



# Hollow fiber supported liquid membrane extraction for ultrasensitive determination of trace lead by portable tungsten coil electrothermal atomic absorption spectrometry

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## ABSTRACT

Hollow fiber supported liquid membrane extraction (HF-SLME) was used to separate and enrich trace lead from a large volume of 250 mL water sample to a final tiny volume of 30  $\mu\text{L}$  of 1-octanol, 5  $\mu\text{L}$  of which was injected into a tungsten coil electrothermal atomic absorption spectrometer (W-coil ET-AAS) for determination of lead. Some important parameters that influenced the extraction and determination were investigated in detail, such as the concentration of ammonium pyrrolidine dithiocarbamate (APDC), pH of sample solution, stirring rate, extraction time, pyrolysis current, atomization current, carrier gas flow rate, as well as interferences. Under the optimized conditions, a practical enrichment factor of 499 and a limit of detection ( $3\sigma$ ) of  $0.2 \text{ ng mL}^{-1}$  were obtained. The calibration curve was linear in the range of  $0.5\text{--}10 \text{ ng mL}^{-1}$ . The relative standard deviation (RSD) was 5.6% for five measurements of a  $4 \text{ ng mL}^{-1}$  lead standard solution. The accuracy of this method was examined by the analysis of certified reference water samples (GBW(E)080398 and GSBZ(E) 50009-88) for lead. Finally, the proposed method was applied to the determination of lead in local tap water, pond water and river water, with recoveries in the range of 96–109% for spiked samples.

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## 1. Introduction

It is well known now that lead can accumulate in the living organisms and exert high-toxic potential on human being and animals. Unfortunately, as one of the most widely used heavy metals, lead is almost ubiquitous in food, water and air [1]. Especially, inorganic or organic lead-containing compounds can be found in a variety of commercial products and industrial materials, including paints, plastics, storage batteries, bearing alloys, and ceramics. Since lead can be accumulated in the organisms, the toxicity of lead should not be ignored even at very low levels. Therefore, the analytical method for lead should be very sensitive, and frequently requires a preconcentration step [2]. Ideally, the analysis can be conducted on-site by using a portable instrument in many cases.

Hollow fiber supported liquid membrane extraction (HF-SLME) is one of the promising pre-separation and preconcentration techniques, and therefore has attracted considerable attention in recent years [3–7]. The microextraction principle of HF-SLME has been well-summarized in a recent review [8]. Several groups have worked on HF-SLME for the preconcentration of metals, such as Cd and Cu [9–13]. Hu et al. determined some trace elements by ETV-ICP-MS after

extraction by hollow fiber two-phase extraction [14]. In fact, a recent new trend for extraction schemes has been focused on miniaturized preconcentration methods and their coupling with detection approaches with both microsampling volume and good sensitivity [15]. In this context, tungsten coil electrothermal atomic absorption spectrometry possesses the merits of low cost and simplicity [16], and is often characterized as a typical microsampling detection scheme. Although a relatively simple power supply compared to a graphite furnace is still required, the heating rate of a tungsten coil (30 K/ms) is about ten times faster than that of a graphite tube (2–4 K/ms). Additionally, using a portable charge coupled device (CCD) as a detector, portable instrumentation for field analysis is possible [16,17]. Therefore, in this study, HF-SLME was used with W-coil ET-AAS for the determination of trace lead in water samples. 1-Octanol was used as liquid membrane and the acceptor solution. Two-phase extraction mode was adopted, and no chemical modifier was used during the determination of lead by portable W-coil ET-AAS.

