RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2016, **6**, 49076

A novel supramolecular aggregated liquid–solid microextraction method for the preconcentration and determination of trace amounts of lead in saline solutions and food samples using electrothermal atomic absorption spectrometry

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A novel supramolecular aggregated liquid–solid microextraction method was developed for the preconcentration and determination of trace amounts of lead in saline solutions and food samples. The technique was based on catanionic assemblies of cetyltrimethylammonium bromide and sodium dodecyl sulphate surfactants as a new green extraction solvent for use in a dispersive microextraction method coupled with electrothermal atomic absorption spectrometry. This technique benefits from the safe and green properties of the supramolecular aggregates rather than the hazardous and volatile organic solvents commonly used in liquid–liquid microextraction methods. The main component of the dispersive solvent is water and a direct interaction between the extraction solvent and the analyte is possible. The separation behaviour of the sodium dodecyl sulphate/cetyltrimethylammonium bromide solvent phase and various parameters influencing the extraction efficiency of lead (*e.g.* pH, salt concentration, centrifugation time, amount of ligand and extraction solvent) were investigated and optimized. Under the optimum conditions, linearity was observed in the range 0.1–2.0 ng mL^{-1} lead with a correlation coefficient of 0.996 and a limit of detection (S/N = 3) of 0.047 ng mL^{-1}. The relative standard deviations were 6.5 and 5.2% for five repeated measurements of 0.4 and 1.0 ng mL^{-1} lead solutions, respectively. The effects of some common anions and cations on the lead signal were investigated. The proposed method was successfully applied to the determination of lead in sea water and some food samples. The accuracy of the method was confirmed by analysing a certified reference material.

Received 11th February 2016
Accepted 3rd May 2016

DOI: 10.1039/c6ra03874c

www.rsc.org/advances

Introduction

The monitoring of trace amounts of heavy metal pollutants from industrial and agricultural processes is essential as a result of their wide distribution in the environment.[1,2] Lead is one of the most toxic metals and can accumulate in the body from contaminated air, water and food.[3,4] Harmful effects of lead contamination include a reduction in enzymatic activity and damage to the kidneys, liver, brain and central nervous system. Lead can also act as a carcinogen and is classified by the US Environmental Protection Agency as a group B2 human carcinogen.[5–7] As a result of these harmful effects, the World Health Organization has established a maximum allowable limit of 10 ng mL^{-1} for lead in drinking water.[8]

Flame atomic absorption spectrometry (AAS),[9] electrothermal AAS (ET-AAS),[10] inductively coupled plasma atomic emission spectrometry (ICP-AES)[11] and ICP mass spectrometry[12] are the most common analytical methods used to determine lead. Flame AAS is simple and is available in most laboratories, but its poor detection limit (at μg mL^{-1} levels) is not sufficient for the determination of trace amounts of lead. ICP-AES has good sensitivity and can determine lead at ng mL^{-1} levels, but is not widely applied in routine analysis as a result of instrumental complexity and high costs. ET-AAS is relatively cheaper and has a high sensitivity using only a few microlitres of sample.[13]

Despite improvements in the performance of modern analytical instruments, the determination of heavy metals in real samples is limited as a result of their low concentrations and sample matrix effects.[14] To remedy these shortcomings, two different microextraction techniques – solid-phase microextraction[15] and liquid phase microextraction[16] – have been developed. Solid-phase extraction benefits from a low consumption of organic solvent and a high preconcentration factor; however, in determining lead, a derivatization step is also needed.[2,17] Dispersive liquid–liquid microextraction

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(DLLME) is a popular techniques as a result of its high enrichment factor, speed and simplicity.[17]

Much effort has been made to replace the toxic organic solvents used in extraction techniques with supramolecular green solvents. The hydrophilic and hydrophobic parts of surfactants in supramolecular solvents lead to various interactions, including hydrogen bonds, ionic, π-cation, dipole–dipole and dipole–induced dipole interactions and, as a consequence, various compounds with different polarities can be extracted into these solvents.[18] Surfactant aggregates are not volatile or flammable as a result of their high water content, which makes them very safe.

