Talanta 84 (2011) 109–115

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Ion pair-based dispersive liquid–liquid microextraction for gold determination at ppb level in solid samples after ultrasound-assisted extraction and in waters by electrothermal-atomic absorption spectrometry

I. De La Calle, F. Pena-Pereira, N. Cabaleiro, I. Lavilla, C. Bendicho*

Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Facultad de Química, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain

ARTICLE INFO

Article history:
Received 11 October 2010
Received in revised form
30 November 2010
Accepted 19 December 2010
Available online 25 December 2010

Keywords:
Ultrasound-assisted extraction
Dispersive liquid–liquid microextraction
Gold
ng g^{-1} levels
Environmental samples

ABSTRACT

A new methodology was developed for the determination of ultratrace levels of gold in water samples, soils and river sediments. Dispersive liquid–liquid microextraction was used to preconcentrate the ion pair formed between $AuCl_4^-$ and $[CH_3(CH_2)_3]_4N^+$ in a microliter-range volume of chlorobenzene using acetone as disperser solvent. When solid samples were analyzed, the method consisted of a combination of ultrasound-assisted extraction and dispersive liquid–liquid microextraction with final detection by electrothermal-atomic absorption spectrometry. Since an HCl medium was required for the formation of the $AuCl_4^-$ complex, HCl together with HNO_3 was used as extractants for ultrasound-assisted extraction. After optimization, the enrichment factor obtained was 220 for water samples. Moreover, the extraction efficiency was around 96%. The repeatability, expressed as relative standard deviation ranged from 3.6% to 9.7%. The instrumental detection limit was 8.4 ng L^{-1}, whereas the procedural detection limits were 42 ng L^{-1} for water samples and 1.5 ng g^{-1} for environmental solid samples.

1. Introduction

Gold is a noble metal that occurs at very low levels in the nature, except in the limited gold ores or in certain alluvial deposits. However, the use of gold is widely extended in jewellery, medicine, dentistry, industry, electronics, cosmetic and even in food and drinks [1,2]. On the other hand, cytotoxicity has been observed for gold nanoparticles functionalized with cationic side chains [3], therefore, gold determination in waters or other samples shows an increasing interest due to the enormous production on gold nanoparticles around the world.

As a result of the low levels of gold in most environmental samples, a variety of preconcentration methods for gold have been developed such as solid phase extraction (SPE) [4], cloud point extraction (CPE) [5,6], coprecipitation [7] and liquid–liquid extraction (LLE) [8] in order to meet the sensitivity requirements of different detection techniques. However, many preconcentration approaches involve tedious procedures with multiple steps [4]. Several reviews have been published on this subject [9–11].

LLE has been widely employed for extraction and preconcentration of both organic and inorganic analytes. One of the multiple options for the extraction of metallic ions by LLE is based on the formation of ion pairs followed by their extraction in organic solvents. In this way, quaternary ammonium salts (e.g. tetrabutylammonium ion, Bu_4N^+; trioctyl methyl ammonium ion, $MeOc_3N^+$), organometallic cations (e.g. tetraphenylarsonium ion, Ph_4As^+; tetraphenylphosphonium ion, Ph_4P^+; triphenyltin ion, Ph_3Sn^+) or cationic colorants (e.g. rhodamine B) have been applied with this aim. These cationic species form non-solvated ion pairs with anionic species such as $SnCl_6^{-2}$, $AuCl_4^-$, $Co(SCN)_4^{-2}$, $Fe(SCN)_6^{-3}$, MnO_4^-, ReO_4^-, $TlCl_4^-$, $HgBr_4^{-2}$ and $SbCl_6^-$ [12]. Several approaches involving the formation of different ion pairs with $AuCl_4^-$ and subsequent solvent extraction have been reported in the literature [13]. However, it should be pointed out that at present, LLE is not recommended due to the large volumes of toxic organic solvents apart from being labour-intensive [14].

The development of sample pretreatment approaches involving a minimization of solvent consumption and waste generation, as well as integration of steps is one of the main objectives pursued by the green analytical chemistry [15,16]. In this context, Rezaee et al. [17] introduced in 2006 the technique named dispersive liquid–liquid microextraction (DLLME) for the extraction of organic compounds. DLLME consists of a miniaturization of the LLE, which results in a drastic reduction of the extractant phase volume (usually an organic solvent) [16]. As a result of the reduced extractant phase volume as compared to LLE [18], environmental and human hazards are minimized and this technique can be considered as green [16]. DLLME studies related to ion metals involve

---

* Corresponding author. Tel.: +34 986 812281; fax: +34 986 812556.
E-mail address: bendicho@uvigo.es (C. Bendicho).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.12.031

the use of complexing reagents, ligandless-dispersive liquid–liquid microextraction (LL-DLLME) and ion-pair forming agents, the first approach being the most widely used. Thus, ammonium pyrrolidine dithiocarbamate (APDC) and diethyl dithiophosphoric acid (DDTP) have been used for complexing Cd [19] and Pb [20]. LL-DLLME has been applied for the determination of Ag [21], Cu [22] and Pd [23]. The ion-pair based approach has only been employed for gold following the formation of an ion pair between the $AuCl_4^-$ complex and different counter ions such as Victoria Blue R [24], dicyclohexylamine [25] and between the $AuCN_2^-$ complex with Astra Phloxine (R) [26].

Since 2007, more than forty papers have appeared in the literature concerning metal extraction using DLLME. Samples analyzed were mostly waters [19,27] due to the simplicity and low matrix effects found with these samples [28].

