



Chromium speciation using aqueous biphasic systems: Development and mechanistic aspects



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ABSTRACT

The two principal oxidation states of chromium diverge significantly in their biological and toxicological properties, and it is very important to distinguish between them. Develop procedures that are efficient, fast, easier and cheaper for chromium speciation is an analytical challenge. Chromium speciation was investigated using aqueous biphasic systems (ABS) formed by polyethylene oxide (PEO1500) or a triblock copolymer (L64), an electrolyte (Li_2SO_4 , Na_2SO_4 , MgSO_4 , $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$, or $\text{C}_4\text{H}_4\text{Na}_2\text{O}_6$) and water, without the presence of any extractant. Cr(III) was favorably partitioned to the electrolyte-rich phase (ERP) of the ABS, whereas the Cr(VI) was preferentially concentrated in the macromolecule-rich phase (MRP) in most analyzed ABS. The fluorescence spectroscopy data revealed that the Cr(III) and Cr(VI) separation process is governed by specific interactions between the ethylene oxide segments in the macromolecules and the Cr(VI) species, which do not occur for Cr(III) species. The extraction percentage (%E) of chromium species from the ERP to the MRP was affected by pH, tie-line length (TLL), electrolyte nature, and macromolecule hydrophobicity. For the ABS comprising of PEO1500 + Na_2SO_4 + H_2O , TLL = 50.89% (m/m), 25 °C and pH 2.0, the %E values for Cr(III) and Cr(VI) were 0.0100 and 99.9%, respectively. The speciation of Cr(III) and Cr(VI) that was achieved in this ABS resulted in an excellent separation factor ($S_{\text{Cr(VI),Cr(III)}}$) of 1.00×10^8 .

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1. Introduction

Chromium is a trace element and highly reactive pollutant which spreads into ecosystems from a variety of industrial activities, such as electroplating, leather tanning, steel works, refractories, pigments, mining, textile dyeing, chromate preparation and timber processing companies [1–3]. Cr(III) and Cr(VI) are the most stable and prevalent forms of this element in the environment [3]. The toxicological as well as biological properties of chromium are known to depend strongly on its oxidation state [4]. Thus, the quantification of total chromium does not provide sufficient information for understanding its toxicity, bioavailability, biotransformation and dissemination routes [4].

Cr(III) is an essential nutrient for humans, playing a vital role in the metabolism of glucose, lipids, and proteins [1,2,4–6]. In contrast, the toxic form, Cr(VI), is a suspected carcinogen, inhibits enzymatic sulfur uptake in the cell and is harmful to the lungs,

liver, and kidneys [1,7]. Because of their toxicity differences, precise and reliable methods for the quantification of each species of chromium is more important than the total chromium measurement [4].

Many analytical techniques such as flame atomic absorption spectrometry (FAAS) [5,8–11], inductively coupled plasma–atomic emission spectrometry (ICP–AES) [12–14], inductively coupled plasma–mass spectrometry (ICP–MS) [15–17], electrothermal atomic absorption spectrometry (ET–AAS) [18–20] and luminescence spectroscopy [21,22] have been used for chromium determination. However, because these techniques determine only the total chromium, several additional procedures have been developed to separate the different chromium species to determine each species. These include liquid–liquid extraction [23–25], solid-phase extraction [8,9], solid-phase extraction using chelating resins [1,10], co-precipitation [5,11,26], high performance liquid chromatography (HPLC) [4,15,27], electromembrane extraction [27], chronoamperometric biosensors [28] and cloud-point extraction [2,18,20].

As some of these procedures have high operational costs, are time-consuming or make use of solvents that cause environmental

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problems, the development of a simple, inexpensive, and efficient procedure for the speciation of chromium is essential. The use of aqueous biphasic systems (ABS) or aqueous two-phase systems (ATPS) has the potential to be an interesting approach for chromium speciation. These systems do not use organic solvents; rather, they are based on green chemistry principles, are predominantly formed by water, and their minority components (polymers and electrolytes) are nonvolatile, recyclable, nonflammable and offer safety and cost benefits [29,30]. ABS have been applied in the separation of proteins [31,32], the determination of phenol compounds [33,34] and extraction of the dyes [35,36] and metallic ions [29,30,37–39].