The term cloud-point extraction (CPE)[19] refers to the phase transfer of non-ionic surfactant aggregates from a homogenous solution to a cloudy system at a temperature higher than the cloud-point temperature of the surfactants; this can be very high for thermally unstable compounds.[18,20] However, in ionic surfactants the phase separation phenomenon coacervation is induced at much lower temperatures by either adding high concentrations of inorganic salts,[21] a surfactant with an opposite charge,[22] a co-surfactant such as 1-octanol,[23] an amphiphilic counter ion[24] or inducing pH changes.[25] Thus, unlike in CPE, there is no need to adjust the temperature.

The anionic surfactant sodium dodecyl sulphate (SDS) and the cationic surfactant cetyltrimethylammonium bromide (CTAB) have been used in extraction techniques because of their ready availability and low price.[26–29] SDS shows an acid-induced phase separation behaviour. Usually SDS solutions of a few percentages are prepared in the presence of high concentrations of hydrochloric acid (about 4 mol L^{-1}); the solutions are stirred and then centrifuged for several minutes to achieve phase separation.[25,27] No phase separation is obtained in the absence of highly concentrated HCl, however, despite the high ionic strength (2.0 M) and high temperature (90 °C).[27] CTAB has an even more complex manner of phase separation. A mixture of almost 0.5% surfactant in the presence of saturated sodium chloride is prepared and stirred for few minutes to obtain a cloudy solution.[23,29] A few microlitres of a co-surfactant, such as 1-octanol, are then added, followed by further stirring and centrifugation to obtain phase separation. One of the main problems in phase separation using CTAB is that it is crucially important to use an appropriate concentration of the co-surfactant.

A mixture of cationic and anionic surfactants, known as a catanionic system, has many unique properties depending on the concentrations of the surfactants, their alkyl chain length, the temperature and the molar ratio.[30] In these systems, the two oppositely charged surfactants can interact to form a pseudo-double-tailed zwitterionic surfactant with an effectively smaller head group and an increased volume for the hydrophobic portion,[31] which makes accumulation easier. As a result, they can produce several different types of aggregated microstructure, such as vesicles, lamellar or multilayer phases, precipitates and rod-like micelles, which show more surface activity than either of the pure surfactant microstructures.[32,33] The interaction between these microstructures and various substances has been reported previously.[34–36]

In conventional coacervation techniques, supramolecular aggregates are formed *in situ* by adding a surfactant and other components into the sample solution with several minutes of stirring and centrifugation to assist the separation of the supramolecular solvents from the homogeneous solution. We prepared mixtures of SDS and CTAB at different molar ratios in propanol–water. They were then dispersed in saline lead solutions as the extraction solvent, similar to a DLLME strategy, to speed up the microextraction process. Lead forms a complex with sodium diethyldithiocarbamate and it was preconcentrated into the SDS/CTAB microstructure aggregates. After centrifugation, the separated phase was dissolved in a few microlitres of propanol and analysed using ET-AAS. Various parameters such as the molar ratio of SDS : CTAB, the pH, the amount of ligand and extraction solvent, the percentage of sodium nitrate and the centrifugation time were investigated and optimized.

Experimental

Instrumentation

We used an Analytik Jena Model novAA 400p atomic absorption spectrometer equipped with an electrothermal atomizer, deuterium background correction, MPE 60 autosampler and a lead hollow cathode lamp operated at 217 nm and 8 mA with a monochromator spectral band pass of 0.8 nm. Pyrolytic coated graphite tubes with a L'vov platform and 99.996% purity Ar were used. A Metrohm, 632 pH meter with a glass combined electrode was used to adjust the pH and a Centurion Scientific centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany) was used to accelerate the phase separation.

Reagents and samples

All chemicals were of analytical-reagent grade and deionized distilled water was used in all aqueous solutions. A stock solution of 1000 mg L^{-1} lead was prepared by dissolving appropriate amounts of lead nitrate (Merck, Darmstadt, Germany) in 2% nitric acid solution. The working standard solutions were prepared by stepwise dilution in 0.5% nitric acid. Sodium diethyldithiocarbamate (≥97%) was obtained from Merck and a 2% w/v solution was prepared in deionized water. Propanol (99.7%), ammonia solution (NH_3 25%), ammonium nitrate (NH_4NO_3, ≥98%), nitric acid (HNO_3, 65%), hydrogen peroxide (H_2O_2, 30%), ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ≥98%) and palladium (Pd, 99.99%) were purchased from Merck. CTAB (95%) and SDS (98%) were obtained from Sigma-Aldrich and used without further purification. All glassware was soaked in 10% HNO_3 for at least 24 h before use and then washed with deionized water. The pH values of the working solutions were adjusted by either adding ammonia or nitric acid solutions.