More efforts need to be made so as to extend the applicability of DLLME to solid matrices. At this point, ultrasound-assisted extraction (UAE) could be a suitable option instead of more intensive pretreatments prior to the use of DLLME.

The proposed method was applied to the determination of Au in solid samples, such as soils and sediments, and in water samples at a lower concentration level (ng g^{-1} and ng mL^{-1}, respectively) than in other papers published recently. Amin [29] quantified Au at $\mu g L^{-1}$ levels in water, mg g^{-1} in jewel samples and $\mu g g^{-1}$ in ore samples following solid-phase extraction. Kocúrová et al. [26] determined Au at the mg L^{-1} level in pharmaceutical samples following preconcentration by DLLME, using 145 μL of toluene and 145 μL of CCl_4 for microextraction. De La Calle et al. [30] carried out the ultrasound-assisted extraction of Au from environmental solid samples, thus avoiding acid digestion for pre-treatment. However, the method was not sensitive enough for gold determination at the ppb level.

The goal of this work is to develop a pre-treatment method for Au determination in solid matrices at ultratrace level by combining UAE and DLLME in tandem prior to detection by electrothermal-atomic absorption spectrometry.

2. Experimental

2.1. Reagents and standards

Ultrapure water was obtained from a PETLAB ultrapure water production system (Peter Taboada, Vigo, Spain). All chemical products used were of analytical-reagent grade. A gold standard solution (1000 mg L^{-1} Au (III) as $HAuCl_4$) in 10% v/v HCl was obtained from (Prolabo, Leicestershire, England). Tetrabutylammonium bromide 99% of purity $[CH_3(CH_2)_3]_4NBr$ (Aldrich, Steinheim, Germany). 69% m/v nitric acid (Prolabo), 37% m/v hydrochloric acid (Prolabo), 95% m/v sulphuric acid (Prolabo), 30% m/v hydrogen peroxide (Merck, Darmstadt, Germany) and 40% m/v hydrofluoric acid (Merck) were used for extraction after dilution with ultrapure water. Dichloromethane (Panreac, Barcelona, Spain), trichloromethane (Panreac), carbon tetrachloride/tetrachloromethane (Panreac), bromobenzene (Aldrich) and chlorobenzene (Aldrich) were attempted as potential organic extractant phases. Methanol (Prolabo), acetone (Prolabo), ethanol (Prolabo) and acetonitrile (Prolabo) were tested as disperser solvents.

2.2. Instrumentation

All measurements were carried out with a Thermo Electron Corporation® series M5 atomic absorption spectrometer (Cambridge, UK) equipped with deuterium background corrector. A Thermo GF95 graphite furnace, a Thermo FS95 furnace autosampler and a hollow cathode multielemental lamp of Ag/Au were employed as radiation source (Thermo Scientific, Cambridge, UK). The instrumental parameters are given in Table 1. Longitudinal-heated graphite tubes with integrated L'vov platform were provided by the same manufacturer.

Table 1
Instrumental parameters and temperature program for gold determination.

Parameter		Au		
Instrumental parameters				
Wavelength (nm)		242.8		
Spectral band pass (nm)		0.5		
Lamp current (mA)		7.5		
Signal measurement		Peak area		
Read time (s)		3		
Program time (s)		112		
Stage	Temperature (°C)	Hold time (s)	Ramp (°C/s)	Gas flow-rate Ar (L/min)
Temperature program				
Drying 1	80	30	30	0.2
Drying 2	120	30	15	0.2
Pyrolysis	400	30	30	0.2
Atomization	2400	3	0	0[a]
Cleaning	2800	3	300	0.2

[a] Read stage.

A cup-horn sonoreactor UTR 200® (Dr. Hielscher Company, Teltow, Germany) with 200 W of maximum output power and 24 ± 1 kHz of operating frequency was employed for ultrasound-assisted extraction of gold from the different samples. A Sonic and Materials (Danbury, CT, USA) ultrasonic probe (50 W power, 20 kHz frequency) equipped with a titanium microtip of 3 mm diameter was also tried to assist DLLME.

A Denver (Norfolk, United Kingdom) microcentrifuge was used for rapid separation of liquid and solid phases after ultrasound-assisted extraction. A Sigma 2-16 versatile Centrifuge (Dorval, Canada) was used for rapid separation of the organic solvent (few microliters of chlorobenzene) at the bottom of the vial from the aqueous solution after DLLME.

A 100-μL microsyringe (Hamilton model 1710N CTC, Reno, Germany) was used to collect the sedimented organic phase and to accurately dose the volume of the different organic phases studied.

2.3. Sample collection and conditioning

2.3.1. Water samples

Three water samples were collected from Avia River (Ribadavia), Castrelo de Miño Dam (Castrelo de Miño) and Arenteiro River (O Carballiño) in Galicia (northwest of Spain). Samples were acidified immediately with nitric acid to pH = 2 so as to prevent adsorption of the metallic ions onto the flask walls. Samples were filtered before analyses through cellulose nitrate filter with a pore size of 0.45 μm (Sartorious, Goettingen, Germany) to remove suspended particulate matter.

2.3.2. Environmental solid samples

Three certified reference materials (CRMs) were used to evaluate the accuracy of the proposed methodology: NIST SRM 2782 Industrial Sludge, NIST SRM Montana Soil 2710 and NIST SRM Montana Soil 2711 from National Institute of Standards and Technology (United States). Powdered samples were stored at 4 °C and no additional grinding was performed. Certificates for CRMs ensured a particle size less than 75 μm in SRM 2782 and less than 74 μm in SRM 2710 and SRM 2711.

