

## Ultrasound-Assisted Emulsification–Microextraction Combined with Flame Atomic Absorption Spectrometry for Determination of Trace lead in Water Samples

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(Received on 8<sup>th</sup> September 2010, accepted in revised form 21<sup>st</sup> February 2011)

**Summary:** The process of ultrasound-assisted emulsification–microextraction (USAEME) was successfully applied for the extraction and preconcentration of trace lead from water samples, prior to flame atomic absorption spectrometry (FAAS). In the proposed approach, dithizone was used as a chelating agent; carbon tetrachloride was selected as extraction solvent. Some effective parameters on the microextraction and the complex formation were selected and optimized. These parameters included extraction solvent type as well as extraction volume, time, temperature, and pH, the amount of the chelating agent, and salt effects. Under optimum conditions, an enrichment factor of 91 was obtained from only 7.0 mL of water sample. The calibration graph was linear in the range of 3.76–600  $\mu\text{g/L}$  with a detection limit of 1.14  $\mu\text{g/L}$ . The relative standard deviation (R.S.D) for ten replicate measurements of 20 and 600  $\mu\text{g/L}$  of lead were 3.23 and 2.56%. This proposed method was successfully applied to tap water, river water and sea water, and accuracy was assessed through the analysis of certified reference water or recovery experiments. Operation simplicity, low cost, high enrichment factor, and low consumption of the extraction solvent are the main advantages of the proposed method.

### Introduction

Lead (Pb) is known to be a toxic metal that accumulates in the human body throughout the lifetime [1]. Typical symptoms of lead poisoning are abdominal pain, anaemia, headaches and convulsions, chronic nephritis of the kidney, brain damage and central nervous-system disorders [2]. The U.S. Environmental Protection Agency (EPA) has classified lead as a Group B2 human carcinogen [3]. The World Health Organization (WHO) has established the maximum allowable limit of 10  $\mu\text{g/L}$  for lead in drinking water [4]. Therefore, highly sensitive determination methods of trace Pb in environmental samples need to be established [5–7]. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment required. However, direct determination of metal ions at trace levels by FAAS is limited, not only due to insufficient sensitivity, but also to matrix interference. Under these circumstances, in order to determine trace levels of Pb, a separation and enrichment step prior to the determinations may be beneficial. Several methods have been proposed for separation and preconcentration of trace Pb, including liquid–liquid extraction (LLE) [8], coprecipitation [9, 10], solid phase extraction (SPE) [11, 12] and cloud point extraction (CPE) [13, 14]. However, liquid–liquid extraction (LLE), as the oldest preconcentration and separation technique in

analytical chemistry [15], is time-consuming and requires large amounts of organic solvents [16]. Compared with LLE, SPE offers simpler operation, a higher enrichment factor, and ease of automation, but the amounts of elution solvents are still relative large [17, 18]. CPE is a comparatively simple, cheap and less toxic method [19, 20], but it also has several limitations associated with it. For instance, because of the viscosity of the surfactant-rich phase, samples prepared this way cannot be injected directly into conventional analytical instruments. As well, the surfactants bear chromophores, which interfere with UV detection by overlapping with the analyte signal [18].

Modern trends in analytical chemistry now lean towards the simplification and miniaturization of sample preparation, as well as the minimization of the organic solvent used. Jeannot and Cantwell developed a liquid-phase microextraction (LPME) technique in 1996, which is based on analyte partitioning between a drop of organic solvent (extraction phase) and a bulk aqueous sample [21]. Several different types of LPME have been developed, including single drop microextraction (SDME) [22–24], hollow fiber LPME [25, 26], homogeneous liquid–liquid extraction (HLLE) [27, 28] and solidified floating organic drop microextraction (SFODME) [29, 30]. Microextraction techniques are fast, simple, inexpensive,

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environmentally friendly, and compatible with many analytical instruments. Nevertheless, some drawbacks, such as instability of the droplet and relatively low precision, are often reported [31].

