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Dispersive Liquid-Liquid Microextraction Combined with Electrothermal Atomic Absorption Spectrometry for Determination of Trace Lead in Drinking Water Samples

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A new method of dispersive liquid-liquid microextraction combined with electrothermal atomic absorption spectrometry was proposed for the determination of trace lead using sodium diethyldithiocarbamate as chelating reagent. Several factors influencing the microextraction efficiency of lead and the subsequent determinations, such as extraction and disperser solvent type and their volume, pH, concentration of diethyldithiocarbamate and extraction time were investigated. Under the optimum conditions, the detection limit of the proposed method was 0.006 ng mL^{-1} for lead and the relative standard deviation was 3.5 % (c = 0.1 ng mL^{-1}, n = 7). The proposed method was successfully applied to the determination of trace lead in mineral water samples and the recoveries for the spiked samples was in the range of 96-108 %.

Key Words: Dispersive liquid-liquid microextraction, Electrothermal atomic absorption spectrometry, Lead, Drinking water.

INTRODUCTION

It is well known that lead is one of the most toxic elements to human health because they cause servious effects on metabolic processes[1]. The U.S. Environmental Protection Agency has classified lead as a Group B2 (probable) human carcinogen[2]. And the intake of food and drinking water are the most important ways for lead entering into human body. As a result, the maximum allowable level of lead in drinking water has nowadays been severely restricted by international regulations on water quality. The World Health Organization has established the maxium allowable limit of 10 μg L^{-1} for lead in drinking water[3]. Therefore, it is important to develop sensitive and simple method for monitoring the lead level in drinking water sample.

Currently, the most common elemental detectors are the flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry and mass spectrometry (ICP-OES/MS). Of the above mentioned methods, electrothermal atomic absorption spectrometry is still a powerful technique for the determination of trace and ultratrace elements in different samples because it combines the characteristics of relative simplicity, cheaper cost, low sample volume requirements and low detection limits(in the same level with ICP-MS)[4].

However, in many cases, direct determination of metals at trace or ultratrace elements by ETAAS is often difficult, not only because of its insufficient sensitivity, but also because of matrix effects. To solve this problem, separation-preconcentration procedures are often involved prior to analysis by ETAAS. Preconcentration is a very important issue for improvement of sensitivity and separation is an efficient technique to reduce the interference of sample matrix[5]. Various separation-preconcentration procedures have been used for this purpose, including liquid-liquid extraction[6, 7], solid phase extraction[8, 9], ion exchange techniques[10], coprecipitation[11] and cloud point extraction[12,13].

Recently, a new mode of microextraction named dispersive liquid-liquid microextraction (DLLME)[14-17], which based on ternary component solvent system such as cloud point extraction and homogeneous liquid-liquid extraction (HLLE)[18] was proposed. In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected into aqueous samples containing analytes. Then the cloudy solution was formed and a drop of organic phase was sedimented in the bottom of the conical tube after centrifugation. The determination of analytes in sedimented phase can be performed by different kinds of instrumental analysis techniques, such as FAAS, GFAAS, ICP-OES and ICP-MS. Compared with other LPME, DLLME offers the advantages of simplicity of operation, rapidly, low sample volume, low cost and high enrichment factor[19].

The combination of DLLME and ETAAS is a kind of perfect combination of miniaturized sample preparation procedure and microamount sampling detection technique. The aim of this work is to develop a method by combining DLLME with ETAAS for the determination of trace lead in drinking water sample. The factors affecting the efficiency of microextraction were investigated in detail. The developed method was successfully applied to drinking water samples with satisfactory results.

EXPERIMENTAL

The measurements were performed with a Shimadzu AA6300 atomic absorption spectrometer (Japan) equipped with a heated graphite tube atomizer. Deuterium lamp background correction was employed to correct the non-specific absorbance. A lead hollow cathode lamp operated at 8 mA was used as the radiation source. The heating programs employed for lead determination was given as follows: the drying temperature was 100 ºC, ramp 10 s, hold 10 s; the ashing temperature was 400 ºC, ramp 10 s, hold 10 s; the atomizing temperature was 1800 ºC, hold 4 s; the cleaning temperature was 2000 ºC, hold 2 s.

The pH values were controlled with a PHS-3C pH-meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). The phase separation was assisted by a centrifuge (80-1 model, Jintan Instrument Limited Company, Jiangsu, China) in 10 mL calibrated conical tubes.

All reagents used were analytical-reagent grade. The stock standard solutions(1.000 g L^{-1}) of lead was prepared by dissolving appropriate amounts of lead nitrate (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) in deionized water. Solution(1%, m/v) of sodium diethyldithiocarbamate (Shanghai Reagent Company, Shanghai, China) was prepared fresh daily in deionized water. HCl(pH 1.0-2.0), acetate-acetic acid buffer (pH 3.0-5.0) and NaOH solution (0.1 mol L^{-1}) were used for pH adjustment. Different stock solutions of potentially interfering ions(1.000 g L^{-1}) were prepared according to the conventional method. Working solutions were prepared daily by appropriate dilutions of stock solutions. The laboratory glassware was kept in a 5 % (v/v) nitric acid solution overnight. Afterwards, it was rinsed thoroughly with deionized water and dried.

