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

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ABSTRACT

A microextraction procedure for the speciation of very low concentrations (0.005–0.2 $\mu g\ L^{-1}$) of chromium is discussed. To the aqueous sample (10 mL), diluted hydrochloric acid, sodium chloride and a small amount of tributylphosphate (80 μL) 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 $\mu g\ L^{-1}$ chromium. The relative standard deviation for ten consecutive microextractions of a 0.1 $\mu g\ L^{-1}$ 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.

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 $\mu g\ L^{-1}$, and several states of the same country have set a maximum of 50 $\mu g\ L^{-1}$, which in others has been lowered to 0.2 and 2.5 $\mu g\ L^{-1}$ for Cr(VI) and Cr(III), respectively. In some countries the maximum permitted concentration is 20 $\mu g\ L^{-1}$ [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 $\mu g\ g^{-1}$, 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 0.005–0.3 $\mu g\ g^{-1}$. 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

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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 μL 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 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 MΩ 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 μg mL^{-1}) were prepared from $Cr(NO_3)_3 \cdot 9H_2O$ and $K_2Cr_2O_7$ (Fluka, Buchs SG, Switzerland), respectively, in water, and diluted daily to obtain appropriate working solutions. Tributylphosphate (TBP) was obtained of Sigma-Aldrich Chemie (Germany). The rest of the chemicals used were obtained from Fluka.

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, μL		30	
Chemical modifier		None	
Background correction		Zeeman	
Furnace program			
Step	Temperature, (°C)	Ramp, (s)	Hold, (s)
1: Dry	120	1	20
2: Dry	300	10	20
2: Ash	1200	10	15
3: Atomization [a,b]	2200	0	5
4: Clean	2600	1	5

[a] Stopped internal gas flow.
[b] Reading stage.

2.3. General procedure

To 10 mL of the sample solution containing chromium in the 0.005–0.2 μg L^{-1} range, 1 mL of 5 mol L^{-1} hydrochloric acid solution and 0.3 g sodium chloride were added. Next 80 μL TBP were added and the mixture submitted to ultrasounds for 10 min. After centrifuging for 5 min at 4000 rpm, 30 μL 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 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 southeastern Spain. These later samples were filtered and maintained in plastic containers at 4 °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 room temperature. Then, depending on the physical characteristics, they were broken into small pieces, or the superficial paint was scraped off, to be submitted to lixiviation with diluted hydrochloric acid. To portions (0.3 g) of the samples 15 mL of a 0.1 mol L^{-1} hydrochloric acid solution were added and the mixture magnetically stirred for 2 h at 37 °C. After filtration through a chromatographic type membrane, 10 mL of the supernatants were submitted to the general procedure.

3. Results and discussion

3.1. Optimization of the microextraction process

The literature reports [29] that Cr(VI) is extracted in acidic medium with a solution of TBP in hexane. The use of hydrochloric acid instead of sulfuric or nitric acid results in an improvement of the extraction yield. It has been suggested that chloride plays a relevant role in the process that has been schematized as:

$$HCrO_4^- + 2H^+ + Cl^- + nTBP_{(org)} \rightleftarrows [HCrO_3, nTBP]_{(org)} + H_2O$$

in which the value of n was experimentally found to be in the 2.3–3 range. The literature also reports that the extraction process improves when the TBP concentration increases [29]. With this in mind, preliminary experiments to maximize extraction were carried out using TBP as the organic phase directly instead of its solution in hexane, the extracts being injected into an electrothermal atomizer to obtain the analytical signal of chromium. As can be seen in Fig. 1 where some of these results are summarized, the extraction in the presence of hydrochloric acid instead of nitric acid was confirmed to be advantageous. Additional experiments were carried out incorporating sodium chloride in the solution in addition to hydrochloric acid. When the chloride concentration was increased to 0.7 M, the analytical signal reached a maximum. This beneficial effect did not occur when sodium chloride was replaced by sodium nitrate or sulfate, confirming the relevance of chloride in the extraction process. Consequently, for the rest of the experiments 0.5 M hydrochloric acid as well as solid sodium chloride were incorporated in the aqueous samples before extracting with pure TBP.

The effect of different periods of ultrasounds and temperature on the extraction of the complex has been studied. Fig. 2 shows the results obtained for the extraction of 0.1 μg L^{-1} Cr(VI) with TBP applying the proposed procedure. As can be seen, at room temperature, the signal was maximal and remains constant after 8 min of ultrasounds treatment. When the temperature of the water bath in which ultrasounds is applied was raised to 50 °C, the signal reached its maximum after 5 min, which was reduced to 3 min at 80 °C. In all cases the chromium solution was at working temperature before adding the TBP.