Despite the importance of chromium speciation, only two studies have proposed the ABS as sample preparation step for the separation of chromium species. Akama and Sali [37] used the ABS formed by tetrabutylammonium bromide (TBAB) and $(\text{NH}_4)_2\text{SO}_4$ to suggest a selective extraction of Cr(VI) in the presence of Cr(III). The system was efficient to extract Cr(VI) for the TBAB rich phase while Cr(III) remained at $(\text{NH}_4)_2\text{SO}_4$ rich phase. The system pH from 1.0 to 9.0 was investigated and the pH range from 1 to 5 was efficient to extract Cr(VI) without interference from the coexisting Cr(III). The Cr(VI) extraction was attributed to the presence of HCrO_4^- ions and the ion pair formation as $\text{HCrO}_4^- \cdot \text{TBAB}^+$. However, the driving force of Cr(VI) extraction behavior was slightly investigated. The quantity of $(\text{NH}_4)_2\text{SO}_4$ added to the system was also examined and the results showed that the increase in the $(\text{NH}_4)_2\text{SO}_4$ amount improved the extraction of Cr(VI). This electrolyte addition results in an unknown ABS phase composition. Then, the authors not worked in defined tie-line lengths and could not determine the effect of ABS components concentration in chromium speciation procedure. Finally, Akama and Sali [37] did not evaluate the effects of the ABS components nature and restricted the investigation to only one system that included a toxic and expensive component (TBAB).

The other investigation of ABS as speciation tool was performed by Roy and Lahiri [39]. The authors used systems formed by a polymer poly(ethylene oxide) with average molar mass (MM) of 4000 g mol^{-1} and five ABS-forming electrolytes (Na_2CO_3 , NaOH, $\text{Na}_2\text{S}_2\text{O}_3$, Na_2HPO_4 , Na_2SO_4). The system constituted by Na_2SO_4 leads to the best condition to selective separation of chromium species. It was verified a great influence of the electrolyte anion in modulate the chromium speciation, but it was not studied the effect of electrolyte cations. The effect of pH range from 1.0 to 7.0, was also examined and at pH 3.0 Cr(VI) was quantitatively extracted to the macromolecule rich-phase (MRP) and Cr(III) remains at electrolyte rich-phase (ERP). The authors attributed the Cr(VI) extraction behavior to the formation of $\text{Cr}_2\text{O}_7^{2-}$ and the transference of Na^+ and K^+ as counter ion for the MRP. This hypotheses confronts the extraction mechanism proposed by Akama and Sali [37]. Then, it is necessary new researches to understand the mechanistic aspects of chromium extraction in ABS for future robust applications. Moreover, similarly to Akama and Sali [37], Roy and Lahiri [39] proposed the electrolyte addition to improve the Cr(VI) extraction. Despite the increment of the percentage extraction of Cr(VI) the present procedure leads to an ABS with indefinite phases composition and the authors also not assessed the effect of the phase components concentration in chromium speciation. Another research gap was the absence of ABS-forming polymer investigation.

The present work studies the influence of two new polymers, five electrolytes, and discusses the driving force behind the chromium speciation process in ABS. The extraction behaviors of Cr(III) and Cr(VI) species were investigated in different ABS composed of (i) polyethylene oxide with an average molar mass (MM) of 1500 g mol^{-1} (PEO1500), an electrolyte (Li_2SO_4 , Na_2SO_4 , MgSO_4 , $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$, or $\text{C}_4\text{H}_4\text{Na}_2\text{O}_6$), and water, or (ii) (polyethylene

oxide)₁₃-(polypropylene oxide)₃₁-(polyethylene oxide)₁₃ with an average MM of 2900 g mol^{-1} (L64), an electrolyte (Li_2SO_4 or Na_2SO_4) and water. The influence of a wider pH range, tie-line length (TLL), electrolyte nature (cations and anions) and polymer hydrophobicity on the %E of the ions were systematically investigated in order to study a chromium speciation in ABS. The procedure for chromium speciation is robust, and a quantitative separation of chromium species can be performed with different ABS systems without the aid of any extractant.

