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PAPER

Preconcentration and determination of As, Cd, Pb and Bi using different sample introduction systems, cloud point extraction and inductively coupled plasma optical emission spectrometry

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This study deals with the development of a method for As, Bi, Cd and Pb preconcentration and determination using cloud point extraction (CPE) and inductively coupled plasma optical emission spectrometry (ICP OES). Hydride generation, pneumatic nebulization and micronebulization/aerosol desolvation were investigated for introducing the surfactant rich phase into the ICP. *O*,*O*-Diethyldithiophosphate (DDTP) was used as complexant and octylphenoxypolyethoxyethanol (Triton X-114) as surfactant. The influence of concentration of HNO_3, HCl, DDTP, Triton X-114, surfactant rich phase in methanol, reductant of As, and $NaBH_4$ was evaluated. The enrichment factors obtained were 10, 18, 12 and 14 for As, Bi, Cd and Pb, respectively. The limits of detection (LODs) of As, Bi, Cd and Pb were 0.055, 0.063, 0.047 and 0.28 μg L^{-1}, respectively. Precision and accuracy were assessed by analysis of certified enriched water (NIST 1643e), oyster tissue (NIST 1566b), tobacco leaves (CTA-OTL-1), bush branches and leaves (GBW 07602) and analyte spiking. Microwave-induced combustion (MIC), sonication, and acid digestion were used for sample preparation. The developed method was applied for extraction and determination of As, Bi, Cd and Pb in river water, wine, fertilizer and urine. Analyte recovery close to 100% and relative standard deviation (RSD) lower than 5% were observed.

1. Introduction

Matrix separation/analyte preconcentration has been used to reduce interference and also improve limits of detection (LODs).[1,2] Among the different methods used for matrix separation/analyte preconcentration, cloud point extraction (CPE) is outstanding.[2–7] Cloud point extraction is based on micelles formation and subsequent separation. Micellar aqueous solution is produced by addition of surfactant. The amount of surfactant added must be such to ensure the formation of micelle aggregates in the solution [the final surfactant concentration must exceed the critical micelle concentration (CMC)]. Once the surfactant concentration exceeds the CMC, the aqueous micellar solution separates into two isotropic phases: a surfactant-rich phase of small volume and a surfactant-poor phase of much higher volume (aqueous). The separation of the phases can be accelerated by increasing the temperature and addition of salt. Any component that binds to the micellar aggregate in solution can be extracted from the original solution and, therefore, be concentrated in the surfactant-rich phase.[8] In the case of inorganic species, which are hydrophilic, complexing agents are used for producing hydrophobic species. These species produced are then extracted into micelles.[2,9]

Reagents such as 8-hydroxyquinoline,[3] *O*,*O* diethyldithiophosphate (DDTP)[1,7,10] and ammonium pyrrolidinedithiocarbamate (APDC)[11] have been used as complexants. DDTP is quite stable in acid medium that is very important because samples are usually decomposed with acid.[7,10] The octylphenoxypolyethoxyethanol (Triton X-114, a nonionic surfactant) has been widely used[11,12] mainly because of the relatively low CPE temperature (between 22 and 25 °C) and low cost.

Analyte preconcentration using CPE can be performed with a small volume of surfactant, which is an advantage of the method. Complexant, pH, ionic strength, surfactant type and concentration, temperature, time of reaction and centrifugation have to be evaluated to make CPE successful. High electrolyte concentration and high acidity can prevent analyte preconcentration and/or CPE. Thus, previous sample preparation must be carefully evaluated.

Atomic absorption (AAS) techniques and inductively coupled plasma optical emission spectrometry (ICP OES) are usually employed for analyte detection after its preconcentration using CPE.[1,13,14] However, CPE in conjunction with ICP OES and hydride generation (HG) has not been much investigated for hydride forming elements. Quite low LODs are expected, especially if an ICP OES spectrometer with axially viewed plasma is used for detection.

