted in equations 7 and 8:

**Table 1.** Percentage extraction (%E) of Cr<sup>III</sup> and Cr<sup>VI</sup> obtained when the chromium species were individually and simultaneously added to PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS

Chromium species addition	E <sub>TP</sub> <sup>Cr<sup>III</sup></sup> / %	E <sub>BP</sub> <sup>Cr<sup>III</sup></sup> / %	E <sub>TP</sub> <sup>Cr<sup>VI</sup></sup> / %	E <sub>BP</sub> <sup>Cr<sup>VI</sup></sup> / %
Individual	8.1 ± 0.1	91.3 ± 0.3	92.5 ± 0.6	7.7 ± 0.4
Simultaneous	5 ± 1	96 ± 2	93.3 ± 0.2	6.7 ± 0.2

E<sub>TP</sub><sup>Cr<sup>III</sup></sup>: extraction percentage of Cr<sup>III</sup> for the top phase; E<sub>BP</sub><sup>Cr<sup>III</sup></sup>: extraction percentage of Cr<sup>III</sup> for the bottom phase; E<sub>TP</sub><sup>Cr<sup>VI</sup></sup>: extraction percentage of Cr<sup>VI</sup> for the top phase; E<sub>BP</sub><sup>Cr<sup>VI</sup></sup>: extraction percentage of Cr<sup>VI</sup> for the bottom phase.

**Table 2.** Determination of Cr<sup>III</sup> and Cr<sup>VI</sup> at different concentration ratios by the proposed method (n = 3)

Cr <sup>III</sup> :Cr <sup>VI</sup> ratio	Spiked / (mg kg <sup>-1</sup> )		C <sub>TP</sub> <sup>Total</sup> / (mg kg <sup>-1</sup> )	C <sub>BP</sub> <sup>Total</sup> / (mg kg <sup>-1</sup> )	Found / (mg kg <sup>-1</sup> )		Recovery / %	
	Cr <sup>III</sup>	Cr <sup>VI</sup>			Cr <sup>III</sup>	Cr <sup>VI</sup>	Cr <sup>III</sup>	Cr <sup>VI</sup>
5:0.5	0.500	0.0500	0.317 ± 0.009	0.48 ± 0.04	0.56 ± 0.05	0.045 ± 0.001	112 ± 10	90 ± 3
5:1	0.518	0.100	0.65 ± 0.01	0.469 ± 0.007	0.516 ± 0.008	0.096 ± 0.002	100 ± 2	96 ± 2
10:1	0.996	0.100	0.64 ± 0.03	0.866 ± 0.004	1.01 ± 0.01	0.092 ± 0.004	92 ± 4	102 ± 1

C<sub>TP</sub><sup>Total</sup>: total chromium concentration obtained using FAAS in the top phase; C<sub>BP</sub><sup>Total</sup>: total chromium concentration obtained using FAAS in the bottom phase.

**Table 3.** Determination of Cr<sup>III</sup> and Cr<sup>VI</sup> in water samples by the proposed method (n = 3)

Sample	Spiked / (mg kg <sup>-1</sup> )		C <sub>TP</sub> <sup>Total</sup> / (mg kg <sup>-1</sup> )	C <sub>BP</sub> <sup>Total</sup> / (mg kg <sup>-1</sup> )	Found / (mg kg <sup>-1</sup> )		Recovery / %	
	Cr <sup>VI</sup>	Cr <sup>III</sup>			Cr <sup>VI</sup>	Cr <sup>III</sup>	Cr <sup>VI</sup>	Cr <sup>III</sup>
Tap water	–	–	nd	nd	nd	nd	–	–
	0.0506	0.498	0.333 ± 0.009	0.39 ± 0.02	0.048 ± 0.001	0.45 ± 0.03	95 ± 3	90 ± 5
WTP	–	–	nd	nd	nd	nd	–	–
	0.0501	0.517	0.32 ± 0.01	0.47 ± 0.02	0.046 ± 0.002	0.55 ± 0.02	91 ± 3	107 ± 4
River	–	–	nd	nd	nd	nd	–	–
	0.0501	0.505	0.310.01	0.405 ± 0.005	0.044 ± 0.002	0.472 ± 0.007	88 ± 4	94 ± 1

nd: not detected; WTP: wastewater treatment plants; C<sub>TP</sub><sup>Total</sup>: total chromium concentration obtained using FAAS in the top phase; C<sub>BP</sub><sup>Total</sup>: total chromium concentration obtained using FAAS in the bottom phase.