2. Experimental

2.1. Chemicals

All reagents were of analytical grade. Milli-Q deionized water (Millipore Corp., Massachusetts, USA) was employed in the preparation of all solutions. Copolymer L64, $\text{K}_2\text{Cr}_2\text{O}_7$ and metallic chromium were acquired from Aldrich (Wisconsin, USA). Cr(III) was obtained dissolving 0.0200 g of chromium metal in 0.500 g of 1:1 HCl with gentle heating. The solution was cooled and diluted to 2.000 g to give $10,000 \text{ mg kg}^{-1}$ Cr(III) stock solution. The polymer PEO1500 was purchased from Synth (Sao Paulo, Brazil). $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, Na_2SO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ and $\text{C}_4\text{H}_4\text{Na}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ were obtained from Vetec (Rio de Janeiro, Brazil). HCl and 1,5-diphenylcarbazide (DPC) were purchased from Merck (Darmstadt, Germany) and Fluka (Missouri, USA), respectively.

2.2. Aqueous biphasic system construction

The ABS compositions – L64 + Li_2SO_4 + H_2O [40], L64 + Na_2SO_4 + H_2O [40], PEO1500 + Li_2SO_4 + H_2O [41], PEO1500 + Na_2SO_4 + H_2O [41], PEO1500 + MgSO_4 + H_2O [41], PEO1500 + $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ + H_2O [42], and PEO1500 + $\text{C}_4\text{H}_4\text{Na}_2\text{O}_6$ + H_2O [42] – were obtained from the literature, and the TLLs are reported in Tables S1–S7. HCl and NaOH solutions in the pH range 1.0–11.0 were prepared from 12 mol L^{-1} HCl or 1.0 mol L^{-1} NaOH. The pH of the ABS was assumed to be equal to the pH of the HCl or NaOH solution. The pH was adjusted according to a pH meter (model Hi 221, Hanna Instruments, Brazil). To obtain the ABS L64 + Li_2SO_4 + H_2O with TLL = 21.51% (m/m), an NaOH or HCl aqueous solution was used as the solvent to prepare stock solutions of L64 at 25.49% (m/m) and Li_2SO_4 at 13.02% (m/m). All macromolecule and electrolyte stock solutions were prepared in this way, but at different pH and macromolecule and electrolyte concentrations, depending on the desired ABS and TLL. The ABS was obtained by mixing 2.00 g of the appropriate macromolecule stock solution and 2.00 g of electrolyte stock solution.

2.3. Extraction of the chromium species

To study the %E of the chromium species, each ABS was obtained by mixing 2.00 g of the macromolecule stock solution and 2.00 g of the electrolyte stock solution (containing chromium) with the assistance of an analytical balance (Model AY-220, Shimadzu, Brazil). The total chromium concentration in the ABS was 4.00 mg kg^{-1} . After mixing the macromolecule and electrolyte stock solutions, the system was manually stirred for 3 min, centrifuged (Heraeus Megafuge 11R, Thermo Scientific, Germany) at 9503g for 5 min and placed in a thermostatic bath (Model MQBTC 99-20, Microquimica, Brazil) at 25.0°C for 20 min. Two clear phases were observed. Aliquots from the MRP and/or ERP were collected and diluted, and the concentrations of Cr(III) and Cr(VI) were determined in triplicate by FAAS (Model AA240, Varian, Australia) against previously determined calibration curves ($R^2 \geq 0.999$). The chromium ions were determined with a deuterium background

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