Due to viscosity and organic content of the surfactant-rich phase, which affects the plasma performance and stability,

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appropriate sample introduction systems and nebulizers are required. For example, flow injection (FI) was used for introducing a small volume of the surfactant-rich phase into plasma,[3] or the analyte present in the surfactant-rich phase was retained in a column made with cotton, eluted with a mixture of nitric acid and propanol and subsequently introduced into plasma.[13] Other examples are employment of free-clogging nebulizer[14] or chemical vapour generation.[5]

Micronebulization/aerosol desolvation has not been investigated for introducing the surfactant rich phase into ICP. Aerosol desolvation promotes better sample transport efficiency to plasma and better sensitivity as a consequence. By using micronebulization/aerosol desolvation analysis of a very low amount of sample is possible.[15,16] This is an advantage since the volume of the surfactant-rich phase is small. On the other hand, more critical effects of organics are expected because the amount of them introduced into the plasma increases due to the higher sample transport efficiency.

The potential of CPE for matrix separation/Cd, Pb, Bi and As preconcentration in different matrices followed by analyte detection using ICP OES is investigated in the present work. Micronebulization/aerosol desolvation and HG are proposed for introducing the surfactant-rich phase into plasma. Different procedures of sample preparation are used. In order to obtain a solution with low acid concentration, microwave induced combustion (MIC)[17] is employed.

2. Material and methods

2.1. Instrumentation

An Optima 2000 DV-ICP OES spectrometer (PerkinElmer, Norwalk, CT, USA) was used. Argon (White Martins/Praxair) was used as plasma gas and auxiliary gas, whereas nitrogen with purity of 99.996% (White Martins/Praxair) was used as purging gas. The main instrumental parameters are summarized in Table 1.

A home made HG system was hyphenated with ICP OES and used for As and Bi determination. This system is described elsewhere.[5] It consists basically of a confluence and a gas liquid separator. In this system, solutions were transported and mixed using the peristaltic pump of the ICP OES spectrometer. The flow rate of sample, HCl and $NaBH_4$ solutions were 1.3, 1.8 and 1.3 mL min^{-1}, respectively. The pneumatic nebulizer used (GemCone)[18] is considered free-clogging and suitable for viscous solutions or having high content of dissolved solids. An APEX-Q system (ESI, USA) with aerosol desolvation was used. Solutions were aspirated through a PFA microconcentric nebulizer fitted into a cyclonic spray chamber that was heated at 140 °C and then transported to a Peltier-cooled multipass condenser where the temperature was set as 2 °C. Partial solvent removal occurs in this system and sample transport efficiency is about 30%. The efficiency of this system is presented elsewhere.[15,16]

Table 1 Instrumental parameters used for ICP OES and sample introduction systems

Parameter	Arsenic	Cadmium and lead	Bismuth
Plasma power/W	1500	1500	1400
Plasma gas flow rate/L min^{-1}	15	15	15
Auxiliary gas flow rate/L min^{-1}	0.2	0.2	0.2
Nebulizer or carrier gas flow rate/ L min^{-1}	0.6	0.6	0.6
Sample introduction	Hydride generation	GemCone; unbaffled cyclonic spray chamber	APEX-Q system; hydride generation
Spectral line/nm	193.696	228.802 (Cd) and 220.353 (Pb)	223.061
Background correction	2 points/ peak	2 points/peak	2 points/peak
Signal processing (peak area)	7 points/ peak	3 (Cd) and 7 (Pb) points/peak	7 points/peak

A heating block (TE-007D Tecnal, Brazil) was used for the fertilizer sample decomposition. A microwave oven Multiwave 3000 (Anton Paar) equipped with quartz vessels was used for MIC. A water bath with temperature control was used as a source of heating and assists CPE while a centrifuge was used for separation of the aqueous and surfactant-rich phases. A Hydraulic Press (15 ton) was used for pellets preparation used in MIC.