The extraction solvent (100 mmol L^{-1}) was prepared using SDS/CTAB in propanol (at different ratios and percentages) in water to obtain stable solutions and was stored in polypropylene tubes. These solutions were stable for at least for 3 weeks in

propanol in water in room temperature. A 0.2% Pd and 1% $NH_4H_2PO_4$ solution was used as a matrix modifier.

Seawater was collected from the Caspian Sea and filtered through a 0.45 μm filter paper to remove any interfering material. A 10 mL volume of seawater was diluted to 50 mL in the presence of appropriate amounts of NH_4NO_3; the pH was adjusted to determine the lead content using the proposed analytical procedure.

Food samples were collected from local stores. A 0.5 g mass of the milled samples or homogenized tomato paste was weighed in separate beakers. A 5 mL volume of HNO_3 and 3 mL of H_2O_2 were added to each beaker, followed by heating on a hot-plate at 150 °C until complete dissolution. After cooling, the contents were filtered through ash-less filter papers into 50 mL volumetric flasks and then diluted to volume with 10% NH_4NO_3. Lead was determined in these solutions using the proposed procedure.

Microextraction method

A 10 mL volume of the lead ion standard or sample solutions containing 10% w/v ammonium nitrate was adjusted to pH 6 and placed in a 15 mL centrifuge tube. Then 0.2 mL of the ligand solution and 0.3 mL of the extraction solvent solution were added using 1.00 mL syringes and a cloudy solution of immiscible SDS/CTAB aggregates was formed. This separated as a white flexible solid layer standing on top of the aqueous phase after centrifugation at 4000 rpm for 3 min. The solid layer was dissolved in 50 μL of propanol after withdrawing the lower aqueous phase with a 10.00 mL syringe. This solution (20 μL) was then injected into the graphite atomizer to determine the lead concentration.

Results and discussion

Optimization of atomizer temperature programme

To achieve the best atomizer temperature programme, a 1 ng mL^{-1} lead ion solution was analysed according to the proposed method. The optimum conditions are shown in Table 1. In this technique, the SDS/CTAB microstructures were used as the extraction agent; these are not volatile and cannot be removed in the drying step. Therefore the SDS/CTAB microstructures must be burned and decomposed before the atomization step. A temperature programme with three pyrolysis steps was used in the presence of 5 μL of matrix modifiers (0.2% Pd and 1% $NH_4H_2PO_4$). The third pyrolysis step at 700 °C for 10 s was sufficient to burn and decompose the solvent matrix, but it was not enough to remove all the ash products. The lead signal decreased at higher temperatures or longer times. Therefore to obtain an accurate and correct auto-zero process before the atomization step, a pre-auto-zero step before the auto-zero process was used to allow enough time to remove all the ash products at lower temperatures (100 °C) with no reduction in the absorbance of lead.

Table 1 Atomizer temperature programme used to determine lead

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)	Gas flow-rate
Drying	110	5	10	Max
Pyrolysis	250	20	20	Max
Pyrolysis	350	20	20	Max
Pyrolysis	700	20	10	Max
Pre-auto-zero	100	—	10	Max
Auto-zero	100	0	6	Stop
Atomization	2000	2000	5	Stop
Cleaning	2450	500	4	Max

SDS/CTAB phase separation behaviour

SDS/CTAB supramolecular aggregates were used as the extraction solvent and the phase separation behaviour of the SDS/CTAB mixture was carefully investigated.

The dodecyl sulphate (SD^-) and cetyltrimethylammonium (CTA^+) ions have opposite charges and interact very strongly to form an insoluble sediment in water.[37] Sediment formed in all the surfactant mixtures at a total concentration of 100 mM at different molar ratios, but dissolved quickly in the presence of water-miscible solvents such as propanol. Table 2a gives the percentages of propanol required to obtain a stable solution. At molar ratios close to 1 : 1, more sediment was formed and a higher percentage of propanol was required to dissolve it. These solutions were stable for at least 3 weeks.