Recently, Assadi and co-workers developed a novel microextraction technique, termed dispersive liquid-liquid microextraction (DLLME) [32]. This technique is based on the formation of tiny droplets of the extractant in the sample solution using a water-immiscible organic solvent (extractant) dissolved in a water-miscible organic dispersive solvent [33]. The advantages of the DLLME method are rapidity, low cost, and high enrichment factors. Its main drawback is the necessity of using a third component (disperser solvent), which usually decreases the partition coefficient of analytes into the extraction solvent [34].

Ultrasonic energy, when applied to solutions, causes acoustic cavitation; that is, bubble formation and implosion. The collapse of bubbles formed by ultrasonic energy results in the generation of extremely high temperatures and pressures at the interface of the collapsing bubble and another phase, leading to enhanced chemical reactivity [35]. In combination, micro-extracting systems and ultrasound radiation provide an efficient preconcentration technique, termed ultrasound-assisted emulsification-microextraction (USAEME), which has been successfully used for the extraction and determination of synthetic musk fragrances, phthalate esters and lindane in aqueous samples [34]. USAEME is based on the implosion bubbles generated by the cavitation phenomenon, which produce intense shock waves in the surrounding liquid, resulting in high-velocity liquid jets. These microjets can cause droplet disruption in the vicinity of collapsing bubbles, and thus improve emulsification by generating a smaller droplet size of the dispersed phase, immediately after disruption. Submicron droplet size leads to significant enlargement of the contact surface between both immiscible liquids, improving the mass-transfer between the phases [36]. Recently, we have successfully determined the trace amounts of cadmium in water samples with this method [37].

In USAEME, the appropriate extraction solvent is rapidly injected by syringe into aqueous samples containing the analyte of interest. After sonication, a cloudy solution forms. This cloudy solution is then centrifuged and the fine droplets sediment at the bottom of the conical centrifuge tube.

The determination of analytes in the sedimented phase can be performed by instrumental analysis. Operation simplicity, low cost, high enrichment factor, and low consumption of the extraction solvent are the main advantages of the proposed method.

The present paper describes the application of ultrasound-assisted emulsification microextraction for the determination of trace lead in water samples, without the addition of the dispersive solvent, thereby overcoming DLLME disadvantages. In order to obtain a high extraction efficiency, the effect of different parameters affecting the complex formation and extraction conditions (such as type and volume of the extraction solvent, pH, the chelating agent amount, extraction time, extraction temperature and ionic strength) were tested. USAEME can be employed with satisfactory results as a simple and efficient extraction and preconcentration procedure for heavy metals in aqueous samples.

## Results and Discussion

### *Effect of Type and Volume of the Extraction Solvent*

The extraction solvent should have special characteristics. It should have a higher density than water, high extraction capability for the compound of interest, and low solubility in water. Carbon tetrachloride ( $\text{CCl}_4$ , density: 1.59 g/mL), chloroform ( $\text{CHCl}_3$ , density: 1.48 g/mL) and carbon disulfide ( $\text{CS}_2$ , density: 1.26 g/mL) were examined in the present study for the extraction of lead. A series of sample solution were studied by using different volumes of the extraction solvent to achieve a 80  $\mu\text{L}$  volume of the sedimented phase. Since the solubility of the extraction solvents in water is different, it was necessary to add an excess amount of extraction solvent, in order to recover a constant volume of the sedimented phase (80  $\mu\text{L}$ ). Therefore, 100, 135 and 120  $\mu\text{L}$  of carbon tetrachloride, chloroform and carbon disulfide were employed, respectively.

In this experiment chloroform, carbon disulfide and carbon tetrachloride as extraction solvents obtained enrichment factors of  $88 \pm 4.4$ ,  $90 \pm 5.1$  and  $91 \pm 4.0$ , respectively. According to these results, variations of the enrichment factors using different extraction solvents are not statistically significantly different. In detail, carbon tetrachloride forms a well stable cloudy solution; the sedimented phase can easily be removed by sampler and has less consumption volume due to its low solubility, while chloroform forms an unstable cloudy solution and

carbon disulfide is difficult to be removed by sampler. Therefore, carbon tetrachloride was selected as the extraction solvent for further studies.