Several real samples were also analyzed to demonstrate the usefulness of the proposed methodology. Eleven sampling points along 88 km were selected according to previous information. Six river sediment samples were collected at the Miño River (Ourense), Arenteiro River (O Carballiño), Arnoia River (Arnoia), Miño River (Salvaterra de Miño), Louro River (Tui) and Lagares River (Vigo). Moreover, soil samples were collected at Rivas (O Irixo), Brués (Boborás), O Lago (Maside), Sampaio (Ribadavia) and Oleiros (Salvaterra de Miño). 2 kg of sample (sediment or soil) were collected at each sampling point using a plastic scoop and kept in polyethylene containers. Once in the laboratory, samples were dried at 60 °C in a heater. After that, they were sieved using nylon sieves to collect the fraction with a particle diameter less than 50 μm, and then stored in polyethylene bottles at room temperature in a desiccator.

2.4. *DLLME procedure for aqueous standards and water samples*

1 mL of concentrated HCl, 0.5 mL of 0.31 M $[CH_3(CH_2)_3]_4NBr$ and 5 mL of gold aqueous standard (0.075–75 $\mu g\,L^{-1}$) or 5 mL of a water sample were poured into a 15-mL polyethylene tube. A mixture of 500 μL of acetone (as the disperser agent) and 35 μL of chlorobenzene (as the extraction solvent) was added to the tube. A white-cloudy solution appeared immediately. The solution was manually shaken for a few seconds, and the mixture was then centrifuged for 2 min at 3000 rpm. Thus, the ion pair $AuCl_4$–$[CH_3(CH_2)_3]_4N$ formed was extracted into the organic phase, which sedimented at the bottom of the tube. Finally, 22 ± 2 μL of the sedimented phase were placed into an autosampler cup of the ETAAS instrument and 15 μL were automatically injected by the autosampler into the graphite tube. Gold absorbance was measured under the operating conditions summarised in Table 1. The temperature program is similar to others where chlorinated solvents are used [25].

2.5. *UAE–DLLME procedure for environmental solid samples*

A portion of 3–30 mg of solid material was weighed into an Eppendorf vial and 1 mL of a 25% v/v HNO_3 + 25% v/v HCl mixture was added to the vial. This acid mixture has been proved efficient for the extraction of gold due to the oxidant properties of nitric acid and the complexing properties of hydrochloric acid (i.e. formation of the complex $AuCl_4^-$ at high HCl concentration) [30]. Ultrasound energy was applied for 20 min at a sonication amplitude of 60% by means of a cup-horn sonoreactor. This system was previously filled with ultrapure water so that ultrasound waves could be efficiently transmitted. After sonication, centrifugation was carried out for 2 min at 5000 rpm. The preconcentration step was performed like in Section 2.4. 900 μL of the sonicated extract were poured into a 15-mL polyethylene tube and then, 0.75 mL of concentrated HCl, 2.5 mL of a 6.2×10^{-2} M $[CH_3(CH_2)_3]_4NBr$ solution and 0.85 mL of ultrapure water were added.

3. Results and discussion

Preliminary experiments were performed in order to ascertain the extractability of the ion pair in organic solvents as well as possible analyte losses in the furnace owing to the use of chlorinated solvents. To this end, LLE was performed by using equal volumes of gold standard solution and organic solvent (chlorobenzene). Calibration lines for gold obtained in aqueous and organic media showed the same slope, thus demonstrating the absence of errors.

In order to find the appropriate conditions for DLLME, experimental parameters such as nature and volume of the extractant solvent and disperser agent, effect of hydrochloric acid and tetrabutylammonium bromide concentration were studied.

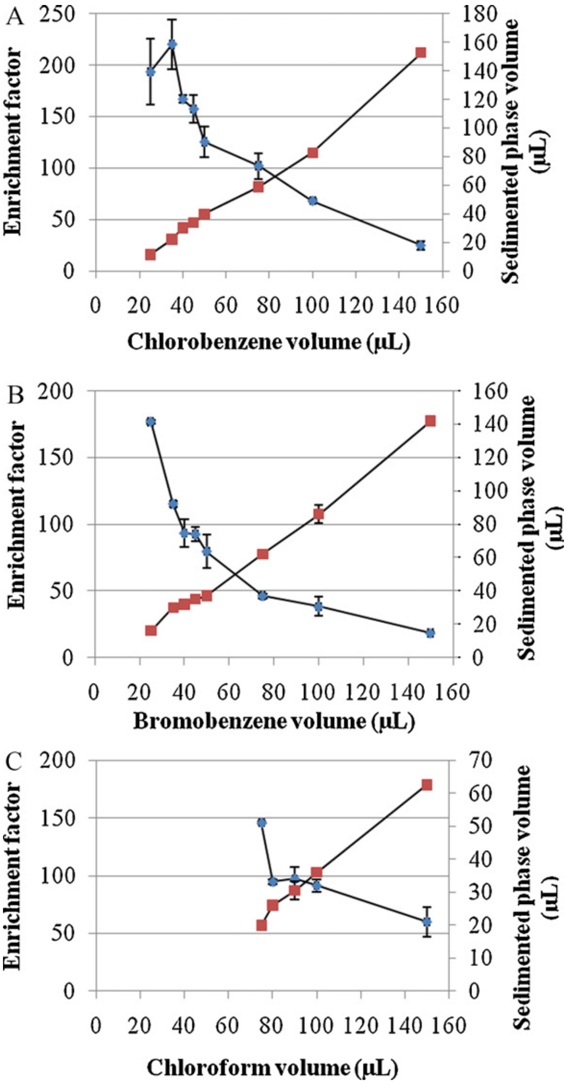

Fig. 1. Effect of the volume of different extractants on both the enrichment factor of Au (♦) and the volume of the sedimented phase (■). (A) chlorobenzene, (B) bromobenzene and (C) chloroform. Experimental conditions were the following: 0.5 $\mu g\,L^{-1}$ Au (III) concentration; 10% v/v HCl concentration; 1.55×10^{-2} M $[CH_3(CH_2)_3]_4NBr$ concentration; 500 μL of methanol.