$$C_{Cr^{III}}^{ABS} \times m_{ABS} = C_{Cr^{III}}^{Found} \times m_{Add} \quad (7)$$

$$C_{Cr^{VI}}^{ABS} \times m_{ABS} = C_{Cr^{VI}}^{Found} \times m_{Add} \quad (8)$$

where  $m_{Add}$  is the mass of the sample added in the ABS, while  $C_{Cr^{III}}^{Found}$  and  $C_{Cr^{VI}}^{Found}$  are the concentrations of Cr<sup>III</sup> and Cr<sup>VI</sup> in the water samples calculated using the proposed method in this study, respectively.

Under the optimized conditions, the recovery percentages (%R) and relative standard deviations (RSDs) of the chromium species were calculated (Table 2). The %R ranged from 90 to 112%, with RSDs between 1 and 10%. These results show that the proposed method can be applied in the determination of chromium species using an ABS and FAAS. The quantitative %R of each chromium species was also measured at different Cr<sup>III</sup> to Cr<sup>VI</sup> ratios, suggesting that the variation in the chromium concentration of the system does not affect the recovery of the species.

Recovery experiments were also conducted for the tap, wastewater treatment plant, and Piracicaba River water samples spiked with known amounts of Cr<sup>III</sup> and Cr<sup>VI</sup> (Table 3). The Cr<sup>III</sup> and Cr<sup>VI</sup> concentrations were within the concentration limit recommended by national and international organizations.<sup>9-12</sup> The %R ranged from 88 to 107%, with RSDs between 1 and 5%. These findings suggest that the water matrix had little to no interfering effects during the analysis.

Speciation of chromium species at high concentrations in the electroplating wastewater samples

The proposed method was also applied for the determination of Cr<sup>III</sup> and Cr<sup>VI</sup> species in electroplating wastewater samples containing high chromium contents. In addition to chromium species, wastewater can contain other metal ions, such as Cu<sup>II</sup>, Fe<sup>II</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup>, which were determined using FAAS (Table 4).

**Table 4.** Determination of metal ions in electroplating wastewater by FAAS (n = 3)

Metal ion	Concentration / (mg kg <sup>-1</sup> )
Cr <sup>III</sup> + Cr <sup>VI</sup>	9630 ± 190
Cu <sup>II</sup>	106 ± 1
Fe <sup>II</sup> /Fe <sup>III</sup>	45.8 ± 0.3
Ni <sup>II</sup>	224 ± 2
Zn <sup>II</sup>	2.54 ± 0.03

The speciation of Cr<sup>III</sup> and Cr<sup>VI</sup> in electroplating wastewater samples was performed using PEO1500 + Na<sub>2</sub>SO<sub>4</sub> ABS and FAAS. The concentration of each species in the water samples was determined using equations 9, 10, 7, and 8, respectively.

$$0.925 \times C_{Cr^{III}}^{ABS} + 0.0805 \times C_{Cr^{VI}}^{ABS} = \frac{2.00 \times C_{TP}^{Total}}{4.00} \quad (9)$$

**Table 5.** Comparison between the proposed method and standard method for the determination of Cr<sup>III</sup> and Cr<sup>VI</sup> in electroplating wastewater (n = 3)