2.2. Reagents, solutions and materials

All chemicals were of analytical-grade. Water purified (to 18.2 MΩ cm) in a Milli-Q system (Millipore) was used to prepare all reagents, solutions and samples. Nitric acid (65% m/m), HCl (37% m/m), H_2O_2 (30% m/m) and CH_3OH (all from Merck) were used. The HNO_3, HCl and CH_3OH used were further purified by sub-boiling distillation (a Milestone duo PUR 2.01E system was used). Sodium tetrahydroborate ($NaBH_4$, Vetec, Brazil) was employed for As and Bi determination using HG. DDTP $[(C_2H_5O)_2P(S)SNH_4]$ from Aldrich and Triton X-114 from Sigma were used for As, Cd, Pb and Bi preconcentration. A 5.0% (m/v) DDTP stock solution was prepared by the dissolution of the reagent in water. A 5.0% (m/v) Triton X-114 stock solution was prepared by weighing 2.5 g of the reagent in a polypropylene vial and adding 50 mL of water. Antifoam Y-30 from Sigma-Aldrich was used to reduce foam production in determinations using HG. Potassium iodine (KI) and ascorbic acid ($C_6H_8O_6$) from Vetec were used for As reduction. Solutions of As, Cd, Pb and Bi were prepared in 0.14 mol L^{-1} HNO_3 by serial dilution of mono-element stock solutions (Titrisol, Merck) containing 1000 mg L^{-1} of the analyte. The calibration solutions concentration and respective acid concentration varied according to the analyte as will be seen later. The calibration solutions were also submitted to CPE in the same way as that of samples.

A 6.0 mol L^{-1} ammonium nitrate (Merck) solution was used as igniter for MIC. A small disc (15 mm of diameter and mass of 12 mg) of paper with low ash content was also used to aid the combustion process. A more detailed procedure of sample preparation using MIC is described elsewhere.[14]

2.3. Samples and sample preparation

Samples of the following certified reference materials (CRMs) were analyzed: water (NIST 1643e) and oyster tissue (NIST 1566b) from the National Institute of Standards and Technology, bush branches and leaves (GBW 07602) from the Institute of Nuclear Research of China, and oriental tobacco leaves

(CTA-OTL-1) from the Institute of Nuclear Chemistry and Technology of Poland. The solid samples of the CRMs were decomposed using MIC. Approximately 300 mg of powder sample were pressed into pellets, weighed directly on filter paper and then placed on a quartz holder positioned inside a quartz vessel to which 6 mL of absorbing solution (0.4 mol L^{-1} HNO_3) was previously added. Then, 50 μL of ammonium nitrate solution was immediately added to the paper. After closing the quartz vessels and placing them in the rotor they were pressurized with oxygen at 20 bar for 2 min and the rotor placed inside the microwave oven. Next, the mixtures inside the vessels were irradiated by microwave for 60 s at 1400 W followed by cooling for 20 min. The resultant solutions were transferred to graduated polypropylene vials and the volume completed to 25 mL using water. A sample of bush branches and leaves (GBW 07602) was also prepared by sonication; aliquots of 300 mg in 25 mL of 2.4 mol L^{-1} HCl were sonicated for 30 s at 80 W using a probe. An ultrasonic processor (Unique, Brazil) equipped with a 4 mm diameter titanium tip was used. The sonicated mixture was subsequently centrifuged for 10 min at 3200 rpm. Aliquots of the supernatant were then submitted to CPE.

Fertilizer and white wine purchased in the local market, river water (from Rio Guaíba, RS, Brasil) and urine (from a volunteer) were analyzed. Aliquots of 0.100 g of the fertilizer (previously pulverized in agate mortar) were weighed and transferred to PTFE flasks to which 1.0 mL HNO_3 and 1.0 mL H_2O_2 were added. The mixture was left to stand for a period of 12 h. Subsequently, the flasks were closed with screw caps and the mixture heated at 100 °C for 4 h. After cooling at room temperature, the obtained solutions were transferred to graduated polypropylene vials and the volume completed to 25 mL using water.[19] The river water was collected in a cleaned polyethylene bottle and just filtered (a Whatman filter paper for fast filtration was used). The urine and wine samples were sonicated with a probe for 30 s at 80 W. Then, they were ten-fold diluted with water before being submitted to CPE. Analyte recovery tests were performed in order to verify the accuracy and precision of the method for wine, river water and fertilizer analysis. The liquid samples were spiked before being submitted to CPE whereas the fertilizer was spiked before decomposition.