3.1. *Optimization of DLLME*

3.1.1. *Nature and volume of the extraction solvent*

Dichloromethane (CH_2Cl_2), tetrachloromethane (CCl_4), chloroform ($CHCl_3$), chlorobenzene (C_6H_5Cl) and bromobenzene (C_6H_5Br) were tried as organic solvents in this work. These organic solvents were chosen according to their density, higher than water in all cases, and ranging from 1.10 to 1.58 $g\,cm^{-3}$ [31]. Dichloromethane (CH_2Cl_2) was rejected since it was fully soluble in the sample solution after the formation of the cloudy solution. Tetrachloromethane (CCl_4) was also discarded because of its inability to extract the ion pair formed likely due to its non-polar nature [31].

In Fig. 1, a comparative study of the effect of chloroform, chlorobenzene and bromobenzene on the extraction of the ion pair is shown. The volume of the organic solvents was varied from 25 to 150 μL for chlorobenzene and bromobenzene, and from 75 to 150 μL for chloroform, because of the total solubility of chloroform at lower volumes. As can be seen, chlorobenzene allows obtaining the higher enrichment factor. Sedimented phase volumes

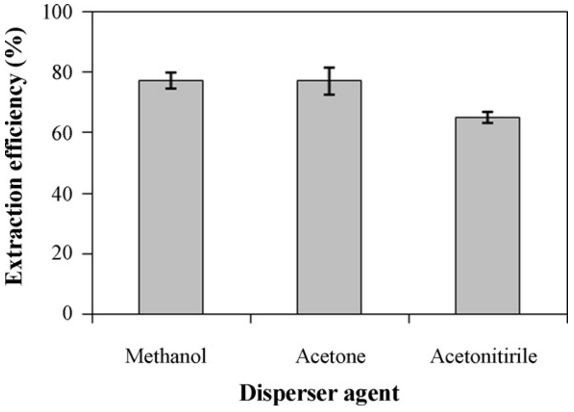

Fig. 2. Effect of the extractant on the extraction efficiency of Au. Chlorobenzene was used as extractant and the volume of the three disperser solvents (methanol, acetone and acetonitrile) was 500 μL. Experimental conditions were the following: 0.5 μg L^{-1} Au (III) concentration; 10% v/v HCl concentration; 1.55×10^{-2} M $[CH_3(CH_2)_3]_4NBr$ concentration; 35 μL of chlorobenzene.

smaller than 20 μL were not enough for being injected into the graphite furnace. A volume of 35 μL of chlorobenzene (representing *ca.* 22 μL of the sedimented phase) provided an enrichment factor of 220 (extraction efficiency of 77%). The same volume of bromobenzene provided an enrichment factor of 115 (extraction efficiency of 61%). 75 μL of chloroform gave rise to an enrichment factor of 145 (extraction efficiency of 59%). The use of larger volumes of organic solvent gave rise to a decrease in the enrichment factor as a result of dilution. Due to the high volumes of chloroform required and the lower enrichment factor obtained with bromobenzene, chlorobenzene was selected for further studies.

3.1.2. Nature and volume of disperser solvent

The disperser solvent is used in DLLME to enhance the extraction kinetics, since it allows the formation of tiny drops of extractant phase, which improves the mass transfer of the analyte as a result of the increased liquid–liquid interface [18]. In addition, the sedimented phase volume depends on the nature and volume of disperser solvent [31]. The organic extractant and disperser agent should be mixed in advance so as to obtain the same remaining volume of sedimented phase. Several organic solvents were attempted as dispersers on the basis of their miscibility with both the organic and aqueous phases. Methanol (CH_3OH), acetone (CH_3COCH_3) and acetonitrile (CH_3CN) were assayed as disperser agents at the same conditions and using the same volume (i.e. 500 μL) (Fig. 2).

The extraction efficiency achieved using methanol and acetone was almost the same, so acetone was chosen as disperser agent because of its lower toxicity.

The effect of the acetone volume was studied in the range 0.25–2 mL. In order to achieve a constant volume of sedimented phase the volumes of acetone and chlorobenzene were changed simultaneously, so that the volume of the sedimented was 22 ± 2 μL. The studied volume ratios of acetone (mL)/chlorobenzene (μL) were 0.250/35, 0.5/35, 0.75/35, 1/40 and 2/40. Finally, a 0.5 mL volume of acetone was chosen for subsequent experiments, since it provided the highest extraction efficiency (Fig. 3A).

3.1.3. Effect of hydrochloric acid concentration

The hydrochloric acid concentration is a key parameter on the formation of the $AuCl_4^-$ complex previous to the formation of the ion pair. Furthermore, an acidic medium (low pH) is suitable for the extraction of ion pairs in conventional LLE [12]. Maeck et al. assayed concentrations of 0.2 to 5 M of HCl in the extraction of gold as quaternary amine complexes [32]. The excess of HCl has a positive effect on the ion pair formation and extraction. The extraction efficiency increased on increasing the hydrochloric acid concentration up to 20% v/v (i.e. 2.3 M), so further experiments were carried out at this concentration (Fig. 3B).