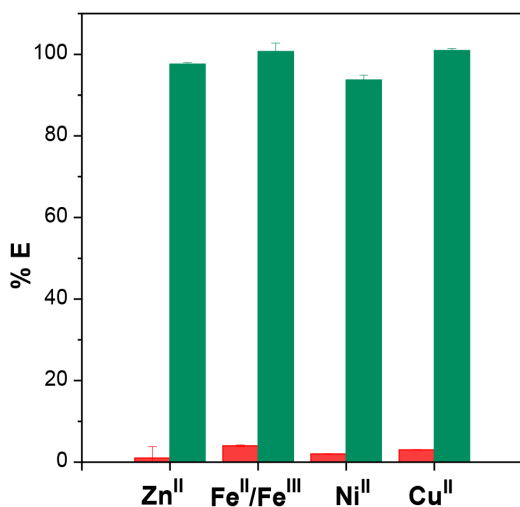
Species	C <sub>TP</sub> <sup>Total</sup> / (g t <sup>-1</sup> )	C <sub>BP</sub> <sup>Total</sup> / (g t <sup>-1</sup> )	Standard method / (g t <sup>-1</sup> )	Proposed method / (g t <sup>-1</sup> )	Error / (g t <sup>-1</sup> )
Cr <sup>III</sup>	10.5 ± 0.1	2.86 ± 0.05	1.92 ± 0.25	1.66 ± 0.05	-0.26
Cr <sup>VI</sup>			7.92 ± 0.05	8.41 ± 0.05	0.49

C<sub>TP</sub><sup>Total</sup>: total chromium concentration obtained using FAAS in the top phase; C<sub>BP</sub><sup>Total</sup>: total chromium concentration obtained using FAAS in the bottom phase.

$$0.0770 \times C_{Cr^{III}}^{ABS} + 0.913 \times C_{Cr^{VI}}^{ABS} = \frac{2.00 \times C_{BP}^{Total}}{4.00} \quad (10)$$

The experimental results obtained for the determination of Cr<sup>VI</sup> using the standard method and the proposed method are listed in Table 5. Based on the calculated values, the Cr<sup>III</sup> and Cr<sup>VI</sup> concentrations obtained from the proposed method are comparable to the values from the standard method.

High extraction of the Cu<sup>II</sup>, Fe<sup>II</sup>/Fe<sup>III</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup> ions to the BP, with E<sub>Cu</sub><sup>BP</sup> = 101 ± 0%, E<sub>Fe</sub><sup>BP</sup> = 101 ± 2%, E<sub>Ni</sub><sup>BP</sup> = 93.7 ± 1.1%, and E<sub>Zn</sub><sup>BP</sup> = 97.6 ± 0.4%, was achieved (Figure 2). It is generally known that without an extracting agent, metal ions spontaneously partition to the BP when extracted in an ABS because of the weak interaction between the ions and the macromolecule.<sup>46,47,50</sup> As a result, the polymer chain is free to interact with the predominant Cr<sup>VI</sup> species because the associated metal ions do not have a significant effect on the separation and determination of Cr<sup>III</sup> and Cr<sup>VI</sup> species in the electroplating wastewater samples.



**Figure 2.** Percentage extraction of Zn<sup>II</sup>, Fe<sup>III</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> in the presence of Cr<sup>III</sup> and Cr<sup>VI</sup> using PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS. (■) Top phase and (■) bottom phase.

#### Analytical figures of merit

Table 6 lists the analytical features of the proposed method. External calibration plots were constructed and excellent linearity was obtained, with a determination

coefficient of 0.999. Standard analytical curves with a linear range of 0.05 to 0.500 mg kg<sup>-1</sup> were used to determine the limit of detection (LOD) and limit of quantification (LOQ). The LOD and LOQ were calculated to be 3.3 × s/S and 10 × s/S, respectively, where s is the standard deviation of the ordinate intercept and S is the slope of the standard curve. The preconcentration coefficient (K) for spiked samples (n = 5, Cr<sup>VI</sup> = 10.0 mg kg<sup>-1</sup>) was determined using  $K = \frac{Q_{Cr}/Q_M}{Q_{Cr}^0/Q_M^0}$ , where Q<sub>Cr</sub> and Q<sub>Cr</sub><sup>0</sup> are the quantities of the chromium in the concentrate and in the sample, respectively, and Q<sub>M</sub><sup>0</sup> and Q<sub>M</sub> are the quantities of the matrix before and after preconcentration, respectively. The RSDs for five Cr<sup>VI</sup> extractions (n = 5, c = 0.0150 mg kg<sup>-1</sup>) and five Cr<sup>III</sup> extractions (n = 5, c = 0.0230 mg kg<sup>-1</sup>) were obtained. Recovery studies for Cr<sup>III</sup> and Cr<sup>VI</sup> were also performed for wastewater samples from treatment plants, the tap, and the Piracicaba River to estimate the accuracy of the presented procedure, expressed as %R (Table 6).

