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Determination of lead and cadmium using an ionic liquid and dispersive liquid–liquid microextraction followed by electrothermal atomic absorption spectrometry

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A B S T R A C T

A procedure for the determination of ultratrace levels of lead and cadmium using dispersive liquid–liquid microextraction followed by electrothermal atomic absorption spectrometry (ETAAS) has been developed. The ionic liquid, 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_8MIm][NTf_2]), is formed *in situ* and used to extract the lead and cadmium complexes with ammonium pyrrolidinedithiocarbamate. The very fine droplets of ([C_8MIm][NTf_2]) allow effective dispersion without the need for organic solvents. After centrifugation, the concentrations of lead and cadmium in the sedimented phase can be determined by ETAAS. Using a 10 mL aqueous sample, the enrichment factor of the procedure was 280 and detection limits of 0.2 and 3 ng L^{-1} were obtained for cadmium and lead, respectively. The relative standard deviations for 10 replicates at the 10 ng L^{-1} cadmium and 0.2 μg L^{-1} lead levels were 6.5 and 7.3%, respectively. The method was successfully applied to the analysis of waters as well as to lixiviates obtained from toys made of plastic materials.

1. Introduction

Cadmium and lead are important metals from a public health point of view. Both are released to the environment from a large number of sources including hazardous waste sites, and as a result of burning fossil fuels, mining, smelting and other industrial activities. The presence of cadmium in water is mainly due to the corrosion of galvanized pipes, the discharge from metal refineries and runoff from waste batteries and paints, while lead in the water supply can be attributed the corrosion of household plumbing systems. Food and cigarette smoke are the primary sources of cadmium exposure for the general population. The primary target of both cadmium and lead toxicity are the kidneys, while lead is also a well-known neurotoxin [1].

The maximum permitted values of cadmium and lead in drinking water have been set at 5 and 15 μg L^{-1}, respectively, by the United States Environmental Protection Agency (EPA) [2], while the European Union (EU) has established limits of 5 and 10 μg L^{-1}, respectively [3]. Spanish legislation sets the same limit for cadmium [4] but 25 μg L^{-1} for lead, although this will be revised downwards in January 2014 as a result of EU legislation.

The bibliography mentions a wide variety of levels for both cadmium and lead in potable waters: 0.06–4.3 and 0.07–15.8 μg L^{-1}, respectively [5–7]. It is clear that the measurement of such low concentrations needs sensitive measuring procedures suited to the type of samples in question, among which can be counted FAAS [8,9], ETAAS [10,11], ICP-AES [12,13], ICP-MS [14–16] and voltammetry [17,18].

Electrothermal atomic absorption spectrometry (ETAAS) is suitable for the determination of trace levels of both metals. However, despite its sensitivity, it is necessary to include a preconcentration step due to the low levels present in drinking waters. Several procedures have been developed for this [19], including liquid–liquid extraction [20], coprecipitacion [21,22], ionic exchange [23], chelating resins [24] and solid phase extraction [25,26]. These approaches allow sensitivity to be increased although few of them can be considered as environmentally friendly as they use substantial amounts of organic solvents.

In recent years, several microextraction techniques involving minimal amounts of organic solvents have been proposed for preconcentration purposes: bioabsorption [27], the use of other absorbents [28], cloud point extraction (CPE) [29,30], single drop microextraction (SDME) [31–33], liquid phase microextraction [34] and hollow fiber liquid phase microextraction (HF-LPME) [35,36].

Among the different microextraction techniques developed, dispersive liquid–liquid microextraction (DLLME) [37] shows

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excellent enrichment characteristics and is very fast. In this technique, analyte extraction is practically instantaneous because of the enormous contact surface between the receptor and donating phases. To achieve dispersion a third solvent can be used in both phases [38] and ultrasounds [39].

In recent years there has also been a growth of interest in replacing volatile organic solvents by ionic liquids (ILs), which possess many of the advantages of classic organic solvents, and also have low vapor pressure and good thermal stability [40–43]. Such characteristics have frequently led to conventional organic solvents being replaced by ILs in microextraction processes, including DLLME procedures. The most widely used IL dispersion strategies have been based on temperature control [44], ultrasounds [45], shaking [46] or the use of disperser solvents [47]. However, ILs present their own associated problems in that they may be difficult to introduce into the instruments for measurement.