Dispersive liquid-liquid microextraction procedure: First, 4.0 mL of standard solution of lead or sample solution of lead was placed in a 10 mL calibrated conical tube. Then, 0.5 mL DDTC (as chelating reagent) solution (1 %, m/v) was added and the pH was adjusted to 5.5. After that, the 0.5 mL of acetone(as disperser solvent) containing 25 µL of carbon tetrachloride (as extraction solvent) was rapidly injected into sample solution by a syringe. A cloudy solution was formed in the conical tube and phase separation was assisted by centrifugation (3000 rpm, 5 min). A small droplet of carbon tetrachloride was sedimented in the bottom of conical tube. 10 µL sedimented phase was withdrawn into the microsyringe and then injected into the ETAAS for analysis.

Sample preparation: The mineral water samples were purchased in the supermarket and the water sources of the three different mineral water products were Qiandao Lake in Zhejiang province, Kunlun Mountain and Deep Ocean in Yantai, respectively. And no special sample pretreatment was required for this clean water samples.

RESULTS AND DISCUSSION

Effect of extraction solvent and its volume: The type of extraction solvent used in DLLME is an essential consideration for efficient extraction. It should have higher density than water, extraction capability of the interested compounds and low solubility in water. Three kinds of solvents: carbon tetrachloride, chloroform and chlorobenzene were compared in the extraction of lead. According to the procedure in 2.3, to achieve 20 µL volume of the sedimented phase at the bottom of the conical tube, 30 µL, 70 µL and 50 µL of carbon tetrachloride, chloroform and chlorobenzene were required, respectively. Therefore, tetrachloride has a lower solubility in water than other two extraction solvents.

According to the procedure (using different volume to obtain 20 µL sedimented phase for the three different extraction solvent), the variations of the enrichment factors (caculated by the ratio of analyte concentration in the sedimented phase and the initial analyte concentration) for the three extraction solvents were not statistically significantly different. Carbon tetrachloride forms a well stable cloudy solution and the achieved sedimented phase could be easily removed by sampler. However, chloroform forms an unstable cloudy solution and carbon disulfide was difficult to be removed by sampler. Therefore, carbon tetrachloride was chosen as the extraction solvent.

To examine the effect of the extaction solvent volume, the DLLME procedures using acetone solution containing different volume of carbon tetrachloride were carried. By increasing the volume of carbon tetrachloride from 15 µL to 40 µL, the volume of the sedimented phase increases from 8 µL to 26 µL. It was found that by increasing the volume of CCl_4, the analytical signal for Pb increased with the increasing of extaction solvent volume in the first and then kept nearly constant.

Effect of disperser solvent and its volume: In DLLME, the disperser solvent should be miscible with both extraction solvent and aqueous sample. For the sake of acquiring the most suitable disperser solvent, three kinds of disperser solvents such as acetone, methanol and ethanol were tested. A series of standard solutions were investigated by using 0.5 mL of each disperser solvent containing 25 µL of CCl_4. It was found that acetone was the best disperser solvent as it could achieve the highest signal intensity of lead. So, acetone was selected as disperser solvent in the following experiment.

The effect of the volume of disperser solvent on the signal intensity of lead was also examined. Because different volume of acetone led to different volume of sedimented phase using the same volume of extraction solvent, in order to acquire the same volume of sedimented phase, the volume of disperser solvent and extraction solvent changed simultaneously. The experimental results indicated that analytical signal increased in the first and then decrease with increasing volume of acetone. It should be pointed out that a well cloudy solution could not form when using low volume of acetone and the

solubility of complex in water increased when using large volume of acetone. So, 0.5 mL acetone was chosen in the following work.

Influence of pH: It is well known that pH of the sample solution was one of the important factors affecting the formation of complexes. Fig. 1 displayed the effect of pH on the signal intensity of Pb. As can be seen, the signal intensity of Pb increased with the increasing of pH from 2.0-5.5 and the signal intensity of Pb keep constant at the pH range of 5.5-7.0. Therefore, a pH 5.5 was selected for further study.

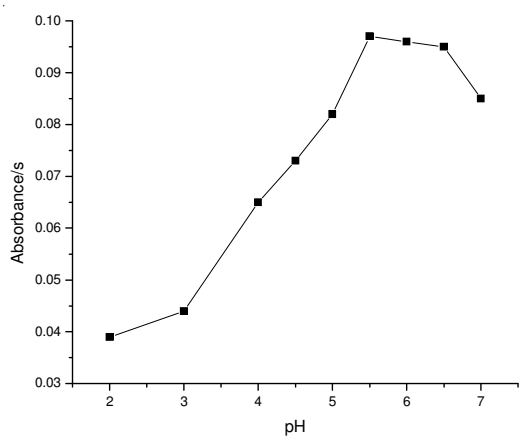

Fig. 1 Effect of pH on the absorbance of lead. Condition: lead standard solutions (0.1 ng mL^{-1}, 4.0 mL), 0.5 mL DDTC solution (0.010 g/mL), pH 2.0-7.0, 0.5 mL disperser solvent (acetone) containing 25 mL extraction solvent (CCl_4).