## 2. Experimental

### 2.1. Apparatus

A prototype portable W-coil ET-AAS instrument was used for the determination of lead, with a schematic instrumental arrangement shown in Fig. 1. A constant temperature magnetic stirring meter

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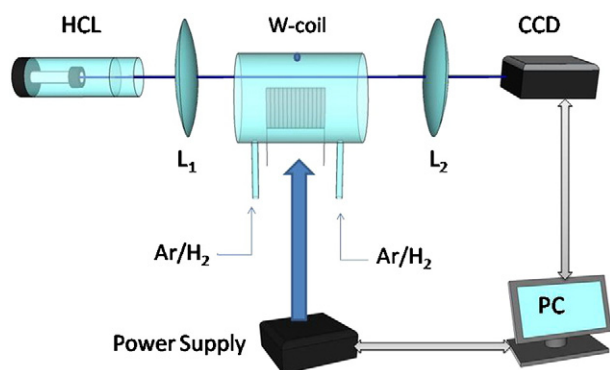


Fig. 1. Schematic diagram of the W-coil AAS instrument.

(Zhongrong Instrument Corporation, Shanghai, China) was used for stirring for the extraction. A lead hollow cathode lamp (HCL) (Ningqiang Source Co., Hengshui, China) was operated at a current of 8 mA. A W-coil obtained from a commercially available slide projector bulb (Model HLX 64633, OSRAM, Germany) was used as the atomizer, which was placed in a glass cell with two fused silica windows. The light from the lead HCL was focused through a fused silica lens ( $f=50$  mm, Gangdong Scientific Development Inc., Tianjin, China) to a point of 1 mm above the W-coil. Unabsorbed radiation was focused through another fused silica lens ( $f=50$  mm) to the entrance slit of a CCD spectrometer (USB 2000, Ocean Optics, Inc., Dunedin, FL, USA). Data were collected and saved using the software (OOIBased32) recommended by the CCD manufacturer and subsequently processed with Microsoft Excel. The software parameters were as follows: integral time, 50 ms; average, 1; flash delay, 100. The emission lines of 283.3 nm and 286.6 nm were selected for quantification and near-line background correction, respectively. Peak-height was used for quantification. A commercial DC power supply (Model HY 1791-10S, Huai'an Yaguang Electronics Ltd. Co., Huai'an, China) was employed for the power of the W-coil. The temperature of the W-coil was calculated by the formula mentioned in Ref. [18]. The mixture gas of argon and hydrogen was used to prevent W-coil from oxidation. The sampling volume was 5.0  $\mu\text{L}$  in this work considering the micro-amounts of samples after extraction. The heating program and related temperatures of the W-coil atomizer were summarized in Table 1, which included both situations without extraction and with HF-SLME.

## 2.2. Reagents and materials

The stock standard solution of Pb (II) ( $1 \text{ mg mL}^{-1}$ ) was purchased from the National Center for Reference Materials (Beijing, China). Working solutions were prepared daily by appropriate dilution of the stock solution with double distilled water (DDW). The chelating agent, 0.01% (m/V) ammonium pyrrolidine dithiocarbamate (APDC, Fluka) solution, was prepared by dissolving appropriate amount of APDC in DDW. Sodium acetate, acetic acid, sodium hydroxide and 1-octanol used in this experiment were obtained from Kelong Chemical Reagent Corporation (Chengdu, China). All the chemicals were at least

analytical-grade. Sodium acetate (NaAc) and acetic acid (HAc) buffer solution was used in this work to adjust the pH of the sample solutions. The polypropylene hollow fiber (320  $\mu\text{m}$  i.d., 50  $\mu\text{m}$  wall thickness, 0.1  $\mu\text{m}$  pore size) was purchased from Kaihong Membrane Coporation (Hangzhou, China). A 25- $\mu\text{L}$  microsyringe (Anting Corp., Shanghai, China) was used for sampling and flushing the hollow fiber. Tap water was collected in our laboratory, and pond water and river water were obtained on or near our campus (Chengdu, China).