In this paper, an IL-DLLME procedure is used for the determination of very low concentrations of lead and cadmium in waters and in lixiviates obtained from plastic toys. The procedure is based on an interesting idea first reported by Yao and Anderson [48] for the preconcentration of aromatic compounds from water and later verified for the particular case of the speciation of chromium traces in water samples [49]. In this method an insoluble IL is formed by mixing two soluble reagents in a straightforward ion-exchange reaction. Although neither organic extractants nor disperser solvents are used, this procedure does in fact count as DLMME, since dispersion follows the formation of tiny droplets of the water-insoluble IL formed. In this way, the lead and cadmium complexed with ammonium pyrrolidine dithiocarbamate (APDC) [19,50] can be separated and measured by ETAAS.

2. Materials and methods

2.1. Instrumentation

An atomic absorption spectrometer (model 800, Perkin-Elmer, Shelton, USA) equipped for Zeeman-effect background correction, with a transversely heated graphite tube atomizer and AS-800 autosampler were used. The autosampler was not used, and the organic samples were pipetted manually into the atomizer. Pyrolytic graphite platforms in pyrolytically coated tubes were obtained from the same manufacturer (part number B050-4033). Argon at 250 mL min^{-1} was used as inert gas, except during atomization, when it was stopped. Cadmium and lead hollow cathode lamps (Perkin-Elmer) were used as the radiation sources. See Table 1 for the instrumental parameters.

2.2. Reagents and samples

All the solutions were prepared using pure water (18 MΩ cm) obtained with a Millipore system (Millipore, Bedford, MA, USA). Polypropylene vessels were used instead of glass to store the solutions in order to minimize contamination. The plastic vessels were washed with 1% (v/v) concentrated nitric acid solution, and then water. However, for the DLLME procedure 15-mL glass tubes were used, to minimize the adherence of the ILs formed to the tube walls.

The cadmium (II) and lead (II) standard solutions (1000 μg mL^{-1}) were prepared from $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ (Aldrich, St. Louis, MO 63103, USA), in pure water, from which working standard solutions were obtained by dilution. The 0.5 mol L^{-1} solution of ammonium pyrrolidine dithiocarbamate (APDC) was prepared by dissolving the compound (Sigma-Aldrich Chemie GmbH, Germany) in methanol of high purity. Solutions (1 mol L^{-1}) of 1-octyl-3-methylimidazolium chloride ([C_8MIm]Cl) and lithium bis(trifluoromethylsulfonyl) imide ([NTf_2]Li), (from IOLITEC, Heilbronn, Germany) were prepared by dissolving 1.15 and 1.43 g, respectively, in 50 mL of ultrapure water. For comparison purposes, 1-octyl-3-methylimidazolium bis((trifluoromethyl sulfonyl)imide ([C_8MIm][NTf_2]) from IOLITEC was used. A 0.2 mol L^{-1} aqueous solution of (1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (Triton X-114) from Sigma was used as sticking agent. All the other chemicals used were from Fluka.

Bottled water samples were bought in a supermarket and the tap water came from the Murcia University mains supply. The seawater samples were taken from a nearby port on the Mediterranean coast. All the samples were filtered and kept in plastic containers at 4 °C until analysis, which took place within a period of 48 h. In addition, ten plastic toys of a variety of shapes and colors were bought in low-price outlets. None was labeled as having been manufactured in the EU. The toys were washed with water and dried at room temperature, before being broken into small pieces or having the paint scraped off prior to lixiviation with diluted hydrochloric acid.

2.3. General procedure

1 mL of a 1 mol L^{-1} nitric acid solution and 200 μL of a 0.5 mol L^{-1} APDC solution were added to a 15-mL glass tube containing 10 mL of a sample solution of cadmium (0.7–20 ng L^{-1}) or lead (0.01–0.4 μg L^{-1}). To this solution, 100 μL of the [C_8MIm]Cl solution and 100 μL of 0.2 mol L^{-1} Triton X-114 solution were added, and the mixture was homogenized by gently shaking. Next, 100 μL of the [NTf_2]Li solution were added, leading to the formation of a turbid solution as the IL formed dispersed. Centrifugation (3000 rpm for 5 min) led to a low volume (33 ± 1 μL) of the IL being recovered in the bottom of the tube. Using a chromatographic syringe, 30 μL of this sedimented phase were injected into the electrothermal atomizer, and the program depicted in Table 1 was run. If maximum sensitivity is unnecessary, the same microextraction process can be used for both analytes carrying out two separate 10 μL injections.