To examine the effect of the extraction solvent volume, the solutions containing different volumes of carbon tetrachloride were subjected to the same USAEME procedures. According to Fig. 1, which shows the curve of absorbance versus volume of the carbon tetrachloride (50-130  $\mu\text{L}$  at 10  $\mu\text{L}$  intervals), increasing the volume of carbon tetrachloride initially increases the absorbance, until at 100  $\mu\text{L}$  it reaches the maximum amount and remains nearly constant. Thereby, in the subsequent studies, 100  $\mu\text{L}$  carbon tetrachloride was used as the optimum volume of the extraction solvent.

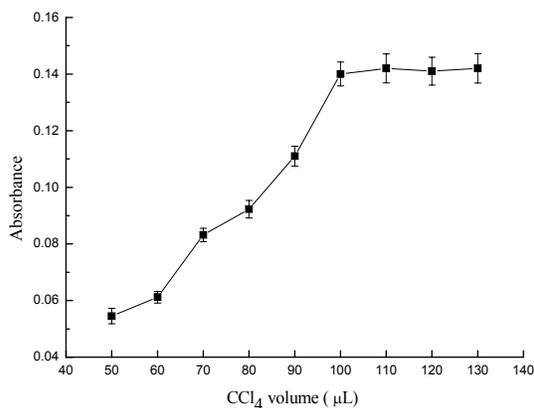


Fig. 1: Effect of the volume of extraction solvent ( $\text{CCl}_4$ ) on the absorbance of Pb obtained from USAEME. Extraction conditions: water sample volume, 7.0 mL; dithizone volume, 90  $\mu\text{L}$ ; pH 6.0; concentration of Pb, 600  $\mu\text{g/L}$ ; extraction time, 10 min; extraction temperature, 45°C.

#### *Influence of pH*

The separation of metal ions by USAEME involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of the sedimented phase, whereby the desired preconcentration is obtained. pH plays a unique role on metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of lead from water samples was studied in the range of 2.0–10.0 by using nitric acid, ammonium acetate, phosphate and ammonium chloride. As can be seen in Fig. 2, the highest signal intensity of Pb was obtained at pH 6.0. The progressive decrease in

extraction of lead at low pH is due to competition of the hydrogen ion with the analyte for reaction with dithizone. At higher pH values, the hydrolysis of cations occurs. Thus, the value of pH 6.0 was selected for the following experiments.

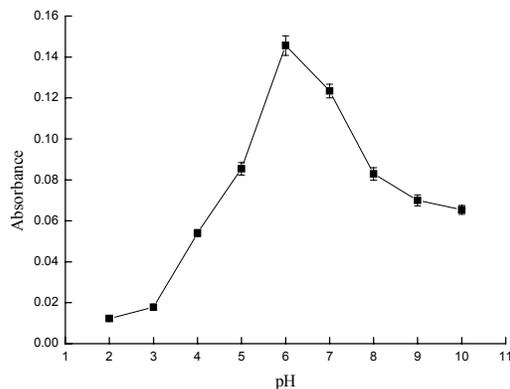


Fig. 2: Effect of pH on the absorbance of Pb obtained from USAEME. Extraction conditions: water sample volume, 7.0 mL; dithizone volume, 90  $\mu\text{L}$ ; extraction solvent ( $\text{CCl}_4$ ) volume, 100  $\mu\text{L}$ ; concentration of Pb, 600  $\mu\text{g/L}$ ; extraction time, 10 min; extraction temperature, 45°C.