2.4. Cloud point extraction

Aliquots of sample solution ranging from 1 to 7 mL were transferred to graduated polypropylene vials. For As determination, KI and $C_6H_8O_6$ (ascorbic acid) were added to the solution in order to obtain only As(III) species, which reacts with DDTP. After addition of KI and $C_6H_8O_6$ the mixture was allowed to stand for 30 minutes. Next, DDTP and Triton X-114 solutions were added and the volume of the mixture was completed to 14 mL using water and/or acid solution. The optimal concentrations of all reagents in the final mixture were investigated and they are summarized in Table 2. The mixture was heated in a water bath in order to accelerate the separation of the phases, centrifuged at 3200 rpm for 10 min and then cooled in an ice bath for 10 min. The aqueous phase was removed by inversion of the vial and the surfactant-rich phase was subsequently taken by using a Pasteur pipette. The final volume of the surfactant-rich phase ranged from 50 to 150 μL. Different amounts of methanol were added to the surfactant-rich phase, depending on the sample introduction system used. Dilution with methanol was followed by addition of 1.0 mL of 0.60 mol L^{-1} HCl for As, 0.5 mL of 0.70 mol L^{-1} HNO_3 or 1.0 mL of 0.5 mol L^{-1} HCl for Bi, and 1.0 mL of 0.70 mol L^{-1} HNO_3 for Cd and Pb.

Table 2 Conditions established for As, Cd, Pb and Bi preconcentration using CPE, and As and Bi hydride generation

Condition	As	Cd and Pb	Bi
DDTP concentration (% m/v)	0.25	0.20	0.15
Triton X-114 (% m/v)	0.05	0.15	0.15
Extraction medium and concentration/ mol L^{-1}	HCl/ 0.96	HNO_3/ 0.28	HNO_3/ 0.40
Temperature/°C	50	50	50
Period of heating/min	20	20	20
Surfactant rich-phase volume/μL	50	150	150
Volume of methanol added to the surfactant rich-phase/μL	100	50	100
HCl concentration for hydride generation/ mol L^{-1}	4.8	—	3.0
$NaBH_4$ concentration (% m/v)	0.5	—	0.5

3. Results and discussion

3.1. Analyte preconcentration and detection

Arsenic. Initially, the influence of HCl concentration on As preconcentration was evaluated. According to Fig. 1(a), the highest signal of As was obtained in the presence of 0.96 mol L^{-1} HCl. It is known that As(V) does not react with DDTP[4] and for that reason a reducing agent was added.[20,21] The presence of HCl and heating were not sufficient to reduce whole As(V). In this case, addition of potassium iodide (KI)/ascorbic acid (aa) increased by 30% the signal of As in the solution submitted to preconcentration. According to the results obtained, KI/aa did not interfere in the CPE and the surfactant-rich phase did not prevent As hydride generation. The concentration of Triton X-114 was fixed at 0.05% (m/v). The smallest volume possible of surfactant was used in order to avoid excessive production of foam in the gas–liquid separator. Due to its effect in the plasma, the volume of methanol added to reduce the viscosity of the surfactant rich phase must also be low. Even by using hydride generation, vapour of methanol can be transported to plasma. Tests were made using 50 to 400 μL of methanol. The arsenic signal increased with the increase of methanol up to 100 μL remaining constant thereafter. However, the precision worsened with the increase of methanol. Hence, the volume of methanol was fixed at 100 μL.

With respect to As hydride generation, better sensitivity was observed for 4.8 mol L^{-1} HCl and 0.5% (m/v) $NaBH_4$. Aqueous solution not submitted to CPE was also analyzed just for comparison. The best conditions for As hydride generation in solution not submitted to CPE mismatched with those for solution submitted to CPE. The differences may be due to the different medium and also foaming production into the gas–liquid separator. Anyway, this inconvenience did not preclude obtaining accurate results because the calibration solutions were also subjected to CPE.

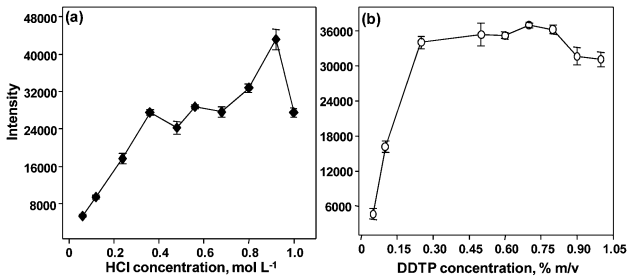

Fig. 1 Influence of the reagents concentration on As [20 μg L^{-1} of As(v)] pre-concentration in (a) and (b). KI: potassium iodine; aa: ascorbic acid. *Conditions*: 0.20% m/v DDTP, 0.05% m/v Triton X-114 and 100 μL of methanol in (a) and in (b) 0.05% m/v Triton X-114, 0.96 mol L^{-1} HCl, 0.5% m/v KI/aa and 100 μL of methanol. Hydride generation conditions: 0.5% m/v $NaBH_4$ and 4.0 mol L^{-1} HCl.