Calibration was carried out by using aqueous standard solutions submitted to the DLLME procedure.

2.4. Procedure for water samples and for lixiviates obtained from plastic toys

The water samples were directly submitted to the general procedure without any additional treatment. To obtain lixiviates from the toy samples, 400 mg portions were treated with 20 mL of a 0.1 mol L^{-1} hydrochloric acid solution and subjected to magnetic stirring for 2 h at 37 °C. The resulting suspensions were filtered through a 0.45 μm membrane filter before using a 10 mL aliquot and following the general analytical procedure.

3. Results and discussion

3.1. Ionic liquid as acceptor phase

The use of ionic liquids as an alternative to organic solvents in microextraction processes is only possible if the IL in question shows low water solubility and viscosity. As already demonstrated [51], the water solubility of ILs based on imidazolium depends on the length of the cation's alkaline chain and the number of hydrogens substituted in the imidazolium cation, as well as on the constituent anion. Thus, it has been reported that the solubility of ILs changes with the anion in the following order

Table 1
Instrumental parameters.

Instrumental parameters[a]	Lead		Cadmium
Lamp current (mA)	14 (HCL)		4 (HCL)
Wavelength (nm)	283.3		228.8
Bandwidth (nm)	0.7		0.7
Atomizer type	Platform		
Injected sample volume (μL)	30		
Chemical modifier	None		Palladium nitrate (300 mg L^{-1})
Background correction	Zeeman		
Furnace heating program[a]			
Step	Temperature (°C)	Ramp (s)	Hold (s)
1: Dry	110	5	20
2: Dry	300	5	30
3: Pyrolysis	600 (Pb), 500 (Cd)	15	20
4: Atomization[a,b]	1800 (Pb), 1200 (Cd)	0	4
5: Clean	2600	1	5
Sequence for cadmium determination			
Step A: pipette 30 μL of the modifier and run step 1			
Step B: inject sample or standard and run the entire program			

[a] Flow of argon stopped.
[b] Reading step.

Table 2
Ionic liquids used.

Substance	Abbreviation	Molecular formula	Molecular mass (g)	ρ (g cm^{-3})	η (cp)	Melting point (K)
1-octyl-3-methylimidazolium chloride	([C_8MIm]Cl	$C_{12}H_{23}ClN_2$	230.78	1.01	337	285.4
Lithium bis(trifluoromethylsulfonyl)imide	[NTf_2]Li	$C_2F_6LiNO_4S_2$	287.08	1.33	–	507
1-octyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C_8MIm][NTf_2]	$C_{14}H_{23}F_6N_3O_4S_2$	475.47	1.33	119	–

$[BF_4]^- > [C(CN)_3]^- > [PF_6]^- > [[NTf_2]Li]$. In this study 1-octyl-3-methylimidazolium chloride ([C_8MIm]Cl) was used as the cation and lithium bis(trifluoromethylsulfonyl)imide ([NTf_2]Li) as the anion (both water soluble, even at high concentrations and easily obtained) for the formation of 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_8MIm][NTf_2]). Table 2 shows some of the physical properties of these compounds. Note that [C_8MIm][NTf_2] is liquid at room temperatures and presents a manageable degree of viscosity.

For rapid phase transfer, the contact area between the donating and receiving phases must be high. In our case, this was achieved by using an exchange reaction (methatesis reaction), which leads to the formation of droplets of an insoluble IL made up of its constituents, both of which are water soluble:

$$[C_8MIm]Cl + [NTf_2]Li \rightarrow [C_8MIm][NTf_2] + LiCl$$

If neutral complexes of metallic ions exist in these conditions in the medium, they can be extracted in the resulting IL due to their high solubility in this solvent. This method has already been used to extract aromatic compounds from water [48] and for the extraction of chromium complexes [49], and represents a simplification of DLLME since the use of dispersant is unnecessary. It is also faster because warming/cooling cycles or ultrasounds are avoided.

Experimentally, it was found that the use of 100 μL [C_8MIm]Cl 1 mol L^{-1} and 100 μL [NTf_2]Li 1 mol L^{-1} permitted a dispersed phase in 10 mL of aqueous phase to be obtained, which, after centrifugation at 3000 rpm for 5 min gave an IL condensed phase at the bottom of the tube, which was quantified at about 33 μL. This volume was very close to the theoretical prediction [52], bearing in mind the density of [C_8MIm][NTf_2].