#### *Influence of the Amount of Dithizone*

The effect of the amount of dithizone ( $10^{-2}$  mol/L) on the absorption was studied, and the results are shown in Fig. 3. The amount of dithizone was increased until the total extraction of Pb was obtained. The absorbance was stable when the dithizone volume was higher than 80  $\mu\text{L}$ , indicating complete complexation. When the amount of dithizone is higher than 100  $\mu\text{L}$ , the analytical signal decreases. This effect is probably caused by competition between complexing agent molecules, which are in excess in the solution, and Pb-complex molecules for extraction solvent interaction. Thus, elevated concentrations of complexing agents caused a negative effect on Pb extraction from aqueous phase and decreased the enrichment factor. In this study, a dithizone volume of 90  $\mu\text{L}$  was chosen to account for other extractable species that potentially interference with the assaying of Pb.

#### *Effect of the Extraction Time*

Time plays an important role in the emulsification and mass transfer phenomena. In USAEME, extraction time is defined as the time between injection of extraction solvent and the end of

the sonication stage. The effect of extraction time was examined in the range of 5-35 min under constant experimental conditions. The results showed that the signals of lead were increased by increasing the extraction time up to 10 min. After 10 min, the absorbance remained nearly constant. Thus, in the following experiments 10 min was selected as the extraction time.

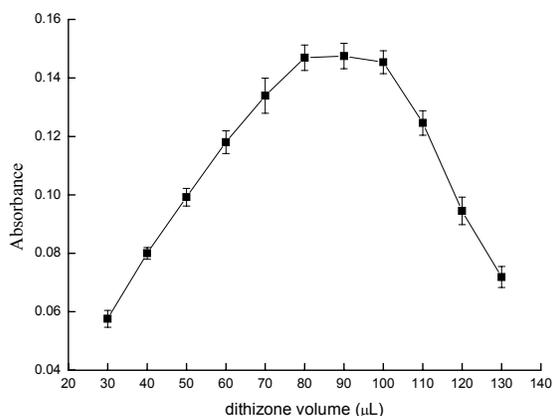


Fig. 3: Effect of dithizone volume on the absorbance of Pb obtained from USAEME. Extraction conditions: water sample volume, 7.0 mL; pH 6.0; extraction solvent ( $\text{CCl}_4$ ) volume, 100  $\mu\text{L}$ ; concentration of Pb, 600  $\mu\text{g/L}$ ; extraction time, 10 min; extraction temperature, 45°C.

#### Effect of Extraction Temperature

Temperature affects organic solvent solubility in water as well as the emulsification phenomenon. Thus, this affects the mass-transfer process and the extraction efficiency. To determine the influence of the extraction temperature, 7.0 mL aqueous solution containing 600  $\mu\text{g/L}$  of lead was extracted at different temperatures ranging from 20°C to 70°C. At temperatures lower than 35°C, it was difficult to get a homogeneous emulsion resulting in a prompt phase separation. Therefore, the mass-transfer process was limited to a short amount of time, leading to poor extraction efficiency, and consequently low absorbance. In the 35-55°C temperature range, the emulsification was easily achieved and the highest absorbance obtained at 45°C. At a temperature higher than 55°C, carbon tetrachloride was partially dissolved into the aqueous bulk, leading to the reduction of the analytical signal. Hence, 45°C is recommended for further studies.

#### Effect of Salt

For investigating the influence of ionic strength on performance of USAEME, various experiments were performed by adding varying NaCl amount from 0% to 5% (w/v). Other experimental conditions were kept constant. By increasing the NaCl from 0% to 5%, the volume of the sedimented phase increases slightly from 80  $\mu\text{L}$  to 82  $\mu\text{L}$ . The results showed that salt addition has no significant effect on the enrichment factor, perhaps because of the two opposite effects of salt addition in USAEME of lead: One involves increasing the volume of the sedimented phase, which decreases the enrichment factor, and the other is the salting-out effect that increases the enrichment factor [38, 39]. Therefore, the enrichment factor is nearly constant by increasing the amount of sodium chloride, and the extraction experiments were carried out without adding salt.