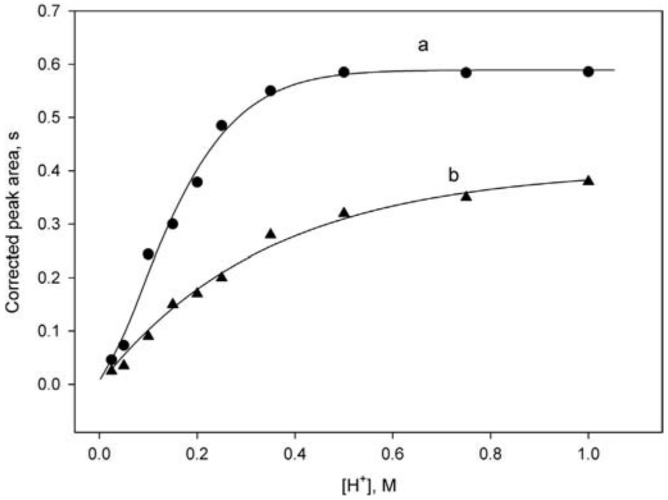

Fig. 1. Effect of the acidity on the analytical signal due to a 0.14 μg L^{-1} Cr(VI) solution submitted to the DLLME procedure. Curves a and b correspond to hydrochloric and nitric acid, respectively.

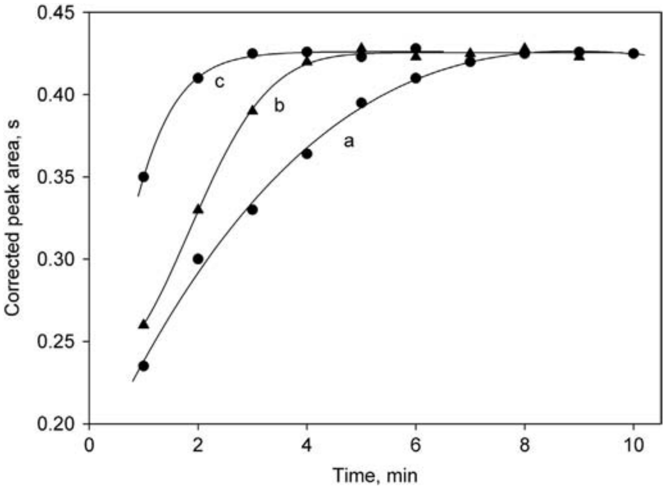

Fig. 2. Effect of the ultrasounds. Curves a, b and c correspond to room temperature, 50 °C and 80 °C, respectively. All the data were obtained with a 0.1 μg L^{-1} Cr(VI) solution submitted to the DLLME process.

The values of the signal shown in Fig. 2 have been corrected taken into account the change in the volumes due to the variation of the temperature. Indeed, as the temperature increases, the solubility of TBP in the aqueous phase also increases, which meant that a lower extract volume was obtained. During centrifugation the solution cooled down, and a slight opalescence was observed in the experiments carried out at the highest temperatures. This effect was not observed when ultrasounds were applied at room temperature. In light of these findings, application of ultrasounds for 10 min at room temperature is recommended.

To achieve separation of the disperse phase, the liquid was centrifuged at various speeds and times, and 4000 rpm for 5 min was found to be sufficient. It should be noted that although TBP is lighter than water and it remained on the aqueous phase, its presence as a well defined drop made it easy to withdraw by means of a micropipette or chromatographic syringe.

Since TBP is slightly soluble in water (approximately 6 g L^{-1} at room temperature) the volume of the organic phase remaining after the microextraction process was clearly below that initially added. It was experimentally found that when 10 mL aliquots of aqueous phase were extracted with 60, 80, 100, and 120 μL TBP, the volumes of organic phase recovered were 30, 42, 53, and 64 μL, respectively. The maximum volume that can be used in the final ETAAS measurement without a risk of overflowing the platform is 30 μL. Consequently, 80 μL are recommended for 10 mL of aqueous sample. In this way, 30 μL organic extract can be reliably taken by means of a chromatographic syringe, and injected in the atomizer. Experiments were made placing the organic liquid into small inserts situated in the autosampler of the spectrometer but repeatability did not improve over manual direct injection, which is consequently recommended.