When a few hundred microlitres of these solutions were dispersed into 10 mL of saline aqueous solutions containing sufficient NH_4NO_3, a cloudy solution with an insoluble phase appeared and started to separate out slowly. This insoluble phase appeared on top of the aqueous phase as a white, very swollen solid phase (except at a 1 : 1 molar ratio). Phase separation occurred quickly under centrifugation, with a much denser solid layer. In the absence of NH_4NO_3, no cloudy solution appeared and no phase separation was seen, even after several minutes of centrifugation (Table 2b). In the presence of sufficiently high concentrations of NH_4NO_3, only a few minutes of centrifugation were required for phase separation. At higher salt percentages, a decrease will occur. Ions from the inorganic salt can neutralize the excess charge on the surface of the supramolecular aggregates[38] and can aggregate to form a separate phase. A salting-out phenomenon takes place when using NH_4NO_3 that speeds up the phase transition.

When the molar ratio of SDS exceeds that of CTAB, no phase separation occurred and, at a molar ratio of 1 : 1, no stable separate phase was obtained even in a saturated saline solution of NH_4NO_3. However, by increasing the amount of CTAB at SDS : CTAB molar ratios from 1 : 2 to 1 : 20, phase separation occurred independently of pH. Complete phase separation was not seen at higher molar ratios. After centrifugation, the lower aqueous phase could be withdrawn using a 10 mL syringe and the separated phase dissolved easily in 50 μL of propanol (Fig. 1).

No significant change was observed in the phase separation when the cationic part of NH_4NO_3 was replaced by other cations such as Na^+ and K^+. However, no phase separation occurred in the presence of Cl^- instead of NO_3^-. The main part of the

Table 2 (a) The required propanol percentage in water to obtain a stable extraction solvent at different SDS/CTAB mole ratios with a total 100 mM concentration; (b) the phase separation behaviour of the extraction solvents (300 μL) with different NH_4NO_3 percentages in 10 mL aqueous solution

a	SDS : CTAB molar ratio	1 : 1	1 : 2	1 : 3	1 : 4	1 : 5	1 : 6	1 : 7	1 : 8	1 : 9	1 : 10	1 : 15	1 : 20
	Propanol percentage in water required	45	35	30	25	20	15				12	10	
b	Salt percentage in sample solution	Centrifugation time required to achieve complete phase separation (min)											
	6	[a]			20	10	8			10	[a]		
	8	[a]	15–25			5						[a]	
	10	[a]	7–10			3						15	[a]
	12	[a]	3										20
	15–30	[a]	3										

[a] No phase separation or no stable separated phase.

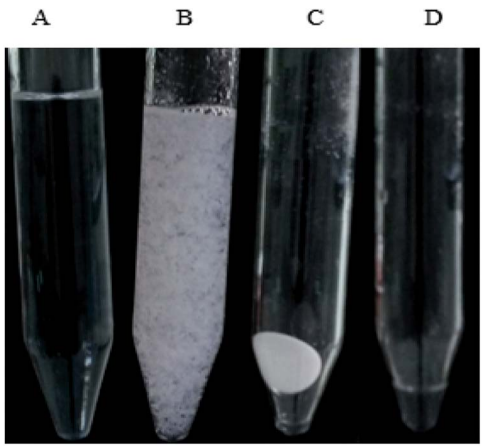

Fig. 1 (A) Solution of 100 mmol L^{-1} SDS : CTAB at a molar ratio of 1 : 6 in water–propanol. (B) After dispersion of 300 μL of the solution in 10% NH_4NO_3 solution. (C) Solid extracted phase after centrifugation for 5 min at 4000 rpm and withdrawal of the lower aqueous phase. (D) After dissolution of the solid layer in 60 μL of propanol.