Influence of diethyldithiocarbamate (DDTC) concentration: The effect of the DDTC amount on the analytical signal is shown in Fig. 2. The signal intensity was increased by increasing the DDTC amount, which is well expected. It seems that slight reduction of extraction in high concentration of DDTC is due to the extraction of DDTC itself, which can easily saturate the small volume of extraction solvent. Therefore, the concentration of 0.010 g/mL DDTC was selected in the following experiment.

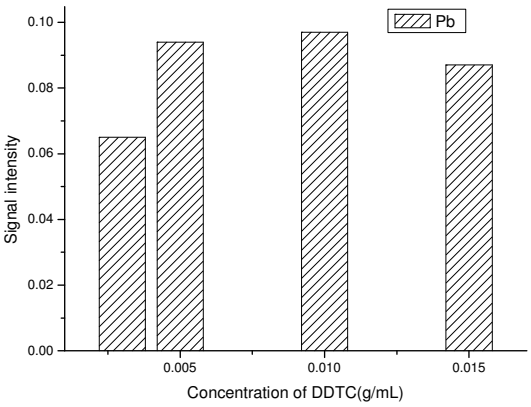

Fig. 2. Effect of DDTC concentration on the absorbance of lead. Condition: lead standard solutions(0.1 ng mL^{-1}, 4.0 mL), 0.5 mL DDTC (0.003-0.015 g/mL) solution, pH 5.5, 0.5 mL disperser solvent(acetone) containing 25 mL extraction solvent(CCl_4).

Influence of extraction time: Extraction time is an important factor influencing the extraction efficiency. In DLLME, extraction time is defined as the time between injection mixture of disperser and extraction solvent and starting to centrifuge. The effect of extraction time on signals intensity was investigated with the time varying from 1 to 10 min. The results indicated that the extraction time has no impact on the extraction efficiency. Because equilibrium state can be achieved quickly in DLLME, the extraction time required can be very short. The short extraction time is one of the remarkable advantages of the DLLME technique.

Interference effects: The effects of common coexisting ions on the recovery of lead were studied. In these experiments, 4.0 mL of solutions contains 0.1 ng mL^{-1} of lead and various amounts of interfering ions were treated according to the recommended procedure. A given spices was considered to interfere if it resulted in a 10 % variation of the signal intensity. The results obtained are given in Table-1.

TABLE-1
TOLERANCE LIMITS OF CO-EXISTING IONS

Ions	Concentration (μg mL^{-1})	Recovery (%)	Ions	Concentration (μg mL^{-1})	Recovery (%)
K^+	1000	104.1	Cr^{3+}	1.40	98.2
Na^+	1000	100.0	Al^{3+}	2.00	100.6
Mg^{2+}	600	97.3	Ag^+	0.08	97.2
Ca^{2+}	500	99.3	Fe^{3+}	0.80	92.1
Ni^{2+}	0.6	95.5	Cu^{2+}	0.10	95.1
Zn^{2+}	1.0	102.1	Cd^{2+}	0.80	93.3
Co^{2+}	0.8	94.6	Hg^{2+}	0.04	97.8

Analytical performance: Under the optimized conditions, the analytical performance of the method was evaluated. Based on the definition of IUPAC, the detection limits(3σ) of this method was 0.006 ng mL^{-1} for lead, the relative standard deviation(RSD) were 3.5 % (c = 0.1 ng mL^{-1}, n = 7). The calibration graph for the preconcentration procedure was A = 0.76693C + 0.05281(R=0.998) for 0.02-0.3 ng mL^{-1}.

Analytical application: The proposed method was applied to the determination of lead in mineral water and the results along with the recovery for the spiked samples were given in Table-2. As could be seen, the recoveries for the three spiked water samples are in the range of 96-108 %.

TABLE-2
RECOVERIES FOR THE DETERMINATION OF TRACE LEAD IN MINERAL WATER SAMPLES (n = 3, ng mL^{-1})

Samples	Added	Found	Recovery (%)
Mineral water (Qiandao Lake)	0	0.080±0.003	-
	0.05	0.134±0.006	108
	0.1	0.186±0.008	106
Mineral water (Kunlun Mountain)	0	ND	-
	0.05	0.048±0.002	96
	0.1	0.104±0.004	104
Mineral water (Deep Ocean)	0	ND	-
	0.05	0.052±0.002	104
	0.1	0.098±0.004	98

" ND "means not determined.

Conclusion

A new method of dispersive liquid-liquid microextraction combined with ETAAS has been described for the determination of lead in mineral water samples. The presented method had a lower limit of detection and higher enrichment factor over other

methods reported in the references. Additional, compared with other modes of liquid phase microextraction, dispersive liquid-liquid microextraction is suitable bath experiment due to very fast extraction.

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