On the other hand, it was experimentally verified that Cr(III) does not form a complex with TBP even at high concentrations, and this fact allows the procedure to be applied for speciation purposes. With this in mind, several of the ways described in the literature to oxidize Cr(III) to Cr(VI) were assayed at very low concentrations. The procedures involving hydrogen peroxide [32] and persulphate [33] in acid medium proved unsatisfactory due to incomplete oxidation even after 15 min of reaction. However, quantitative results were obtained with permanganate [34] after a 10 min reaction provide the medium has a pH above 5. Therefore the addition of permanganate 0.03 mol L^{-1} dropwise to the neutral solution until a slight violet color is obtained and letting the mixture stand for 10 min is recommended to obtain the complete transformation of Cr(III) into Cr(VI). The solution can next be acidified and the hexavalent chromium determined with TBP. It was checked that permanganate in excess did not interfere with the determination.

It should be noted that despite the minimal amount of TBP used, each measurement produces an aqueous waste containing a small amount of TBP. The organic reagent can be recovered by a treatment with a 0.5 mol L^{-1} sodium hydroxide solution, thus facilitating the environmentally friendly disposal of the wastes.

3.2. Optimization of the furnace heating program

TBP proved suitable for ETAAS measurements since the background signals during the atomization stage were low, and well defined absorbance-time atomization profiles were obtained. However, since its boiling point is relatively high (289 °C), a double drying stage was included in the heating program.

The ashing-atomizing graphs shown in Fig. 3A were obtained using platform atomization. Temperatures of 1200 °C and 2200 °C were finally selected for the calcination and atomization stages, respectively. In these experimental conditions the atomization profile was completely developed in less than 5 s (Fig. 3B), and the characteristic mass was calculated to be 8pg. Additional experiments confirmed that no chemical modifier was required.

3.3. Analytical figures of merit. Analysis of real samples

Using the optimized experimental conditions for the preconcentration procedure, a linear relationship between the analytical signal and the chromium concentration in the aqueous phase was found in the 0.005–0.2 μg L^{-1} range. The detection limit was calculated as the analyte concentration providing a signal of three times the standard error of the regression (S_{est}). The slope of a typical calibration graph was 4.28 s μg^{-1} L with an S_{est} value of 0.003, meaning a detection limit of 0.002 μg L^{-1}. The enrichment factor (EF) was calculated as the ratio between the slope of the calibration graph and the slope of another calibration graph obtained with samples that were not submitted to the microextraction procedure but directly measured. This EF was calculated to be 240, which, as can be seen in Table 2, is higher than most of those reported in the literature for other microextraction-based procedures for chromium determination. This value is close to that obtained from the volumes ratio, which suggests the extraction is practically total. This was verified experimentally by making two consecutive extractions of a same aqueous solution of Cr(VI). The results showed an extraction percentage close to 100% (99 ± 4).

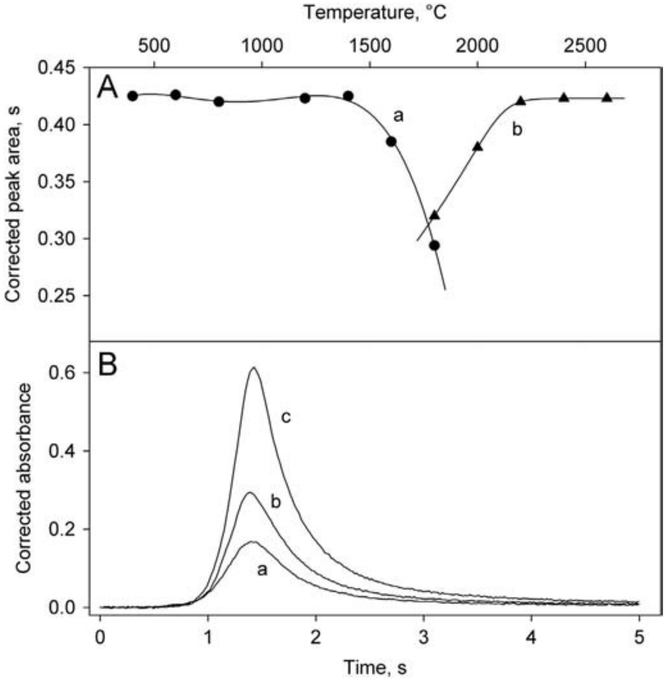

Fig. 3. Graph A: pyrolysis (curve a) and atomization (curve b) plots obtained from a 0.1 μg L^{-1} Cr(VI) solution; Graph B: atomization profiles obtained after the DLMME process. The initial aqueous solutions contained 0.03, 0.075 and 0.15 μg L^{-1} Cr(VI) (curves a, b and c, respectively).

