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# Ultrasound-assisted dispersive liquid–liquid microextraction for the speciation of traces of chromium using electrothermal atomic absorption spectrometry

Ignacio López-García, Marisol Briceño, Yesica Vicente-Martínez, Manuel Hernández-Córdoba\*

Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, E-30071 Murcia, Spain

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## ABSTRACT

A microextraction procedure for the speciation of very low concentrations ( $0.005\text{--}0.2\ \mu\text{g L}^{-1}$ ) of chromium is discussed. To the aqueous sample (10 mL), diluted hydrochloric acid, sodium chloride and a small amount of tributylphosphate (80  $\mu\text{L}$ ) are incorporated, and the mixture is submitted to ultrasounds for 10 min. The organic phase recovered after centrifuging is injected into the electrothermal atomizer, and the signal due to hexavalent chromium obtained. The repetition of the procedure using another aliquot in which all the chromium present is oxidized to Cr(VI) allows the Cr(III) content to be obtained by difference. The enrichment factor is 240 and the detection limit  $0.002\ \mu\text{g L}^{-1}$  chromium. The relative standard deviation for ten consecutive microextractions of a  $0.1\ \mu\text{g L}^{-1}$  chromium solution is close to 8%. The procedure is applied to waters and to the leachates obtained from low cost toys made of plastic materials.

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## 1. Introduction

Chromium is an environmental pollutant resulting mainly from its use in steel making, nickel processing, electrocoating, wood protection, tannery and artificial fertilizers. [1]. The two main forms found in the environment are Cr(III) and Cr(VI), each having its own particular physiological effects [2]. While Cr(III) is considered an essential trace element for maintaining glucose, lipid and protein levels in mammals [3,4], the hexavalent form is toxic for biological systems. Indeed, soluble species of Cr(VI) are highly irritant and toxic for human tissues because of their high oxidation potential and the ease with which they cross biological membranes [5], which explains the enormous interest in developing sensitive and selective procedures for its determination [4].

The Environmental Protection Agency of the United States (EPA) recommends that the concentration of Cr(VI) in water destined for human consumption should not exceed  $100\ \mu\text{g L}^{-1}$ , and several states of the same country have set a maximum of

$50\ \mu\text{g L}^{-1}$ , which in others has been lowered to 0.2 and  $2.5\ \mu\text{g L}^{-1}$  for Cr(VI) and Cr(III), respectively. In some countries the maximum permitted concentration is  $20\ \mu\text{g L}^{-1}$  [6]. Of particular concern is the fact that oxides of chromium are used as pigments in paints, which may be used to decorate toys. Contact with these toys may provoke allergies and, if there is mouth contact (frequent in the case of infants) toxic forms of the metal may enter the organism.

The standard norms for toys (ASTM F963, EN71 and IS 8124-3) set the maximum level of total soluble chromium in painted toys at  $60\ \mu\text{g g}^{-1}$ , although the 88/378/EEC directive, revised in 2009/48/EC, has widened this to include more compounds and organic substances [7,8]. This directive distinguishes between Cr(III) and Cr(VI) depending on the material of which the toy is made. In the case of the hexavalent form, the maximum values that can pass into an aqueous solution are in the range  $0.005\text{--}0.3\ \mu\text{g g}^{-1}$ . Bearing all the above in mind, the objective of this work was to develop a sufficiently sensitive analytical method that allows the speciation of chromium in waters and in the liquid leached from toys without altering the original forms.

A wide repertoire of analytical techniques exists for determining low concentrations of chromium. These include atomic absorption spectrometry (AAS) [2], flow injection analysis combined with inductively coupled plasma mass spectrometry (ICP-MS) [9], liquid

\* Corresponding author. Tel.: +34 868887406; fax: +34 868887682.

E-mail address: [hcordoba@um.es](mailto:hcordoba@um.es) (M. Hernández-Córdoba).

URL: <http://www.um.es/aim> (M. Hernández-Córdoba).

chromatography [10] and the classical spectrophotometric procedure based on the reaction of Cr(VI) with 1,5-diphenylcarbazide [11].

As the assessment of chromium toxicity in solid [12] and liquid [13] matrices requires speciation studies, often involving very low concentrations, a preconcentration procedure is needed that will permit enrichment of the analyte while eliminating the matrix effect. Liquid–liquid extraction (LLE), probably the most widely used conventional procedure for preconcentrating analytes [14], usually requires large quantities of toxic organic solvents in processes that are time-consuming. In recent years the use of liquid–liquid microextraction techniques has attracted much interest since it works at a miniaturized scale, and so requires lower quantities of extractants/solvents [15]. For example, in the case of single drop microextraction (SDME) as little as 3  $\mu\text{L}$  are necessary [16] and using a hollow fiber as a support, it is possible to carry out liquid–liquid–liquid processes in which selectivity is further increased [17]. Dispersive liquid liquid microextraction (DLLME) is an interesting two step microextraction process, in the first of which a suitable mixture of extractant and dispersant is injected in an aqueous phase, thus originating a fine suspension of droplets of receiving phase, which, having a large contact area allows rapid transfer of the analyte. In the second step, a microvolume of the dispersed phase is collected, usually by centrifugation, and directly submitted to measurement in an appropriate detector [15,18–23]. In addition to the use of a dispersing organic solvent [24], other ways such as temperature control [25], ultrasounds [26], mechanical stirring [27] or the in situ formation of an ionic-liquid [28] allows suitable dispersions to be obtained.