#### Effect of Sonication

Sonication and vigorously stirring were compared as emulsification-assistance. By vigorously stirring the solution for 30 min, the analytical signal obtained for lead was comparable to that obtained by sonication for 10 min. Sonication stirring produces smaller droplets of organic solvent in the aqueous bulk than vigorous stirring and results in the generation of a high contact area between the aqueous phase and the extraction solvent. Therefore, the extraction efficiency using sonication stirring was better compared with that obtained by vigorous stirring.

#### Effect of Coexisting Ions

The effects of common coexisting ions in natural water samples on the recovery of lead were studied. In these experiments, 7.0 mL solutions containing 600  $\mu\text{g/L}$  of lead and various amounts of interfering ions were treated according to the recommended procedure. A given species was considered to interfere if it resulted in a  $\pm 5\%$  variation of the absorbance signal. The results obtained are given in Table-1.

#### Analytical Figures of Merit

In the optimum conditions, a calibration graph was obtained by preconcentrating a series of the solutions according to procedure under experiment. Table-2 shows the analytical characteristics of this method. The calibration graph was linear in the range

of 3.76–600  $\mu\text{g/L}$  of lead. The equation of the calibration curve after the preconcentration procedure was given as  $A=2.60 \times 10^{-4}C+0.0136$  with a correlation coefficient of 0.9986 ( $n=10$ ), where  $A$  is the atomic absorbance for lead in the rich phase at 283.3 nm and  $C$  is the concentration of  $\text{Pb}^{2+}$  in the sample solution in  $\mu\text{g/L}$ . The limit of detection and quantification defined as  $3S_B/m$  and  $10S_B/m$  (where  $S_B$  is standard deviation of the blank and  $m$  is the slope of the calibration graph) were 1.14 and 3.76  $\mu\text{g/L}$ , respectively. The relative standard deviation (R.S.D) for ten replicate measurements of 20 and 600  $\mu\text{g/L}$  of lead were 3.23 and 2.56%. Phase volume ratio, calculated as the ratio between the volume of the aqueous phase (8.0 mL) and the final injection volume (0.5 mL nitric acid containing the analyte), was 16 times.

Table-1: Effect of interferences on the recovery of 600  $\mu\text{g/L}$   $\text{Pb}^{2+}$  in water sample using USAEME–FAAS.

Interferent	Concentration ( $\mu\text{g/L}$ )	Interferent/ $\text{Pb}^{2+}$ ratio	Recovery (%)
$\text{Na}^+$	6,000,000	10,000	95.8
$\text{K}^+$	6,000,000	10,000	97.6
$\text{Ag}(\square)$	6000	10	97.5
$\text{Al}(\square)$	60,000	100	98.4
$\text{Ba}(\square)$	60,000	100	96.5
$\text{Cr}(\square)$	60,000	100	96.7
$\text{Cu}(\square)$	60,000	100	98.4
$\text{Ca}(\square)$	30,000	50	97.2
$\text{Mg}(\square)$	30,000	50	98.2
$\text{Fe}(\square)$	30,000	50	97.6
$\text{Mn}(\square)$	30,000	50	95.5
$\text{Fe}(\square)$	24,000	40	98.7
$\text{Bi}(\square)$	24,000	40	96.7
$\text{Zn}(\square)$	18,000	30	100.5
$\text{Cd}(\square)$	18,000	30	99.5
$\text{Ni}(\square)$	18,000	30	96.4
$\text{Co}(\square)$	18,000	30	100.6
$\text{Hg}(\square)$	6,000	10	95.7
$\text{Cl}^-$	6,000,000	10,000	96.2
$\text{Cr}_2\text{O}_7^{2-}$	60,000	100	100.4
$\text{NO}_3^-$	6,000,000	10,000	98.8
$\text{PO}_4^{3-}$	60,000	100	99.4
$\text{CH}_3\text{COO}^-$	600,000	1000	97.5
$\text{SO}_4^{2-}$	60,000	100	101.2

Table-2: Analytical characteristics of USAEME-FAAS for determination of Pb.