The surfactant-rich phase was also introduced into plasma by the micronebulization/aerosol desolvation system employed in the present work. However, the analyte signal did not stabilize and the LOD was worse than that obtained by using HG. Therefore, HG was selected for As determination.

Cadmium and lead. Firstly, the influence of HNO_3 and HCl concentrations on Cd and Pb preconcentration was investigated. It can be observed in Fig. 2(a) and (b) that the signals of both analytes decrease with the increase in the acid concentration. The effect is more pronounced for Cd. Strong acid medium increases the cloud point temperature[7] and disturbs the formation of micellar aggregates. As a result, losses of Cd can occur in the centrifugation step. According to the literature,[22] the acidity of the medium should be kept as low as possible for maintaining the stability of Cd and Pb complexes. Better performance was observed for HNO_3 (Fig. 2(a) and (b)). Thus, this acid was chosen as preconcentration medium. Besides, HNO_3 is usually employed for the decomposition of environmental and biological materials, which means that it is almost always present in the sample solution where the analyte will be preconcentrated. According to Fig. 2, as a compromise condition for measuring Cd and Pb together, the HNO_3 concentration was fixed at 0.28 mol L^{-1}.

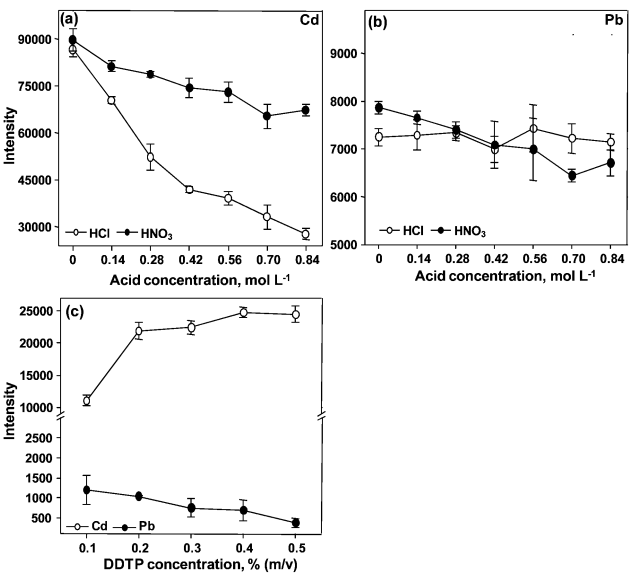

Fig. 2 Influence of the reagents concentration on pre-concentration of Cd and Pb using CPE. A solution containing 20 μg L^{-1} of Cd and Pb was used. *Conditions*: 0.30% m/v DDTP, 0.15% m/v Triton X-114 and 50 μL of methanol in (a) and (b); 0.15% m/v Triton X-114, 0.28 mol L^{-1} HNO_3 and 50 μL of methanol in (c).

With respect to Triton X-114, the highest signals are observed when the surfactant concentration is 0.15% (m/v). The signals of Cd and Pb decrease in the presence of Triton X-114 higher than 0.15% (m/v). This behavior had already been observed by other authors, for Cd and Pb preconcentration in blood[12] and seawater[7] prior to the analytes determination using ETAAS and ICP-MS, respectively. The influence of the DDTP concentration is shown in Fig. 2(c). It can be seen that the signal of Cd increases with the increase of DDTP concentration up to 0.4% (m/v). On the other hand, the signal of Pb decreases with the increase of the complexant concentration. Thus, keeping in mind the possibility of measuring Pb and Cd simultaneously, 0.20% (m/v) DDTP was chosen for both analytes as a compromise condition. In order to reduce the viscosity of the surfactant-rich phase, 50 μL of methanol were added to it. A minimum volume of methanol was added considering the solvent effects in the plasma.