For comparison purposes, the figure of merit LOD of the proposed method and other already described in the literature are given in Table 7.

**Table 6.** Analytical figures of merit for the chromium speciation ABS-FAAS method

Parameter	
Linear range / (mg kg <sup>-1</sup> )	0.0500 to 0.500 or 0.100 to 4.00
LOD (n = 14) / (µg kg <sup>-1</sup> )	5.38
LOQ (n = 14) / (µg kg <sup>-1</sup> )	16.3
RSD (n = 5) / %	0.802 (Cr <sup>VI</sup> ) and 3.53 (Cr <sup>III</sup> )
K	5.87
R / %	88

LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation; K: preconcentration coefficient; R: recovery percentage.

## Conclusions

An environmentally friendly method was proposed for the speciation and determination of chromium species in different water samples. This method uses the PEO1500 + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O ABS at pH 2.00, 25.0 °C, and a TLL of 46.97% (m/m) to separate Cr<sup>III</sup> and Cr<sup>VI</sup> species. The ABS offers advantages, because it is an economical

**Table 7.** Comparison of the proposed method with other reported methods applied for the speciation analyses of chromium

Method	Matrix	LOD	Reference
SPE-FAAS	water, stream sediment, red lentil and vegetable capsules	7.7 µg L <sup>-1</sup>	51
UA-DES-ELPME-FAAS	water	5.5 µg L <sup>-1</sup>	52
USCPE-UV-Vis	water	12.0 µg L <sup>-1</sup>	53
DLLME-UV-Vis	water	7.48 µg L <sup>-1</sup>	54
LLE- handheld UV-Vis	water	7.5 µg L <sup>-1</sup>	55
LLE (traditional)-UV-Vis	water, tannery effluent and electroplating wastewater	80,0 µg L <sup>-1</sup>	22
ABS-AAS	water	60,0 µg L <sup>-1</sup>	38
ABS-FAAS	water	5.38 µg kg <sup>-1</sup>	this work

LOD: limit of detection; SPE-FAAS: solid phase extraction combined with flame atomic absorption spectrometry; UA-DES-ELPME-FAAS: ultrasound assisted-deep eutectic solvent based emulsification liquid phase microextraction method combined with microsample injection flame atomic absorption spectrometry; USCPE-UV-Vis: ultrasound-assisted cloud point extraction coupled with ultraviolet-visible molecular absorption spectrophotometry; DLLME-UV-Vis spectrometry: dispersive liquid-liquid microextraction combined with microvolume ultraviolet-visible molecular absorption spectrophotometry; LLE-handheld UV-Vis: liquid liquid extraction coupled with handheld CCD ultraviolet-visible molecular absorption spectrophotometer; LLE (traditional)-UV-Vis: traditional liquid-liquid extraction coupled with ultraviolet-visible molecular absorption spectrophotometry; ABS-AAS: aqueous biphasic system combined with atomic absorption spectrometry; ABS-FAAS: aqueous biphasic system combined with flame atomic absorption spectrometry.

alternative that uses only non-toxic, biodegradable, and recyclable components. Moreover, chromium measurements were performed using the non-selective and low-cost FAAS technique. ABS-FAAS coupling was also successfully employed for chemical speciation. It was shown that the speciation of Cr<sup>III</sup> and Cr<sup>VI</sup> was possible over a wide concentration range without the use of any extractant or interconversion of the species during the procedure. It was presented that the proposed method in this study is suitable for the determination of chromium species present in tap, treatment plant, river, and electroplating wastewater samples.

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