Analytical parameters	Analytical feature
Linear range ( $\mu\text{g/L}$ )	3.76–600
Slope	$2.60 \times 10^{-4}$
Correlation coefficient	0.9986
Detection limit ( $\mu\text{g/L}$ )	1.14
Quantification limit ( $\mu\text{g/L}$ )	3.76
Relative standard deviation (R.S.D.%) ( $n=10$ , 20 $\mu\text{g/L}$ )	3.23
Relative standard deviation (R.S.D.%) ( $n=10$ , 600 $\mu\text{g/L}$ )	2.56
Enrichment factor <sup>a</sup>	91
Enrichment factor <sup>b</sup>	14.5
Enhancement factor <sup>c</sup>	13.6

<sup>a</sup>The enrichment factor is the ratio of the lead concentration in the organic-rich phase (80  $\mu\text{L}$ ) to that initially in the bulk phase.

<sup>b</sup>The enrichment factor is the ratio of the lead concentration in 0.5 mL 0.1 mol/L nitric acid to that initially in the bulk phase.

<sup>c</sup>The enhancement factor is the slope ratio of the calibration graph after and before extraction.

The enrichment factor (EF) [40, 41] is defined as the ratios of the lead concentration in the organic-rich phase to that in the bulk phase, initially. Equation (1) was used for calculation of the enrichment factor.

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

where  $C_{sed}$  is lead concentration ( $\mu\text{g/L}$ ) in the organic-rich phase after phase separation (80  $\mu\text{L}$  organic-rich phase) and  $C_0$  is the initial concentration of lead ( $\mu\text{g/L}$ ). The enrichment factor was obtained as 91 ( $n=3$ ).

As for the determination of the absorbance for lead in the organic-rich phase, the extraction solvent (80  $\mu\text{L}$ ) was evaporated at room temperature, Finally, the residue was dissolved into 0.5 mL 0.1 mol/L nitric acid, the enrichment factor for the proposed method is 14.5.

The enhancement factor [42], defined as the ratio of the slope of the calibration graph for the USAEME method, to that of the calibration graph in water phase without pre-concentration, was 13.6.

#### Analysis of Natural Waters

The proposed method was applied to the determination of lead in several water samples and the results along with the recovery for the spiked samples were given in Table-3. As could be seen, the recoveries for the addition of different concentrations of lead to water samples were in the range 93.6–100.5%. To verify the accuracy of the proposed procedure, the method was then used for the determination of the content of Pb in National Standard Reference Material for Environment Water (GSBZ50009-88 and GSB07-1183-2000) after the appropriate dilution. These results are presented in Table-3. A good agreement between the determined values and the certified values was obtained.

#### Comparison to other Methods

A comparison of the represented method with other reported preconcentration methods is given in Table-4. In comparison with other reported methods, USAEME has relatively low LOD (1.14  $\mu\text{g/L}$ ), high enrichment factor (91) and low sample consumption (8 mL). These characteristics are of key interest for routine laboratories in trace metal ion analysis.

Table-3: Analytical results of lead determination (dissolved fraction) in certified reference material and spiked natural water samples with the USAEME-FAAS method (n=3).

Sample	Certified	Added	Found <sup>a</sup>	Recovery (%)
GSBZ50009-88 (µg/L)	10.50±0.38	—	10.00±0.43	95.2
	21.00±0.75	—	20.48±0.65	97.5
GSB07-1183-2000 (µg/L)	11.86±0.62	—	11.43±0.55	96.4
	17.79±0.93	—	17.20±0.78	96.7
Tap water <sup>b</sup> (µg/L)	0.0	0.0	<LOD	—
	15.0	14.20±0.63	14.20±0.63	94.7
Sea water <sup>c</sup> (µg/L)	0.0	0.0	8.35±0.38	—
	10.0	18.01±0.76	18.01±0.76	96.6
River water <sup>d</sup> (µg/L)	0.0	0.0	23.28±1.02	99.5
	10.0	14.29±0.50	14.29±0.50	95.6
River water <sup>e</sup> (µg/L)	0.0	0.0	24.83±0.89	100.5
	15.0	14.04±0.64	14.04±0.64	93.6
	20.0	19.66±0.70	19.66±0.70	98.3

<sup>a</sup>Mean of three experiments±standard deviation.