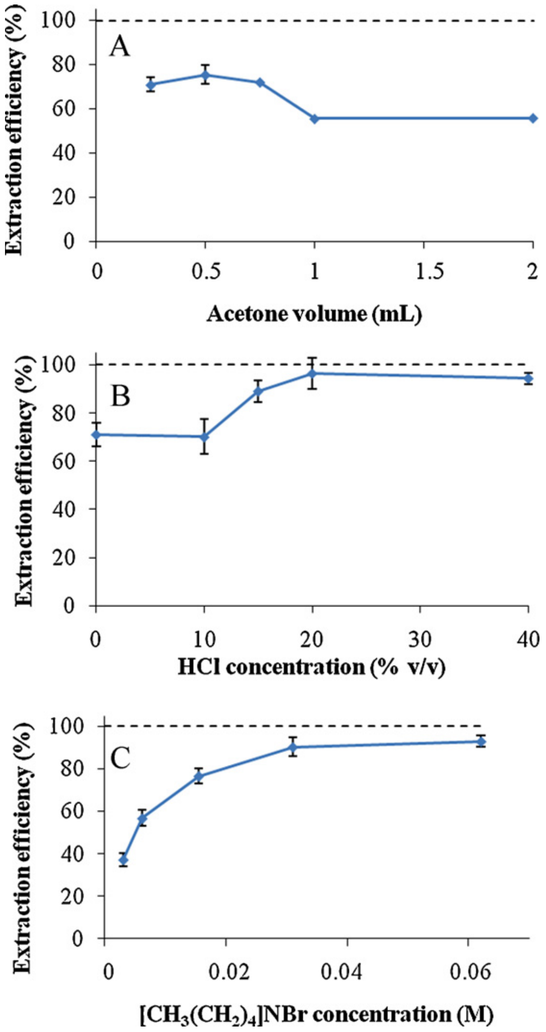

Fig. 3. (A) Optimization curve of acetone volume. Experimental conditions were the following: 0.5 μg L^{-1} Au (III) concentration; 10% v/v HCl concentration; 1.55×10^{-2} M $[CH_3(CH_2)_3]_4NBr$ concentration; 35 μL of chlorobenzene. (B) Optimization curve of hydrochloric acid concentration (% v/v). Experimental conditions were the following: 0.5 μg L^{-1} Au (III) concentration; 1.55×10^{-2} M $[CH_3(CH_2)_3]_4NBr$ concentration; 500 μL of acetone; 35 μL of chlorobenzene. (C) Optimization curve of the tetrabutylammonium bromide concentration (M). Experimental conditions were the following: 0.5 μg L^{-1} Au (III) concentration; 20% v/v HCl concentration; 500 μL of acetone; 35 μL of chlorobenzene.

3.1.4. Effect of the ion-pair-forming agent

Tetrabutylammonium bromide ($[CH_3(CH_2)_3]_4NBr$) was chosen due to its ability to form an ion pair with the tetrachloraurate ion, which can be extracted into an organic solvent [33]. The effect of the $[CH_3(CH_2)_3]_4NBr$ concentration was studied in the range 3.1×10^{-3} to 6.2×10^{-2} M. As is shown in Fig. 3C, an increase in the extraction efficiency of the ion pair occurred with increasing $[CH_3(CH_2)_3]_4NBr$ concentration up to 3.1×10^{-2} M. This concentration of ion pairing agent was selected accordingly for subsequent experiments.

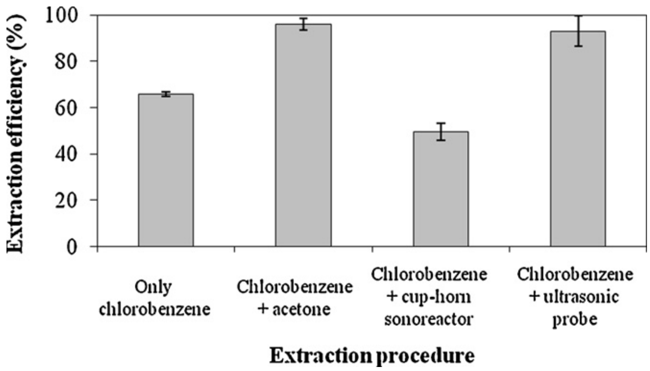

Fig. 4. Effect of the dispersion system on extraction efficiency of Au (use of a disperser agent or ultrasound). Experimental conditions were the following: 35 μL of chlorobenzene; 20% v/v HCl concentration; 3.1×10^{-2} M $[CH_3(CH_2)_3]_4NBr$ concentration; 0.3 $\mu g\,L^{-1}$ Au (III) concentration. (A) Use of only chlorobenzene without any dispersion; (B) use of 500 μL of acetone as disperser agent; (C) application of 5 min of ultrasound at 60% sonication amplitude by a cup-horn sonoreactor; (D) application of 3 min of ultrasound at 50% sonication amplitude by an ultrasonic probe. Ultrasound is applied to assist the dispersive liquid–liquid microextraction.

3.1.5. *Effect of ultrasound energy without the use of disperser agent*

To avoid the use of the disperser agent, ultrasound energy could be applied, which leads to the technique known as ultrasound-assisted emulsification microextraction (or ultrasound-assisted dispersive liquid–liquid microextraction). Ultrasound irradiation can facilitate the dispersion of the extractant solvent in the aqueous phase without using disperser agent [16].