As can be easily understood, the volume of IL formed is of great importance for the reproducibility of the results since even small changes in volume will lead to substantial changes in the signal. When the IL itself is used as extractant, it is very difficult to handle microvolume samples of the same in a reproducible way to carry out the extraction. However, in the conditions proposed, the *in situ* formation of the IL enables excellent reproducibility in the volume of the IL formed (the relative standard deviation was found to be below 5%). In addition, the solubility of the IL formed is reduced due to the presence of an excess of constituent ions in the aqueous phase.

3.2. Optimization of the DLLME conditions

For cadmium and lead extraction, ammonium pyrrolidine dithiocarbamate (APDC) was used. This chemical [53] originates neutral compounds with both Cd(II) and Pb(II). The excellent complexing properties of APDC have been used in several recent microextraction processes [54–60].

A number of experiments were devoted to studying the effect of pH and APDC concentration on the extraction of both Cd(II) and Pb(II) in [C_8MIm][NTf_2], optimizing the experimental conditions for maximum extraction. As can be seen in Fig. 1A, both ions are completely extracted in an acidic medium (pH=1) even when very low APDC concentrations are used. In contrast, maximum extraction of Cd(II) requires the APDC concentration to be raised to 0.008 mol L^{-1} (Fig. 1B). Taking into account the data presented, it is clear that a 0.01 mol L^{-1} concentration of APDC is adequate for Cd(II) and Pb(II) extraction when the pH is close to unity, which can be attained by incorporating 0.1 mol L^{-1} nitric acid in the sample without the need for buffer solutions.

The volume of both the aqueous phase and the final IL recovered must be taken into account if a high preconcentration factor is needed. Since the volume of the IL sedimented after the centrifugation stage must not be very low if a suitable aliquot is to

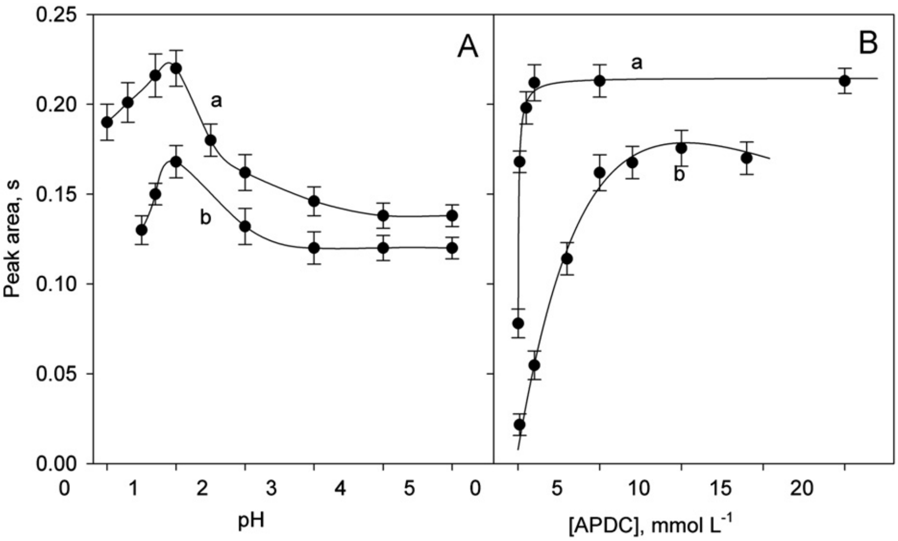

Fig. 1. Effect of pH and APDC concentration on the extraction of lead and cadmium (lines a and b, respectively). Vertical bars indicate the standard deviation ($n=3$).

be taken for injection into the electrothermal atomizer, the volumes of both [C_8MIm]Cl and [NTf_2]Li were maintained at 100 μL. On the other hand, because of the low solubility of the final IL in water, the volume of the sedimented phase was checked to be 33 ± 1 μL, irrespectively of the variation in volume (5–10 mL) of the aqueous phase. The experimental results showed that the concentration of Cd(II) and Pb(II) in the final IL was directly related to the concentration in the initial aqueous sample, indicating extraction was practically complete. Several experiments were run to calculate the extraction percentage, making two successive extractions of the same sample. The calculations gave 98 ± 3 and 99 ± 4% for Cd(II) and Pb(II), respectively.