Micronebulization/aerosol desolvation was also investigated for Cd and Pb determination. The sensitivity was improved, but precision was not acceptable (RSD around 30%). This system was then not employed for further Cd and Pb determination in the surfactant-rich phase due to the bad precision observed. The main reason was the effect of the surfactant and methanol that were present in the plasma, since very good precision (RSD lower than 3%) was observed for Cd and Pb in aqueous solution by using the same nebulizer. In this case the LODs of Cd and Pb were 0.07 and 0.89 μg L^{-1}, respectively. The effect of surfactant and methanol is not the same for all elements. The same effect observed for Cd and Pb was not observed for Bi, as will be seen later.

Bismuth. The influence of HNO_3 and DDTP concentrations were initially evaluated using micronebulization/aerosol desolvation. As shown in Fig. 3(a), the highest average Bi signal is observed for 0.40 mol L^{-1} HNO_3. The effect of DDTP concentration is shown in Fig. 3(b), where it can be observed that the signal of Bi increases up to 0.15% (m/v) DDTP and remains constant thereafter.

It was observed that the concentration of the surfactant used has a great influence on Bi preconcentration. According to Fig. 3 (c), the appropriate concentration ranges from 0.05 to 0.15% m/v Triton X-114. This is in accordance with results published by other authors[23] who used Triton X-114 and dithizone as complexant of Bi. With respect to the amount of methanol added to the surfactant-rich phase, it was less critical in comparison to the conventional pneumatic nebulization. As shown in Fig. 3(d), the highest signal of Bi was obtained for 100 μL of methanol.

Hydride generation was investigated for Bi determination in the surfactant-rich phase. For this, the influence of HCl and $NaBH_4$ was evaluated. As shown in Fig. 4, sensitivity is better for HCl (3.0 mol L^{-1}). Sensitivity increased with the increase in the $NaBH_4$ concentration but the $NaBH_4$ concentration was fixed at

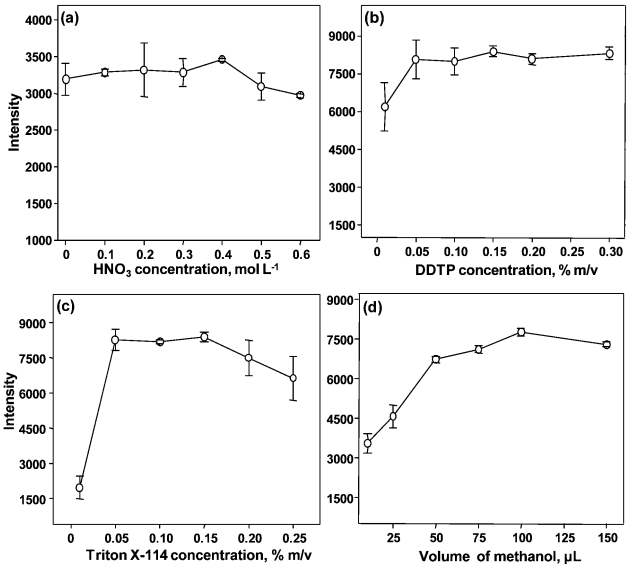

Fig. 3 Influence of the reagents concentration on preconcentration of Bi using CPE. A solution containing 20 µg L^{-1} of Bi was used. *Conditions*: 0.30% m/v DDTP, 0.15% m/v Triton X-114 and 50 µL of methanol in (a); 0.15% m/v Triton X-114, 0.40 mol L^{-1} HNO_3 and 50 µL of methanol in (b); 0.15% m/v DDTP, 0.40 mol L^{-1} HNO_3 and 50 µL of methanol in (c); 0.15% m/v DDTP, 0.15% m/v Triton X-114 and 0.40 mol L^{-1} HNO_3 in (d).

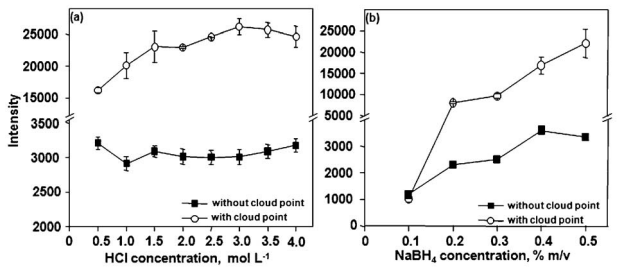

Fig. 4 Influence of the reagents concentration on hydride generation of Bi using CPE. A solution containing 15 µg L^{-1} of Bi was used. *Conditions*: 0.40 mol L^{-1} HNO_3, 0.15% m/v DDTP, 0.15% m/v Triton X-114 and 100 µL of methanol.