A comparative study on the extraction efficiency of the ion pair by a microvolume of chlorobenzene was performed by applying different dispersion systems, including the use of a disperser solvent, an ultrasonic probe and a cup horn sonoreactor.

The obtained results are shown in Fig. 4. The application of ultrasound energy by means of an ultrasonic probe for 3 min at 50% amplitude with chlorobenzene (35 μL) as organic extractant allows achieving an extraction efficiency of 93%, very close to that obtained adding chlorobenzene (35 μL) + acetone (500 μL) (i.e. 96%). On the other hand, the use of the cup-horn sonoreactor or the extraction without adding any disperser agent proved unsuitable because of the lower extraction efficiency reached. Despite ultrasound-assisted DLLME using an ultrasonic probe provided good performance, the option of a disperser agent was chosen, since faster operation was achieved (i.e. 15 s *versus* 18 min for six samples).

3.2. *Analytical figures of merit*

Under optimized conditions, the calibration line was: $y = (0.905 \pm 0.023)\ [Au] + (0.025 \pm 0.009)$ with a regression coefficient better than 0.998, where y is the integrated absorbance and the gold concentration is expressed in $\mu g\,L^{-1}$. The calibration function was linear in the range 0.075–0.75 $\mu g\,L^{-1}$.

Instrumental limits of detection (LODs) and quantification (LOQs) for gold, calculated according to the 3 s/m and 10 s/m criteria (being s the standard deviation of 10 consecutive blanks and m the slope of the calibration curve), were 8.4 and 28 $ng\,L^{-1}$, respectively. When aqueous samples were analyzed, the procedural limits of detection and quantification were 42 and 140 $ng\,L^{-1}$, respectively. Finally, when solid samples were analyzed, the procedural limits of detection and quantification for 30 mg of sample were 1.5 and 5.2 $ng\,g^{-1}$, respectively.

Repeatability expressed as relative standard deviation (RSD) ranged from 4.0 to 8.6% for water samples, from 5.5 to 9.7% for certified reference materials and from 3.6 to 9.2% for environmental solid samples.

The enrichment factor was calculated from the following equation:

$$EF = \frac{C_{sed}}{C_0} \qquad (1)$$

where EF, C_{sed} and C_0 are the enrichment factor, the analyte concentration in the sedimented phase and the initial concentration in the aqueous sample, respectively. The C_{sed} was calculated from the calibration graph obtained by conventional LLE-ETAAS using a mixture with 650 μL of Au (III) aqueous standard (concentration in the range 25–150 $\mu g\,L^{-1}$), 100 μL of concentrated HCl, 0.250 μL of 0.031 M $[CH_3(CH_2)_3]_4NBr$ and 1 mL of chlorobenzene. The resulting enrichment factors were 220 and 415 when using a sample volume of 5 and 10 mL, respectively.

The extraction efficiency of the DLLME method, defined as the percentage of total analyte amount extracted into the sedimented phase was calculated from Eq. (2):

$$EE = \left(\frac{C_{sed}}{C_0}\right)\left(\frac{V_{sed}}{V_{aq}}\right) \times 100 \qquad (2)$$

where EE, V_{sed} and V_{aq} are the extraction efficiency, the volume of the sedimented phase and the volume of the sample solution, respectively. Finally, the extraction efficiency achieved was 96.4%.

3.3. *Analytical applications*

3.3.1. *Gold determination in real water samples*

Gold levels in the water samples analyzed were below the detection limit. The suitability of calibration with aqueous standard solutions was verified by performing spiking experiments in river and dam water samples. The achieved recovery of a spike containing 0.3 $\mu g\,L^{-1}$ Au ranged from 91 to 110% (Table 2). The Student t-test was applied, and no significant differences were found (i.e. t_{exp} was lesser than t_{crit} in all cases).

3.3.2. *Gold determination in certified reference materials*

At the best of our knowledge, this is the first attempt to combine DLLME with an effective sample pre-treatment method such as ultrasound-assisted extraction for trace element analysis.

Appropriate conditions were applied for the extraction of gold from environmental certified materials (Table 3). Ultrasonic extraction of gold from solid samples was carried out prior to the DLLME step. A volume of 450 or 900 μL (depending on the gold concentration in the sample) from the extract obtained upon sonication was added to a 5 mL-vial (2.5 mL of 3.1×10^{-2} M $[CH_3(CH_2)_3]_4NBr$, 1 mL of concentrated HCl). Moreover, spiking experiments were performed in order to check for possible matrix effects in the formation of the ion pair and the subsequent determination of gold by ETAAS. Spikes of 0.3 $\mu g\,L^{-1}$ Au gave a recovery of 94.4 ± 11.6% for SRM 2782, 101.9 ± 6.0% for SRM 2710 and 97.5 ± 7.0% for SRM 2711.

The Student t-test was applied to CRMs. The gold concentration found in CRMs was in good agreement with the indicative values (t-test, $p = 0.95$). t_{exp} (2.0–2.6) was less than t_{crit} in all cases.

3.3.3. *Gold determination in sediments and soils*

The combined methodology UAE–DLLME was applied to the determination of gold in sediment and soil samples. As shown in Table 4, the proposed methodology allows determining the concentration of gold at the $ng\,g^{-1}$ level. The sampling points showing higher gold concentration were soils of Rivas (100 ± 23 $ng\,g^{-1}$) and Brués (249 ± 54 $ng\,g^{-1}$), which were exploited as gold ores until 1910 [34].

Table 2
Determination of gold in natural water samples.