The enrichment factors (EF) were calculated using the ratios between the slopes of the calibration lines obtained from aqueous solutions submitted to the DLLME procedure and the slopes of calibration lines obtained from solutions that were not extracted. The results were very similar for Cd(II) and Pb(II). When volumes of 5 and 10 mL were used for the aqueous phase, the experimental enrichment factors calculated were 150 and 280, respectively. It should be noted these values are similar to the ratio of the volumes of the aqueous sample used to the IL recovered, thus confirming that DLLME was complete.

Additional experiments were devoted to checking the effect of the extraction time, defined as the interval of time elapsing from the mixing of the reagents to the beginning of the centrifugation stage. Maximum analytical signals for cadmium and lead were obtained even with an extraction time as short as 15 s. On the other hand, it was experimentally found that the incorporation of up to 1 mol L^{-1} sodium chloride in the aqueous sample did not affect the analytical signal, which suggests that the procedure is suitable for seawater samples.

3.3. Optimization of the furnace heating program

The presence of the IL used as acceptor phase affected the atomization profile of cadmium in ETAAS, and so the conditions for the heating program in the electrothermal atomizer were optimized in order to obtain maximum analytical signals. As can be seen in Fig. 2, which depicts the cadmium atomization profiles obtained using 500 °C as the calcination temperature, the signal obtained in the presence of the IL (curve a) was about 25% lower than that obtained in its absence (curve b). This decrease could not be overcome even by varying the atomization temperature over a wide range, and so several chemical modifiers, both added as solutions and used as impregnations of the pyrolytic atomizers, were assayed. The use of 30 μL of 300 μg mL^{-1} palladium nitrate proved effective, leading to a considerable improvement in sensitivity. In the case of lead, the presence of the IL did not affect the sensitivity of the detector. The signal remained stable up to a 700 °C calcination temperature. At the same temperature the signal for background absorption was low and represented no problem for quantification purposes, meaning that it was unnecessary to use a chemical modifier,

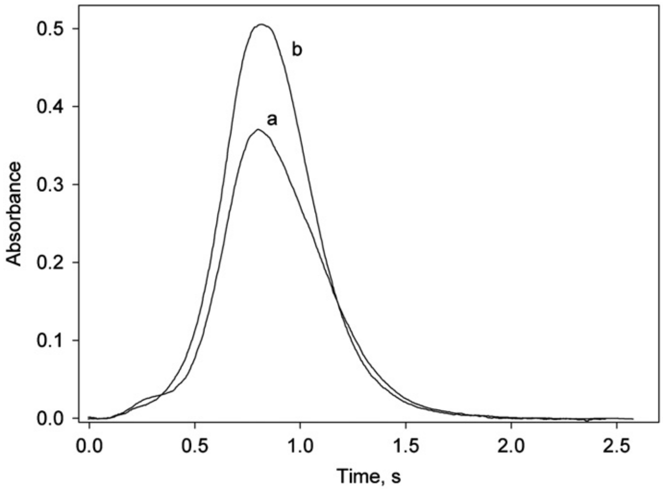

Fig. 2. Absorbance-time profile obtained of 0.15 ng cadmium in the presence (line a) and absence (line b) of the ionic liquid.

The results for the ashing–atomizing curves obtained for Cd(II) and Pb(II) solutions submitted to the extraction procedure are given in Fig. 3. Maximum signals were obtained when 500 and 700 °C were used as the calcination temperature for Cd(II) and Pb(II), respectively. The recommended atomization temperatures for these species are 1200 and 1800 °C, respectively. The heating program finally optimized is given in Table 1. It should be noted that the program uses two drying stages for cadmium determination. Firstly a 30 μL aliquot of the modifier solution is injected and dried. After cooling the atomizer, the IL aliquot is injected and the entire program is run. This way of operation proved effective for achieving chemical modification by the palladium solution and for completely removing any residue of aqueous solution before reaching the calcination temperature.

3.4. *Analytical figures of merit*

Using the conditions described in experimental, a linear relationship between the analytical signal and the cadmium and lead concentration in the aqueous phase was verified in the 0.7–20 ng L^{-1} and 0.01–0.4 μg L^{-1} range, respectively. The detection limits, calculated on the basis of three times the standard error from the calibration graphs were 0.2 and 3 ng L^{-1}, respectively. The repeatability was estimated from ten consecutive experiments at concentrations of 10 ng L^{-1} cadmium and 0.2 μg L^{-1} lead, the relative standard deviations (RSD) being 6.5 and 7.3% for Cd(II) and Pb(II), respectively. The reproducibility was calculated from ten measurements obtained on five consecutive days, and the RSDs were 9.3 and 10.2% for Cd(II) and Pb(II), respectively. A comparison of the main characteristics of the procedure presented here and others reported in the recent literature for the determination of cadmium and lead using microextraction techniques is given in Table 3.