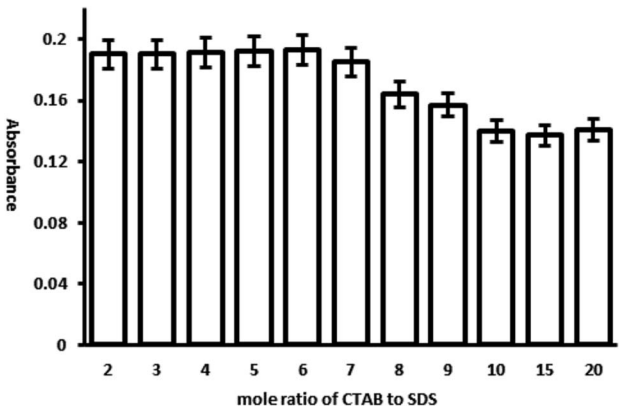

Fig. 2 Effect of SDS : CTAB molar ratio. Conditions: lead concentration, 1.0 ng mL^{-1}; centrifugation time, 3 min; NH_4NO_3 percentage, 15%; extraction solvent volume, 300 μL; pH 6; propanol volume, 50 μL; and NaDDC, 200 ppm. Experiments were performed in triplicate ($n = 3$).

studied solvent was the CTA^+ ion, the net charge of which is positive; the effect of the anionic part of the inorganic salt on the neutralization of the excess charge on the surface of the supramolecules was much higher. The negative charge density of the solvated Cl^- ion was lower and hence NO_3^- is more efficient in the neutralization process and decreases the repulsion between the positively charged head groups. Therefore the phase separation enhanced in the presence of NO_3^- compared with Cl^-.

This methodology could be applied as an efficient, fast and simple technique for the microextraction of various organic and inorganic compounds using SDS/CTAB supramolecular aggregates instead of the toxic organic solvents commonly used in microextraction methods.

Influence of SDS : CTAB molar ratio on the extraction solvent

The phase separation behaviour varied at different molar ratios of SDS : CTAB in the extraction solvents. The sample solutions containing 15% NH_4NO_3 were selected to investigate the effect of the SDS : CTAB molar ratio (Fig. 2). The results are similar to those for the SDS : CTAB molar ratios in the range 1 : 2 to 1 : 6. However, a lower percentage of propanol was required to prepare the extraction solvent at a molar ratio of 1 : 6 and phase separation also occurred at lower amounts of NH_4NO_3. A molar ratio of 1 : 6 was therefore used in subsequent experiments.

Effect of percentage of NH_4NO_3 and centrifugation time

Table 3 shows that the centrifugation time had a complementary effect at lower percentages of NH_4NO_3. The results were almost the same, although using a higher percentage of inorganic salt (10–30%) led to an improvement in the precision of

Table 3 Effect of NH_4NO_3 percentage and centrifugation time. Conditions: lead concentration, 1.0 ng mL^{-1}; SDS/CTAB molar ratio, 1 : 6; extraction solvent volume, 300 μL; pH 6; propanol volume, 50 μL; NaDDC, 200 ppm

NH_4NO_3 (%)	Centrifugation time (min)	Absorbance	RSD (%) ($n = 4$)
6	8	0.189	9.5
8	5	0.192	7.3
10–30	3	0.195	5–6

the microextraction method. A 10% w/v saline solution was selected as the optimum value.

Effect of extraction solvent volume

The amount of extraction solvent is a critical factor in the preconcentration of lead. Thus different volumes of the extraction solvent were used and the maximum absorbance was obtained in the presence of 300 μL of solvent. No phase separation occurred at volumes <200 μL and there was insufficient solvent available for complete microextraction using 200–300 μL of solvent. The volume of the extracted phases was increased gradually and there was a decrease in the absorbance of lead at higher volumes (Fig. 3).

Amounts of 9.36 mg of CTAB and 1.23 mg of SDS in 300 μL of extraction solvent are equal to 0.094 and 0.012% w/v in the sample solution, respectively. These amounts are much less than the concentrations present in conventional microextraction techniques if used separately (about 0.5% w/v for CTAB[25] and 1–5% w/v for SDS[27–29]). Hence this method significantly decreased the consumption of solvent.

Effect of pH and ligand concentration

As the sample pH plays an important part in the formation of metal–ligand complexes, we studied the extraction in the pH range 1–9. The extraction solvent had no significant effect on extraction and the highest lead signals were obtained at pH 5–7, which is consistent with other studies using dithiocarbamates as chelating agents.[39,40] Thus pH 6 was selected for use in further investigations.