This manuscript reports a new DLLME procedure for determining trace levels of Cr(VI) based on its interaction with tributyl phosphate (TBP) in acidic medium [29–31]. In this case dispersion is achieved by ultrasounds, no chemical dispersant being necessary. Since Cr(III) is not extracted, the procedure permits the speciation of the two forms of chromium at very low concentrations.

## 2. Experimental

### 2.1. Instrumentation

All the measurements were carried out with a model 600 atomic absorption spectrometer (Perkin-Elmer, Shelton, USA) equipped with a Zeeman-effect background correction device and a transversely heated graphite atomizer. Pyrolytic graphite platforms inserted into pyrolytically coated tubes were obtained from the same manufacturer (part number B050-4033). Argon flowing at 250  $\text{mL min}^{-1}$  was the inert gas. Measurements were carried out using a chromium hollow cathode lamp (Perkin-Elmer) as the radiation source. Integrated absorbance was always used as the analytical signal. The instrumental parameters are summarized in Table 1.

A 50 W ultrasound bath (ATU, Valencia, Spain) was used for the sample treatment.

### 2.2. Reagents and samples

All the solutions were prepared with pure water (18  $\text{M}\Omega\text{ cm}$  resistivity) obtained with a Milli-Q system (Millipore, Bedford, MA, USA). All the glassware and plasticware (polypropylene) was washed with 1% (v/v) concentrated nitric acid solution, and then rinsed with water before use.

The chromium (III) and (VI) stock standard solutions (1000  $\mu\text{g mL}^{-1}$ ) were prepared from  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  (Fluka, Buchs SG, Switzerland), respectively, in water, and diluted daily to obtain appropriate working solutions. Tributylphosphate

**Table 1**  
Instrumental parameters and furnace heating program.

Parameter			
Lamp current, mA	30 (HCL)		
Wavelength, nm	357.9		
Bandwidth, nm	0.7		
Atomizer	Platform		
Injected sample volume, $\mu\text{L}$	30		
Chemical modifier	None		
Background correction	Zeeman		
Furnace program			
Step	Temperature, ( $^{\circ}\text{C}$ )	Ramp, (s)	Hold, (s)
1: Dry	120	1	20
2: Dry	300	10	20
2: Ash	1200	10	15
3: Atomization <sup>a,b</sup>	2200	0	5
4: Clean	2600	1	5

<sup>a</sup> Stopped internal gas flow.

<sup>b</sup> Reading stage.

(TBP) was obtained of Sigma-Aldrich Chemie (Germany). The rest of the chemicals used were obtained from Fluka.

### 2.3. General procedure

To 10 mL of the sample solution containing chromium in the 0.005–0.2  $\mu\text{g L}^{-1}$  range, 1 mL of 5  $\text{mol L}^{-1}$  hydrochloric acid solution and 0.3 g sodium chloride were added. Next 80  $\mu\text{L}$  TBP were added and the mixture submitted to ultrasounds for 10 min. After centrifuging for 5 min at 4000 rpm, 30  $\mu\text{L}$  of the organic liquid were taken with a chromatographic-type syringe, injected into the electrothermal atomizer and the heating program (Table 1) was run. The signal in this way obtained corresponded to hexavalent chromium.

To determine the total chromium content, another 10 mL sample aliquot was taken, and a 0.03  $\text{mol L}^{-1}$  potassium permanganate solution was added dropwise until a slight pink color was observed. The aliquot in this way prepared was allowed to stand for 10 min and next the hydrochloric acid solution and sodium chloride were incorporated and the above described procedure was repeated. The analytical signal corresponded to the total chromium content which permitted the concentration of trivalent chromium to be calculated by difference.

### 2.4. Determination of chromium in water samples

Tap water was collected from the mains supply of the University of Murcia and was analyzed both directly and after passing through a domestic water purifier system. Five bottled water samples were purchased in a supermarket. The seawater samples were obtained from near the shore, close to a harbor in south-eastern Spain. These later samples were filtered and maintained in plastic containers at 4  $^{\circ}\text{C}$  until they were analyzed (less than 48 h) by the general procedure.

On the other hand, two standard reference materials, namely NIST 1640a (trace elements in natural water) and NASS-6 (seawater reference material for trace metals) with a certified content of total chromium were obtained of National Institute of Standards and Technology and National Research Council Canada, respectively.

### 2.5. Determination of chromium in the lixiviates of plastic toys

Ten toys made of plastic materials and of different shapes and colors were purchased in low-priced markets and submitted to a treatment regulated by the European Union [7,8]. For this purpose, the samples were first thoroughly washed with water and dried at

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