Samples	Added (μg L^{-1})	Found value (μg L^{-1}) $\bar{x} \pm t \cdot s\sqrt{n}$	Recovery (%)	RSD (%)	t_{exp}
Avia River	0	–			
	0.3	0.28 ± 0.06	95	8.6	0.9
Castrelo de Miño (dam water)	0	–			
	0.3	0.33 ± 0.04	110	4.7	3.3
Arenteiro River	0	–			
	0.3	0.27 ± 0.03	91	4.0	4.2

t_{crit} = 4.303 for n = 3; RSD is the relative standard deviation.

Table 3
Determination of gold in certified reference materials.

CRM	Indicative value $\bar{x}$ (μg g^{-1})	Found value $\bar{x} \pm t \cdot s\sqrt{n}$ (μg g^{-1})	Recovery (%)	RSD (%)	t_{exp}
SRM 2782 Sewage Sludge	2.2	2.4 ± 0.4	110	6.3	2.6
SRM 2710 Montana Soil	0.6	0.55 ± 0.07	93	5.5	2.4
SRM 2711 Montana Soil	0.03	0.028 ± 0.007	96	9.7	0.8

t_{crit} = 4.303 for n = 3; RSD is the relative standard deviation.

Table 4
Analytical results (ng g^{-1}; n = 3) for the determination of gold in river sediments and soil extracts using UAE–DLLME–ETAAS.

Sampling point	Found value $\bar{x} \pm t \cdot s\sqrt{n}$ (ng g^{-1})	RSD (%)
Miño River sediment (Ourense)	<LOQ	–
Arnoia River sediment (Arnoia)	<LOQ	–
Arenteiro River sediment (O Carballiño)	5.8 ± 1.3	9.2
Miño River sediment (Salvaterra de Miño)	7.1 ± 0.6	3.6
Louro River sediment (Tui)	80 ± 12	5.9
Lagares River sediment (Vigo)	13 ± 3	8.2
Brués soil (Boborás)	249 ± 54	8.7
Rivas soil (O Irixo)	100 ± 23	9.0
O Lago soil (Maside)	27 ± 5	7.9
Sampaio soil (Ribadavia)	<LOQ	–
Oleiros soil (Salvaterra de Miño)	6.4 ± 0.6	3.6

The LOD for gold is 1.5 ng g^{-1} and the LOQ is 5.2 ng g^{-1} (for 30 mg of mass sample); RSD is the relative standard deviation.

Spiking experiments were also performed in some environmental solid samples. Spikes of 0.3 μg L^{-1} gold gave a recovery of 106 ± 5% for O Lago soil (Maside) and 98 ± 7% for Miño River sediment (Salvaterra de Miño).

3.4. Comparison with other methodologies for gold preconcentration

In Table 5, some alternative methods for separation/preconcentration of gold are compiled and compared with our UAE–DLLME approach. The analysis time was estimated in all cases according to the information provided in the literature. When water samples are analyzed, preconcentration can be directly applied. For environmental solid samples, a sample pre-treatment is required. Shorter pre-treatment times along with a decreased volume of organic solvents and sample mass are achieved with the in-tandem combination of UAE and DLLME. The enrichment factor achieved for water sample approaches the theoretical one due to the high extraction efficiency reached (i.e. 96%). In relation with

Table 5
Comparison of the proposed method with others reported in the literature for preconcentration and determination of gold.

Analytical technique	Matrix (estimated analysis time)	Sample volume or mass	Enrichment factor	Linear range (μg L^{-1})	Detection limit	RSD (%)	Ref.
MW-Hg coprecipitation-TXRF	Urine, roots and dust samples (≈2 h)	20 mL	–	Up to 5	2 ng L^{-1}	20	[7]
SPE–ICP-OES	Geological samples (≈1 h)	0.3 g	50	2–25	47 ng L^{-1}	4.8	[4]
Simplified-CPE–ETAAS	Water (10 min) Copper samples (≈1 h)	50 mL 0.1 g	200	0.01–0.2	2 ng L^{-1} 2 ng g^{-1}	3.6–4.5 1.1–3.6	[5]
MW-CPE–ICP-MS	Water (40 min) Soils (≈2 h)	30 mL 0.2 g	125	0.02–2	0.12 ng L^{-1}	0.8–1.8 1.7–8.6	[6]
LLME–FAAS	Water (5 min)	500 mL	1000	0–10	2.9 ng L^{-1}	3.4	[35]
LLE–ETAAS	Water and wastewater (10 min)	20–50 mL	2	1000–15,000	120 μg L^{-1}	2.1	[8]
DLLME–ETAAS	Water (3 min) Silica ore (≈2 h)	10 mL 0.2 g	388	0.03–0.5	5 ng L^{-1}	4.2 10.6	[24]
DLLME–FAAS and ETAAS	Water (14 min) Pt metal and alloy (≈2 h)	8 mL 0.1 g	60	0.02–1.0	2 ng L^{-1}	2.0–6.1 1.5–3.9	[25]
UAE–DLLME–ETAAS	Water (3 min) Sediment, soils, sewage sludge (25 min)	5 mL 30 mg	220	0.075–0.75	8.4 ng L^{-1} 1.5 ng g^{-1}	4.2 3.6–9.7	This work This work

The preparation and preconcentration steps are: SPE (solid-phase extraction); CPE (cloud point extraction); MW (microwave); LLME (liquid–liquid microextraction); LLE (liquid–liquid extraction); DLLME (dispersive liquid–liquid microextraction); UAE (ultrasound-assisted extraction).
The analytical techniques for determination are: ICP-OES (inductively coupled plasma optical emission spectrometry); ICP-MS (inductively coupled plasma mass spectrometry); ETAAS (electrothermal-atomic absorption spectrometry); FAAS (flame atomic absorption spectrometry); TXRF (total reflection X-ray fluorescence).

the linear range, LOD and precision obtained are comparable to other methods using DLLME or CPE. However it is considered that DLLME is easier and simpler than CPE, due to the tedious steps involved in CPE.