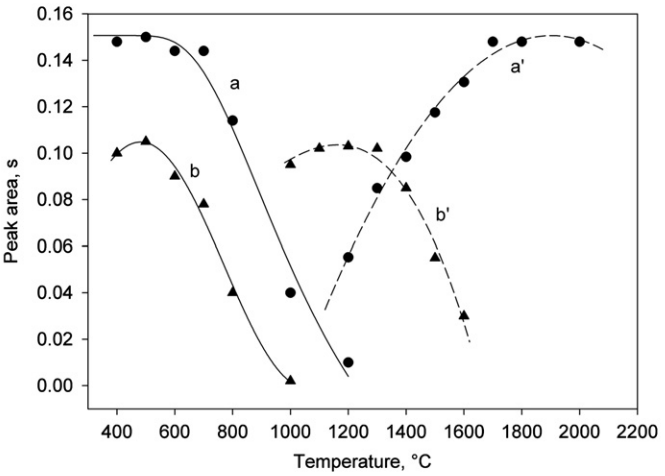

Fig. 3. Ashing–atomizing curves obtained for a 0.13 μg L^{-1} lead solution (lines a and a′) and a 3.4 ng L^{-1} cadmium solution (lines b and b′).

Since the final measurement involved ETAAS, the selectivity was excellent. It was experimentally verified that, as expected, the ions commonly present in waters did not affect the results. For lead determination Ca(II), Mg(II), Hg(II), Ba(II), Zn(II), As(III), Cr(VI), Cu(II), K(I), Ni(II), Co(II) and As(V) were tolerated up to 5 g L^{-1}; Mn (II), Fe(III), Cd(II) and Sb(III) were tolerated up to 1 g L^{-1}, while the level of tolerance of Al(III) was 0.1 g L^{-1}. In the case of cadmium determination the maximum tolerated concentrations were 1 and 5 μg L^{-1} for Hg(II) and Ni(II) respectively. Co(II) and As(V) were tolerated up to 50 μg L^{-1}, and Cu(II) and Fe(III) up to 100 μg L^{-1}. Note that these results mean high interferent/analyte ratios and, due to the sensitivity of the procedure, most of them could be overcome simply by diluting the sample solution.

3.5. *Analysis of real samples*

The optimized procedure was applied to water samples of different origins. Because of the very low concentrations involved, the direct comparison of the results with those found by an alternative procedure was considered unreliable, and standard additions were used instead. As can be seen in Table 4, the

Table 4
Determination of lead and cadmium in water samples.

Sample	Lead[a] (μg L^{-1})		Cadmium[a] (ng L^{-1})	
	Found	Recovery (%)	Found	Recovery (%)
TW[b]	0.043 ± 0.006	99	1.0 ± 0.5	100
BMW[c] 1	< LOD	–	3.8 ± 0.5	98
BMW[c] 2	0.025 ± 0.006	98	2.6 ± 0.5	100
TW+ORS[d]	0.012 ± 0.006	101	0.8 ± 0.5	102
BMCW[e] 1	0.170 ± 0.007	98	14.0 ± 0.6	103
BMCW[e] 2	0.030 ± 0.005	96	2.3 ± 0.5	99
SW[f] 1	0.061 ± 0.006	104	12.5 ± 0.5	101
SW[f] 2	0.044 ± 0.006	99	2.3 ± 0.5	100
SW[f] 3	0.022 ± 0.005	97	4.7 ± 0.5	99
NASS-6	< LOQ	–	30.1 ± 0.6	99
SPS-SW2	25.1 ± 0.3	96	2500 ± 1.6	10

[a] Mean value ± standard deviation (n=3); recovery is the average of three standard additions.
[b] TW: tap water.
[c] BMW: bottled mineral water.
[d] TW+ORS: tap water with reverse osmosis system.
[e] BMCW: bottled mineral carbonated water.
[f] SW: sea water.

Table 3
Characteristics of some microextraction procedures based on ionic liquids for the determination of lead and cadmium.