<sup>b</sup>From drinking water system of Baoding, China.

<sup>c</sup>Beidaihe sea water, Qinhuangdao, China.

<sup>d</sup>Yongding river water, Baoding, China.

<sup>e</sup>Tang river water, Baoding, China.

LOD: limit of detection.

## Experimental

### Apparatus

The experiments were performed with a Hitachi Z-5000 atomic absorption spectrometer (Japan) equipped with Zeeman background correction. A lead hollow cathode lamp operating at 283.3 nm was utilized as the radiation source. The instrumental parameters were adjusted according to the manufacturer's recommendations. All pH measurements were carried out using a pH<sub>3</sub>-3C digital pH meter equipped with a combined glass-calomel electrode (Hangzhou Dongxing Instrument Factory, Hangzhou, China). A Model LD5-2A centrifuge (Beijing Jingli Instrument Factory, Beijing, China)

was used to accelerate the phase separation. A 59 kHz, 200 W ultrasonic bath with temperature control (Shanghai Kudos Ultrasonic instrument Co, Ltd., Shanghai, China) was used to assist the emulsification process of the microextraction technique.

### Reagents and Solutions

A stock standard solution of lead at a concentration of 1000 µg/mL was purchased from the National Institute of Standards (Beijing, China). Working standard solutions were prepared by serial dilutions of the stock solution with deionized water immediately prior to analysis. A solution of 10<sup>-2</sup> mol/L dithizone (Beijing Chemistry Reagent Company, Beijing, China) was prepared by dissolving appropriate amounts of this reagent in tetrahydrofuran (Beijing Chemistry Reagent Company, Beijing, China). The NaCl solution was prepared by dissolving the appropriate amount of NaCl in deionized water. Carbon tetrachloride (CCl<sub>4</sub>), chloroform (CHCl<sub>3</sub>) and carbon disulfide (CS<sub>2</sub>), as extraction solvents were obtained from Tianjin Tianda Chemical Reagent Company (Tianjin, China).

Nitric acid (0.1 mol/L) was used to adjust the pH 2-3, ammonium acetate buffers (0.2 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions resulting in solutions of pH 4-6. For pH 7-8, a phosphate (0.2 mol/L) buffer solution was prepared by adding an appropriate amount of disodium hydrogen phosphate to sodium dihydrogen phosphate. Ammonium chloride buffer solutions (0.2 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions, resulting in solutions of pH 9-10.

Table-4: Characteristic performance data obtained by using USAEME and other techniques in determination of lead.

Method	LOD <sup>a</sup> (µg/L)	R.S.D <sup>b</sup> (%)	Enrichment factor	Sample consumption (mL)	Calibration range (µg/L)	References
CPE-FAAS	2.86	1.39	43 <sup>c</sup>	10	10-460	[43]
SPE-FAAS	6.1	4.7	30 <sup>d</sup>	300	—	[11]
SPE-FAAS	3.7	4.4-2.3	27 <sup>e</sup>	—	—	[12]
Coprecipitation-ICP-OES	3.2	≤5%	20 <sup>d</sup>	200	—	[44]
Coprecipitation-FAAS	3.2	4.2	45	—	0-200	[45]
USAEME-FAAS	1.14	2.56	91 <sup>f</sup>	8	10-600	Represented method

<sup>a</sup>Limit of detection.

<sup>b</sup>Relative standard deviation.

<sup>c</sup>The enhancement factors defined as the ratio of absorbance of preconcentrated samples to that obtained without preconcentration.

<sup>d</sup>Ratio of the aqueous phase to final volume of eluent phase.

<sup>e</sup>The enhancement factor is the slope ratio of calibration graph after and before extraction.