The repeatability of the procedure was estimated in ten consecutive microextractions using a 0.1 μg L^{-1} chromium solution and relative standard deviations of 7.2 and 8.1% were obtained for Cr(VI) and Cr(III), respectively. The reproducibility was calculated from ten microextractions that were carried out using the same sample solution within a five-day period and values of 10.5 and 11.1% were obtained for Cr(VI) and Cr(III), respectively. In addition, microextractions were repeated decreasing the volume of the aqueous sample to 5 mL. In this case, the relative standard deviations for repeatability and reproducibility were 5.2 and 6.1% for Cr(VI) and 8.3 and 8.6% for Cr(III), respectively. To check the reliability of the procedure for speciation purposes, several experiments were carried out using different proportions of both species in the 0.01–0.1 μg L^{-1} range and the recoveries were in the 97–108% range ($n=5$). On the other hand, it is noteworthy that the entire procedure for speciation of a single sample requires about 45 min but the sample throughput may be improved since the ultrasound treatment can simultaneously be carried out with several samples.

The possible effect of ions commonly present in waters was also checked. Nitrate, sulfate, carbonate, calcium, magnesium and potassium did not affect the results even at the 0.1 mol L^{-1} level. A number of ions that could be co-extracted and originate interference were also checked. It was found that Pb(II), Ni(II), Co(II), Cd (II), Mn (II), Cu(II) and Ba (II) at the 1 g L^{-1} level (maximum concentration checked) had no effect on the results. As(III), As (V), Fe(III) and Se(IV) were tolerated up to 0.2 g L^{-1}. An interference was observed in the case of Sb(III) at concentrations higher than 0.01 g L^{-1}. This cannot be considered a serious problem since the Sb/Cr ratio is above 10000. Taking into account the results and the additional selectivity inherent in ETAAS measurements, the procedure was considered as suitable for the determination of traces of chromium in natural and potable waters.

3.4. Analysis of waters and lixiviates obtained from plastic toys

The procedure optimized was applied to the speciation of chromium in water samples of different origin and the results are shown in Table 3. Due to the very low concentrations of chromium involved, a comparison of the results with another procedure was considered unrealistic, and standard additions were used instead. In addition, two standard reference materials which have a certified content of chromium were used to check the reliability of the procedure. For these samples, namely NIST 1640a and NASS-6, the total contents of chromium were found to be 39.98 ± 0.12 and 0.119 ± 0.004 μg L^{-1} that agree with the certified values 40.54 ± 0.30 and 0.118 ± 0.008 μg L^{-1} respectively.

The practical usefulness of the procedure was also checked by applying it to the determination of the small quantities of chromium that can be released from toys made of plastic due to

Table 2
Characteristics of some microextraction procedures for chromium determination.

Species	Complexing agent	Technique	Aceptor phase	Detection	Lineal range, μg L^{-1}	EF	LOD, μg L^{-1}	Ref.
Cr(III), Cr(VI)	APDC	CPE [c]	Aliquat 336+Triton X-114	ICP-MS	0.1–10, 0.3–5	10	0.01, 0.025	[9]
Cr(VI)	APDC	SDME+SIA [a]	toluene	ETAAS	0.5–6	20	0.02	[16]
Cr(III), Cr(VI)	APDC	DLLME	$[C_8MIm]$ $[NTf_2]$	ETAAS	0.01–0.5	300	0.006	[28]
Cr(III)	no	CME [b]	ZrP	ETAAS	0.042–100	10	0.042	[35]
Cr(III), Cr(VI)	APDC	DLLME	Cl_4C	FAAS	0.3–20	270	0.08	[36]
Cr(VI)	APDC	USA-DLLME [d]	$[Hmin][PF_6]$	ETAAS	0.5–8	300	0.07	[37]
Cr(III)	no	SPME	SWCNTs [e]	FAAS	500–10000	30	4.08	[38]
Cr(VI)	Na-DDTC	DLLME	Cl_4C	ICP-OES	1–750	8	0.27	[39]
Cr(III)	PADAP [f]	SFO-DLLME [g]	1-undecanol	ETAAS	0.2–1.3 [h]	800	0.2 [h]	[40]
Cr(III), Cr(VI)	–	SFO-DLLME	TTA [i]	ETAAS	0.03–0.13	327	0.1	[41]
Cr(VI)	APDC	DLLME	Cl_4C	LA-ICP-MS [j]	0–250	154	0.1	[42]
Cr(III), Cr(VI)	DPC [k]	SALLME [l]	1-butyl-3-methylimidazolium tetrafluoroborate	FAAS	3–150	100	1.25	[43]
Cr(III), Cr(VI)	–	DLLME	TBP	ETAAS	0.005–0.2	240	0.002	This work