0.5% (m/v) due to excessive foam production into the gas–liquid separator. Similar LODs were obtained using micronebulization/aerosol desolvation or HG (see Table 3). Therefore, micronebulization/aerosol desolvation or HG can be used for Bi determination in the surfactant-rich phase. The main advantage of micronebulization/aerosol desolvation was lower consumption of reagents in comparison to HG.

3.2. Figures of merit

The figures of merit of the proposed method and calibration curve parameters are summarized in Table 3. The LODs were calculated according to IUPAC (International Union of Pure and Applied Chemistry) recommendations. The LOD was obtained from $b + 3s$; b is the mean concentration of 10 consecutive measurements of the blank and s is the standard deviation. The blank for each element underwent the same procedure of the samples and calibration solutions. The enrichment factor (EF) was calculated by the ratio of the slope of calibration curves obtained (with and without analyte preconcentration) for each system used for introducing the surfactant-rich phase into plasma. The surfactant-rich phase (volume ranging from 50 to 150 µL) needed to be diluted (see Section 2.4) due to the high viscosity or foam production into the gas liquid separator, which decreased the EF. Despite the dilution involved, the LODs found in the present work are of the same order of magnitude or lower than values reported in the literature regarding to As, Cd, Pb and Bi preconcentration using CPE, FAAS or ICP OES.[3,6]

3.3. Samples analysis

The accuracy and precision of the developed method were evaluated by the analysis of certified samples and recovery tests. As can be seen in Table 4, the results obtained for Cd and Pb are in agreement with the certified values (at 95% confidence level) for all analysed samples. This demonstrates that microwave induced combustion (MIC) is adequate for preparing samples of vegetal and animal tissues for Cd and Pb preconcentration and determination using CPE and ICP OES. The acid concentration in the resultant sample solution is low and, therefore, favourable to Cd and Pb preconcentration. Bismuth was detected only in certified water and the concentration found was in agreement with the

Table 3 Figures of merit of the proposed method; hydride generation or micronebulization/aerosol desolvation were used for As and Bi; pneumatic nebulization was used for Cd and Pb

Element/system	Calibration curve/µg L^{-1}	Equation	EF	LOD/µg L^{-1}	LOD[a]/µg g^{-1}
As/CPE-HG	0.50–10.0	$y = 2157x + 2.7$	10	0.055	0.022
As Hydr. generation	2.0–20.0	$y = 205.3x - 6.0$	—	0.15	0.062
Bi/CPE Micr./desolvation	0.5–10.0	$y = 747x + 144$	18	0.063	0.026
Bi Neb/desolvation	5.0–25.0	$y = 41.2x + 23$	—	0.46	0.19
Bi/CPE-HG	0.5–10.0	$y = 4442x + 305$	7	0.057	0.024
Bi Hydr. generation	5.0–25.0	$y = 680x + 25$	—	0.13	0.050
Cd/CPE nebulization	1.0–15.0	$y = 7128x + 1382$	12	0.047	0.018
Cd nebulization	5.0–50.0	$y = 616x + 13$	—	0.18	0.072
Pb/CPE nebulization	5.0–25.0	$y = 487x + 45$	14	0.28	0.12
Pb nebulization	15.0–50.0	$y = 35.6x - 12$	—	4.0	2.4

[a] 300 mg of sample in 30 mL of solution and four fold dilution were taken into account; EF: enrichment factor; LOD: limit of detection.

Table 4 Certified reference materials analysis using CPE and ICP OES. Results are the average and standard deviation of three replicates