4. Conclusions

The combination of UAE and DLLME has been successfully applied for the determination of gold in both liquid and solid samples. The expeditiousness of UAE for fast solid–liquid extraction along with the efficient liquid–liquid microextraction provided by DLLME allows improving sample preparation for determination of gold at ultratrace level. This methodology could be easily adapted for the determination of other elements present at ultratrace level in solid samples, using suitable liquid-phase microextraction approaches after UAE.

Acknowledgements

Financial supports from the Spanish Ministry of Science and Innovation (project CTQ2009-06956/BQU) and the Vigo University (Contract for Reference Research Groups 09VIA08) are gratefully acknowledged. De La Calle also thanks Xunta de Galicia for financial support as a researcher of Maria Barbeito Program and Cabaleiro thanks the University of Vigo for a research grant.

References

[1] R. Eisler, Inflam. Res. 52 (2003) 487–501.
[2] M.F. Guerra, T. Calligaro, Meas. Sci. Technol. 14 (2003) 1527–1537.
[3] C.M. Goodman, C.D. McCusker, T. Yilmaz, V.M. Rotello, Bioconjugate Chem. 15 (2004) 897–900.
[4] S.S. Jibrin, C. Huang, J. Li, N. Zhang, B. Hu, Geostand. Geoanal. Res. 33 (2009) 469–476.
[5] J.L. Manzoori, H. Abdolmohammad-Zadeh, M. Amjadi, Microchim. Acta 159 (2007) 71–78.
[6] N.N. Meeravali, S.-J. Jiang, J. Anal. Atom. Spectrom. 23 (2008) 1365–1371.
[7] J. Messerschmidt, A.V. Bohlen, F. Alt, R. Klockenkämper, Analyst 125 (2000) 397–399.
[8] M.S. El-Shahawi, A.S. Bashammakh, S.O. Bahaffi, Talanta 72 (2007) 1494–1499.
[9] K. Pyrzynska, Spectrochim. Acta B: Atom. Spectrosc. 60 (2005) 1316–1322.
[10] R.R. Barefoot, J. Anal. Atom. Spectrom. 13 (1998) 1077–1084.
[11] M. Balcerzak, Anal. Sci. 18 (2002) 737–750.
[12] M. Valcárcel, M. Silva, Teoría y práctica de la extracción líquido–líquido, 1984 (Alhambra/Madrid).
[13] N.R. Das, S.N. Bhattacharyya, Talanta 13 (1976) 535–540.
[14] S. Dadfarnia, A.M.H. Shabani, Anal. Chim. Acta 658 (2010) 107–119.
[15] S. Armenta, S. Garrigues, M. de la Guardia, Trends Anal. Chem. 27 (2008) 497–511.
[16] F. Pena-Pereira, I. Lavilla, C. Bendicho, Trends Anal. Chem. 29 (2010) 617–628.
[17] M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1–9.
[18] F. Pena-Pereira, I. Lavilla, C. Bendicho, Anal. Chim. Acta 669 (2010) 1–16.
[19] A.N. Anthemidis, K.-I.G. Ioannou, Anal. Chim. Acta 668 (2010) 35–40.
[20] A.N. Anthemidis, K.-I.G. Ioannou, Talanta 79 (2009) 86–91.
[21] S.Z. Mohammadi, D. Afzali, M.A. Taher, Y.M. Baghelani, Talanta 80 (2009) 875–879.
[22] S.Z. Mohammadi, D. Afzali, Y.M. Baghelania, Anal. Chim. Acta 653 (2009) 173–177.
[23] S.Z. Mohammadi, D. Afzali, M.A. Taher, Y.M. Baghelani, Microchim. Acta 168 (2010) 123–128.
[24] M. Shamsipur, M. Ramezani, Talanta 75 (2008) 294–300.
[25] S. Kagaya, D. Takata, T. Yoshimori, T. Kanbara, K. Tohda, Talanta 80 (2010) 1364–1370.
[26] L. Kocúrová, I.S. Balogh, J. Skrlikova, J. Posta, V. Andruch, Talanta 82 (2010) 1958–1964.
[27] P. Liang, L. Peng, P. Yan, Microchim. Acta 166 (2009) 47–52.
[28] A. Sarafraz-Yazdi, A. Amiri, Trends Anal. Chem. 29 (2010) 1–14.
[29] A.S. Amin, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 77 (2010) 1054–1058.
[30] I. De La Calle, N. Cabaleiro, M. Costas, F. Pena, S. Gil, I. Lavilla, C. Bendicho, Microchem. J. (2010), doi:10.1016/j.microc.2010.07.011.
[31] F. Pena-Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta B: Atom. Spectrosc. 64 (2009) 1–15.
[32] W.J. Maeck, G.L. Booman, M.E. Kussy, J.E. Rein, Anal. Chem. 33 (1961) 1775–1780.
[33] O. Bravo, R.T. Iwamoto, Anal. Chim. Acta 47 (1967) 209–214.
[34] J.C. Mirren, Guía dos minerais de Galicia, 1990 (Vigo).
[35] E. Carasek, Talanta 51 (2000) 173–178.