[a] Single drop microextraction and sequential injection analysis.
[b] Capillary micro-extraction with ZrP coated capillary.
[c] Cloud point extraction.
[d] Ultrasonic probe-assisted dispersive liquid–liquid microextraction.
[e] Single-wallet carbon nanotubes.
[f] 2-(5-bromo-2-pyridylazo)-5-(diethyl amino) phenol.
[g] Solidification of floating organic drop dispersive liquid–liquid microextraction.
[h] ng L^{-1}.
[i] 1-undecanol containing 2-thenoyltrifluoroacetone.
[j] Dried-Droplet Laser Ablation ICP-MS.
[k] 1,5-diphenylcarbazide.
[l] Salt-assisted liquid–liquid microextraction with ionic liquid.

Table 3
Determination of Cr(VI) and Cr(III) in water samples.

Sample	Cr(VI) [a] found, μg L^{-1}		Cr(III) [a], μg L^{-1}	
	Direct calibration	Standard additions	Direct calibration	Standard additions
Bottled mineral water 1	0.027 ± 0.003	0.025 ± 0.003	0.012 ± 0.002	0.014 ± 0.003
Bottled mineral water 2	0.029 ± 0.002	0.028 ± 0.007	< LOD	< LOD
Bottled mineral carbonated water 1	0.023 ± 0.002	0.024 ± 0.003	0.015 ± 0.002	0.011 ± 0.003
Bottled mineral carbonated water 2	0.009 ± 0.002	0.007 ± 0.002	< LOD	< LOD
Tap water	0.095 ± 0.005	0.092 ± 0.004	< LOD	< LOD
Tap water with reverse osmosis system	0.032 ± 0.004	0.029 ± 0.002	< LOD	< LOD
Sea water 1	0.037 ± 0.003	0.035 ± 0.003	0.028 ± 0.003	0.029 ± 0.002
Sea water 2	0.040 ± 0.003	0.042 ± 0.004	0.061 ± 0.003	0.059 ± 0.003
Sea water 3	0.148 ± 0.005	0.152 ± 0.005	0.041 ± 0.004	0.043 ± 0.003

[a] Mean value ± standard deviation ($n=3$).

Table 4
Leaching of chromium from toy samples.

Toy	Color	Found [a], ng g^{-1}	
		Cr(VI)	Cr(III)
Stained polymer	Yellow	3.6 ± 0.2	23.2 ± 0.3
Stained polymer	Pink	2.8 ± 0.2	5.1 ± 0.5
Stained polymer	Blue	2.3 ± 0.1	3.6 ± 0.2
Stained polymer	Pink	2.1 ± 0.1	2.5 ± 0.1
Painted surface	Yellow	2.7 ± 0.3	43.2 ± 0.7
Painted surface	Green	2.6 ± 0.2	7.7 ± 0.2
Painted surface	Pink	2.4 ± 0.2	4.5 ± 0.1
Painted surface	Brown	2.1 ± 0.1	3.6 ± 0.1
Painted surface	Purple	2.9 ± 0.2	2.9 ± 0.1
Painted surface	blue	2.2 ± 0.1	1.8 ± 0.2

[a] Mean value ± standard deviation ($n=3$).

the presence of the metal in the paints or additives used during manufacture. This is a subject of interest because children often suck such toys. The European Union has set limits for the maximum quantities that can be leached per gram of sample. The results obtained by using the standardized, regulated norm [7] are given in Table 4. All of them are below the legal limits.

4. Conclusion

The high enrichment factor achieved in the microextraction process together with the sensitivity inherent in ETAAS measurements results in a highly sensitive procedure for chromium. Additional advantages of the procedure are its simplicity, the feasibility of speciation at very low concentrations and the low cost of reagents and instrumentation. The DLLME methodology used is confirmed to be useful and relevant from a Green Chemistry perspective since it allows both a saving of reagents and a minimization of the wastes generated. However, the discontinuous nature of ETAAS renders automation difficult.

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