<sup>f</sup>Preconcentration factor, as the ratio of the concentration of analyte after preconcentration to that without preconcentration giving the same analytical response.

CPE-FAAS: cloud point extraction-flame atomic absorption spectrometry.

SPE-FAAS: solid phase extraction-flame atomic absorption spectrometry.

Coprecipitation-ICP-OES: coprecipitation-inductively coupled plasma-optical emission spectrometry.

Coprecipitation-FAAS: coprecipitation-flame atomic absorption spectrometry.

All reagents used were of analytical reagent grade. Deionized water was used in the preparation of all solutions. The laboratory glassware was kept in 10% nitric acid for at least 24 h and subsequently washed four times with deionized water.

Tap, sea and river water samples used for development of the method were collected in polytetrafluoroethylene (PTFE) containers from Hebei province, filtered using a 0.45  $\mu\text{m}$  pore size membrane filter to remove suspended particulate matter, and stored in a refrigerator in the dark.

#### *Ultrasound-assisted Emulsification-microextraction Procedure*

A 7.0 mL sample of standard solution containing 600  $\mu\text{g/L}$  of lead was poured into a conical centrifuge tube. 1.0 mL acetate buffer and 90  $\mu\text{L}$  dithizone ( $10^{-2}$  mol/L) solution were added, then 100  $\mu\text{L}$  of carbon tetrachloride (extraction solvent) was injected rapidly into the sample solution using a syringe. The tube was immersed into an ultrasonic bath for 10 min at 45°C. As a result, oil-in-water (O/W) emulsions of carbon tetrachloride in water were formed. Emulsions were then disrupted by centrifugation at 3600 rpm for 3 min, which resulted in the organic phase sedimenting at the bottom of the conical tube. The sedimented phase was quantitatively transferred to another test tube and the solvent was allowed to evaporate at room temperature. Finally, the residue was dissolved in 0.5 mL 0.1 mol/L nitric acid and the lead concentration was determined by flame atomic absorption spectrometry. Fig. 4 shows a scheme of the USAEME procedure.

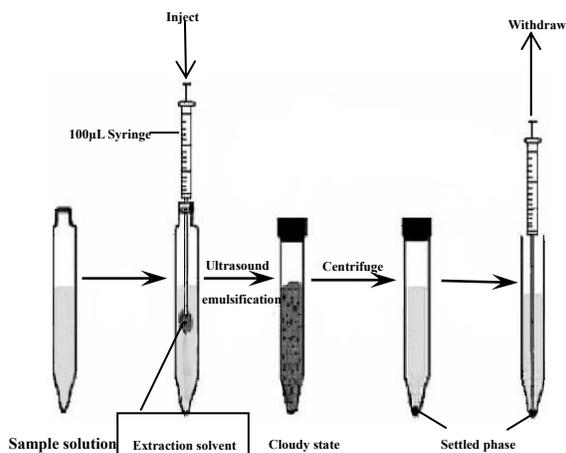


Fig. 4: Ultrasound-assisted emulsification-microextraction procedure.

#### Conclusions

USAEME combined with the flame atomic absorption spectrometry (FAAS) was evaluated for the preconcentration and the determination of the trace amounts of lead (at  $\mu\text{g/L}$  level) from water samples. USAEME is sensitive, efficient and simple method for preconcentration and separation of trace metal with the use of low sample volumes. The high enrichment factor was obtained easily using this method. Besides, it is important to point out that USAEME is a low organic solvent consuming extraction technique, which turns it into a low cost and environmentally friendly technique. In this method, the consumption of the toxic organic solvent (at microlitre level) was minimized without affecting the method sensitivity. Although the obtained results of this research were related to the lead determination, the system could be readily applied to the determination of other metals with the help of various chelating agents, extractable by other organic solvents.

#### Acknowledgements

This project was sponsored both by Development Foundation of the Department of Education of Hebei Province, P R China (ZH2011128), and the Research Development Foundation of the Agricultural University of Hebei.

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