Element	Method	IL	Reagent	EF	Sample volume (mL)	Linear range (μg L^{-1})	LOD (μg L^{-1})	Ref.
Pb	HF-LPME[a]+ETAAS	[C_6MIN][PF_6]	APDC	76	3	0.04–1.0	0.02	[59]
Pb	SDME[b]+ETAAS	[C_4MIN][PF_6]	APDC	76	1.75	0.025–0.8	0.015	[60]
Pb	DLLME+FAAS	[C_6MIN][PF_6]	APDC	40	20	–	1.5	[61]
Pb	TC-LPME[c]+FAAS	[C_6MIN][PF_6]	Dithizone	–	10	0.01–0.2	0.0095	[62]
Pb	SDME-ETAAS	CYPHOS IL 101[d]	5-Br-PADAP[e]	32	1.5	0–4.5	0.0032	[63]
Pb, Cd	DLLME+FAAS	[C_6MIN][PF_6]	DDTC[f]	273,311	10	2–100, 0.1–15	0.6, 0.03	[64]
Cd	Microcolumn-FAAS	[C_4MIN][PF_6]+SiO_2	Dithizone	75	150	1–800	0.6	[65]
Cd	DLLME+FAAS	[C_6MIN][BF_4]+$NaPF_6$	DDTP[g]	78	5	0.2–40	0.07	[66]
Cd	IL-USA-DLLME[h]+ETAAS	[C_6MIN][PF_6]	DDTC	67	10	0.02–0.15	0.0074	[45]
Pb, Cd	DLLME+ETAAS	[C8MIm]Cl+[NTf2]Li	APDC	280	10	0.01–0.4, 0.0007–0.02	0.003, 0.0002	This work

[a] Hollow fiber liquid phase microextraction.
[b] Single drop microextraction.
[c] Temperature-controlled ionic liquid–liquid-phase microextraction.
[d] Tetradecyl(trihexyl)phosphonium chloride.
[e] 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.
[f] Diethyldithiocarbamate.
[g] O,O-diethyldithiophosphate.
[h] Ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction.

Table 5
Migration limits from toys or components of toys that should not be exceeded.

Children's toys	Lead (μg g^{-1})	Cadmium (μg g^{-1})
Brittle, powder-like or pliable toy material	13.5	1.9
Liquid or sticky toy material	3.4	0.5
Scraped-off toy material	160	23

Table 6
Lixiviation of lead and cadmium from toy samples.

Toy color	Content found[a] (ng g^{-1})	
	Lead	Cadmium
Pink	12.5 ± 0.7	0.73 ± 0.04
	0.8 ± 0.4	1.05 ± 0.04
	9.0 ± 0.6	0.21 ± 0.06
Blue	10.5 ± 0.7	0.06 ± 0.03
	18.0 ± 0.8	0.16 ± 0.03
Yellow	6.5 ± 0.5	0.09 ± 0.03
	7.0 ± 0.6	2.91 ± 0.08
Violet	6.5 ± 0.5	0.91 ± 0.04
Brown	8.0 ± 0.6	0.25 ± 0.03

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

recoveries, which ranged from 96 to 105 %, confirmed the reliability of the procedure. The table also includes the results obtained for the reference materials SPS-SW2 batch 125 and NASS-6, with certified lead contents of 25.0 ± 0.1 and 0.006 ± 0.002 μg L^{-1}, respectively, and of cadmium of 2.50 ± 0.02 and 0.0303 ± 0.0019 μg L^{-1}, respectively. As can be seen, there was excellent agreement between these values and those obtained with the proposed procedure.

We also studied the suspected release of both metals from children's toys since the hand-mouth activity of children means that any such release could be dangerous from a health point of view. To this effect, the samples were submitted to a treatment regulated in the European Union [67], and recently modified [68], which assesses the lixiviation from this type of samples. The maximum migration limits accepted by the norm are given in Table 5, while the values found by using the proposed procedure on toys purchased in low-cost shops are shown in Table 6. All the results were clearly below the limits permitted.

4. Conclusions

The formation *in situ* of an IL microvolume allows the extraction of neutral complexes of metallic ions. The introduction of the organic liquid into an electrothermal atomizer results in analytical procedures of high sensitivity and selectivity. In the particular case of cadmium and lead, the detection limits are very low. The distinctive feature of the optimized approach is the fact that no organic solvents or ultrasounds are required to obtain the dispersion.

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