The concentration of chelating agent was investigated in the range 1.17×10^{-5} to 5.84×10^{-3} mol L^{-1} NaDDC. The lead absorbance was improved when the NaDDC concentration increased to 8.76×10^{-4}; it did not change at concentrations $<1.75 \times 10^{-3}$, but decreased at higher concentrations. A concentration of 1.16×10^{-3} (200 μg mL^{-1}) was therefore chosen for subsequent experiments.

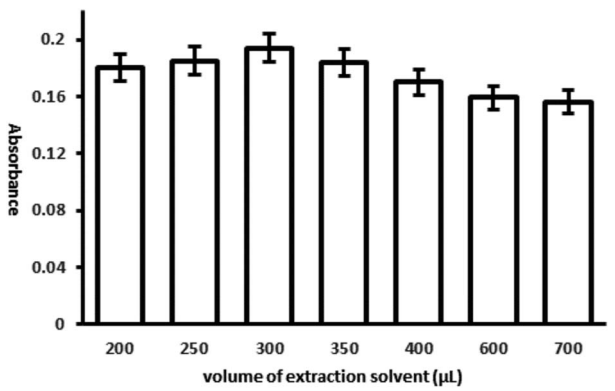

Fig. 3 Effect of volume of extraction solvent. Conditions: lead concentration, 1.0 ng mL^{-1}; SDS : CTAB molar ratio, 1 : 6; NH_4NO_3 percentage, 10% w/v; centrifugation time, 3 min; pH 6; propanol volume, 50 μL; and NaDDC value, 200 ppm. Experiments were performed in triplicate ($n = 3$).

These results show that the highest signals were obtained using 300 μL of the extraction solvent at a 1 : 6 molar ratio of SDS : CTAB. The pH of the lead solution was adjusted to pH 6 and contained 10% w/v NH_4NO_3 and 200 ppm NaDDC; the solution was centrifuged for 3 min. These conditions were used in all subsequent tests.

Effect of coexisting ions

The effect of potential interferences in natural samples on 10 mL of a standard solution containing 1.0 ng mL^{-1} lead in the presence of various individual ions was studied (Table 4). A concomitant ion was assumed to interfere when it resulted in a variation in the analytical signal of ±5%. Although NaDDC is a common chelating agent that can strongly interact with some heavy metals, no significant effect on the absorbance was seen at concentrations 200 times that of lead. These effects were much lower in the presence of alkali metals or common anionic compounds and therefore this method can be used to selectively preconcentrate lead.

Analytical figures of merit

The analytical characteristics of the proposed microextraction method were investigated under the optimized conditions for lead standard solutions. A calibration graph was obtained by analysing seven standard solutions of lead at different concentrations in the range 0.1–2.0 ng mL^{-1} (correlation coefficient 0.996). The regression equation of the calibration graph was $A = 0.1793C + 0.0032$ with a detection limit of 0.047 ng mL^{-1} based on an S/N of 3. The proposed method showed good precision with RSDs of 6.5 and 5.2% for 0.4 and 1 ng mL^{-1} lead, respectively. The separated phases were dissolved in 50 μL of propanol and the final mean volume was 130 μL for five replicate analysis. Therefore the preconcentration factor for the method was about 77. The enhancement factor for the determination of lead calculated by dividing the slopes of the calibration equations before and after preconcentration using the proposed method was 25.3.

Analysis of real samples

The accuracy of the proposed method was evaluated by analysing the CRM-TMDW (drinking water) certified reference material (http://www.highpuritystandards.com/store/home.php?cat=44) with a certified value of 40.0 ng mL^{-1} Pb(II). As the certified

Table 4 Effect of different ions on the determination of 1.0 ng mL^{-1} of lead

Interfering ion	Concentration (μg L^{-1})
As^{3+}, Zn^{2+}	500
Fe^{2+}, Fe^{3+}, Cu^{2+}, Sn^{2+}	200
Mn^{2+}, Ni^{2+}, Bi^{3+}, Co^{2+}	
Cd^{2+}	100
K^+, Na^+, NO_2^-	400 000
CO_3^{2-}, $CH_3CO_3^-$	
SO_4^{2-}	300 000

Table 5 Determination of lead in real samples; results expressed as mean ± standard deviation values based on three replicate analyses