Sample	Analyte	Certified/μg g^{-1}	Found/μg g^{-1}
NIST 1566b (oyster tissue)	As	7.65 ± 0.65	7.30 ± 0.28
	Bi	—	—
	Cd	2.48 ± 0.08	2.42 ± 0.11
	Pb	0.308 ± 0.009	0.320 ± 0.010
GBW 07602 (bush branches and leaves)	As	0.950 ± 0.080	0.270 ± 0.028,[b] 1.022 ± 0.045[c]
	Bi	0.022	nd
	Cd	0.14 ± 0.01	0.13 ± 0.01
	Pb	6.5 ± 0.9	6.3 ± 0.1
CTA-OTL-1 (oriental tobacco) leaves	As	0.539 ± 0.060	0.458 ± 0.030
	Bi	—	—
	Cd	1.12 ± 0.12	1.01 ± 0.01
	Pb	4.91 ± 0.80	4.04 ± 0.08
NIST 1643e enriched water[a]	As	60.45 ± 0.72	62.72 ± 1.98
	Bi	14.09 ± 0.15	14.62 ± 0.65
	Cd	6.568 ± 0.073	6.305 ± 0.007
	Pb	19.63 ± 0.21	19.32 ± 0.54

[a] In μg L^{-1}; sample preparation. [b] MIC. [c] Sonication; nd: not detected.

Table 5 Analysis of non-certified samples using CPE and ICP OES. Results are the average and standard deviation of three replicates

Sample	Analyte	Found/μg L^{-1}	Spiked/μg L^{-1}	Found/μg L^{-1}	Recovery (%)
Urine	As	nd	5.00	5.48 ± 0.30	110
	Bi	nd	10.0	9.74 ± 0.03	97
	Cd	nd	5.00	4.71 ± 0.08	97
	Pb	nd	10.0	10.1 ± 0.18	100
White wine	As	9.51 ± 0.11	5.00	15.0 ± 0.28	110
	Bi	nd	10.0	9.31 ± 0.15	93
	Cd	nd	5.00	4.72 ± 0.08	94
	Pb	nd	10.0	9.61 ± 0.15	96
River water	As	nd	5.00	5.15 ± 0.07	103
	Bi	nd	10.0	9.61 ± 0.26	96
	Cd	nd	5.00	4.91 ± 0.03	98
	Pb	nd	10.0	10.1 ± 0.18	101
Fertilizer[a]	As	0.67 ± 0.04	1.25	1.80 ± 0.05	91
	Bi	nd	2.5	2.31 ± 0.30	92
	Cd	3.95 ± 0.54	2.5	6.58 ± 1.75	105
	Pb	0.71 ± 0.26	2.5	3.21 ± 0.35	100

[a] In μg g^{-1} (nd: not detected).

certified value. This element was not detected in bush branches and leaves whose Bi concentration informed on the certificate is lower than the LOD of Bi (0.026 μg g^{-1}).

With respect to As, it is observed that the mean concentration found in tobacco leaves (CTA-OTL-1) is lower than the certified value. Nevertheless, the concentration range (mean and standard deviation) is not different for a 95% confidence level. The concentration of As found for bush branches and leaves (GBW07602) submitted to microwave induced combustion (MIC) is different from the certified value. But the concentration found agrees with the certified value if the sample is sonicated and submitted to CPE. In this step of the work it was concluded that additional studies are necessary for the decomposition of vegetal samples using MIC with the aim of As determination.

The results obtained for urine, white wine, river water and chemical fertilizer samples are presented in Table 5. Arsenic was detected in white wine and fertilizer, while Cd and Pb were detected only in fertilizer. Bismuth was not detected in any sample analyzed. Despite the fact that wine, urine and fertilizer have complex matrices, good recoveries were found for all analytes, indicating efficient matrix separation. This also demonstrates that the proposed method can be used for the determination of As, Bi, Cd and Pb in different matrices.

4. Conclusions

The results obtained demonstrated that matrix separation/analyte preconcentration using CPE allowed the determination of low concentrations of As, Bi, Cd and Pb in different matrices. Arsenic and Bi at ng L^{-1} level can be determined using CPE for element preconcentration and HG or micronebulization/aerosol desolvation for introducing the surfactant-rich phase in the plasma. Sensitivities for Bi, Cd and Pb improved through the use of micronebulization/aerosol desolvation. However, the precision for Cd and Pb was worse and no improvement of the LODs was observed for these two elements in the surfactant rich phase in comparison to conventional pneumatic nebulization. As known,[9,22] the complexation of the investigated elements with DDTP occurs in acidic medium (HCl or HNO_3). However, in the present work it was observed that for offline preconcentration of

Cd and Pb the acid concentration must be low. In this sense, the use of MIC has proved to be advantageous, since acid concentration in the final solution is low in comparison to conventional decomposition in a microwave oven.

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