Sample	Spiked (ng mL^{-1} or ng g^{-1})	Found (ng mL^{-1} or ng g^{-1})	Recovery (%)
Seawater	0	0.21 ± 0.04	—
	5	5.7 ± 0.3	104.3
Tomato paste	0	25.8 ± 1.4	—
	50	77.4 ± 5.2	103.2
	100	128.4 ± 7.6	102.6
Rice	0	82.3 ± 6.4	—
	50	129.4 ± 9.1	94.2
	100	178.4 ± 12.3	96.1
Wheat	0	20.7 ± 1.3	—
	50	69.4 ± 4.9	97.3
	100	116.2 ± 7.3	95.5
Vetch	0	10.3 ± 1.1	—
	50	59.4 ± 4.6	98.2
	100	111.8 ± 9.3	101.4

concentration in CRM was higher than the upper limit of the linear range of the method, a 40-fold dilution was carried out prior to analysis. Using the proposed method, the lead concentration was determined to be 38.5 ± 2.3 ng mL^{-1}, which is in good agreement with the certified value.

The proposed method was also used to determine the lead concentration in real samples (seawater, tomato paste, milled rice, wheat and vetch) after sample preparation. Recovery tests were carried out by spiking the samples with different concentrations of lead. The dilution factors were five and 100 for seawater and the other real samples, respectively; these were considered in the calculations (Table 5). These results confirmed that this method can be successfully applied to real samples.

Comparing the proposed method with other techniques

Table 6 compares the performance of the microextraction method with some other techniques for determining lead in solution. This method has a good dynamic range, good precision and a detection limit comparable with other methods.

This method has various advantages over DLLME[5] as a result of the replacement of hazardous organic solvents by CTAB and SDS supramolecular aggregates to give a green solvent in which water is the main component used to disperse the extraction solvent and only a low percentage of propanol is sufficient to dissolve the CTAB/SDS mixture. This technique is very simple and does not require any temperature control tools, flow injection system or solid-phase column as in CPE[14] or online SPE[41] methods. It is also easier than single-drop microextraction[42] and DSPE-SS[43] methods, with improved detection limits, and no step is needed to solidify the solvent.[44] Although the linear range of ICP-AES techniques is wider than that for AAS,[11] the latter instrument is much cheaper and its combination with the proposed method provides a cheaper and simpler technique for the determination of lead.

Conclusion

A novel microextraction method was developed using a green solvent composed of CTAB and SDS surfactants in combination with a dispersive microextraction technique. This solvent showed a pH-independent phase separation behaviour in saline solutions. Only a low percentage of propanol in water was needed to dissolve the CTAB/SDS mixtures. Hence the hydrophilic and hydrophobic sites in the extraction solvent have almost direct contact with analytes of various polarities to give a good interaction. This method, in combination with ET-AAS, was applied to the preconcentration and determination of lead in saline solutions and food samples. Although a moderate concentration of inorganic salt is needed for phase separation, these results confirm that this supramolecular aggregate dispersive microextraction method can be used as a simple, safe, fast and low-cost technique for the microextraction of various organic and inorganic compounds from real samples.

Funding

This study was funded by Ferdowsi University of Mashhad.

Conflict of interest

The authors declare that they have no conflict of interest.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Table 6 Comparison of the proposed microextraction method with the other methods for determining lead

Method	LOD (ng mL^{-1})	RSD (%)	Dynamic range (ng mL^{-1})	Ref.
Dispersive liquid–liquid microextraction ET-AAS	0.02	2.5	0.05–1.0	5
Ultrasonic nebulization associated ICP-AES	0.04	3%	0.04–100	11
Cloud-point extraction GF-AAS	0.08	2.8	1–30	14
Online solid-phase extraction GF-AAS	0.012	3.2	0.14–10	41
Single-drop microextraction ET-AAS	0.09	12.8	—	42
Dispersive solid-phase extraction slurry sampling ET-AAS	0.13	2.5–5.9	—	43
Liquid phase microextraction solidification of floating organic drop ET-AAS	0.01	2.8–3.2	0.024–0.4	44
Supramolecular aggregate dispersive microextraction method	0.047	6.5–5.2	0.10–2.0	This work

Informed consent

Not applicable.

Acknowledgements

The authors thank Ferdowsi University of Mashhad for financial support for this work.

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