## 2.3. Extraction procedures

A 15-cm long hollow fiber was connected to the needle of 25- $\mu\text{L}$  microsyringe holding 20  $\mu\text{L}$  of 1-octanol. Then the plunger of the syringe was depressed slowly to flush out 1-octanol to wash the hollow fiber, and this was repeated for five times before it was immersed into 1-octanol for 10 s to impregnate with the pores of the hollow fiber wall to form an organic liquid membrane. Then, the lumen of the hollow fiber was completely filled with 1-octanol, without air bubbles. The two ends of the hollow fiber were heating-sealed with an electric iron bar and enveloped with a strip of aluminum foil. After that, the outside of the hollow fiber was washed with DDW for several times to remove excessive 1-octanol. The effective length of the hollow fiber was about 12 cm with a volume of about 8  $\mu\text{L}$ . The hollow fiber was then immersed into 250 mL sample solution in a 250 mL beaker. By using the same procedure, three more hollow fibers were also immersed into the 250 mL sample solution. Thus, four fibers were used simultaneously for the extraction, which was carried out under a stirring speed of 800 rpm. After extraction for 20 min, the hollow fibers were taken out from the sample solution. The sealed ends of the hollow fibers were cut with scissors, and one end of each fiber was connected to the needle of the microsyringe. The extracting solution in the four hollow fibers was retracted into the microsyringe, and then flushed into a 500  $\mu\text{L}$  polyethylene vial. The volume of collected extracting solution was about 30  $\mu\text{L}$ , of which 5  $\mu\text{L}$  aliquot was injected onto the W-coil for the ET-AAS measurement.

## 3. Results and discussion

### 3.1. Selection of organic solvent

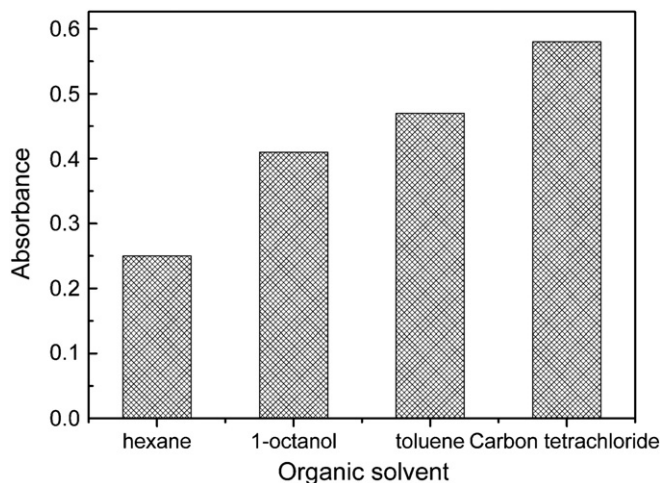
The type of organic solvent immobilized in the pores of the hollow fiber was a critical factor in HF-SLME. Generally, the analyte should be soluble in the selected solvent [19]. On the other hand, the solvent must possess low volatility and low solubility in water, and should not leak from the membrane [20]. Hexane, toluene, carbon tetrachloride and 1-octanol were tested in this study. As can be seen from Fig. 2,  $\text{CCl}_4$  and toluene gave higher enrichment factors than 1-octanol for the analyte, but  $\text{CCl}_4$  and toluene are more volatile and cannot be easily handled. Therefore, in the following investigation, 1-octanol was selected as the extraction solvent for the HF-SLME in this work.

### 3.2. Effect of sample pH

Sample pH plays a critical role in complex formation and subsequent extraction efficiency of the target analyte. APDC was a universal

Table 1  
Heating program and temperature of W-coil.

Step		Desolvation	Pyrolysis	Waiting	Atomization	Cleaning
With HF-SLME	Current (A)	3.2	3.5	0	8.6	9.1
	Temperature (K)	730	950	–	2340	2430
	Lasting time (s)	30	40	20	5	5
Without HF-SLME	Current (A)	3.2	3.4	0	8.5	9.0
	Temperature (K)	730	910	–	2320	2400
	Lasting time (s)	30	20	10	5	5

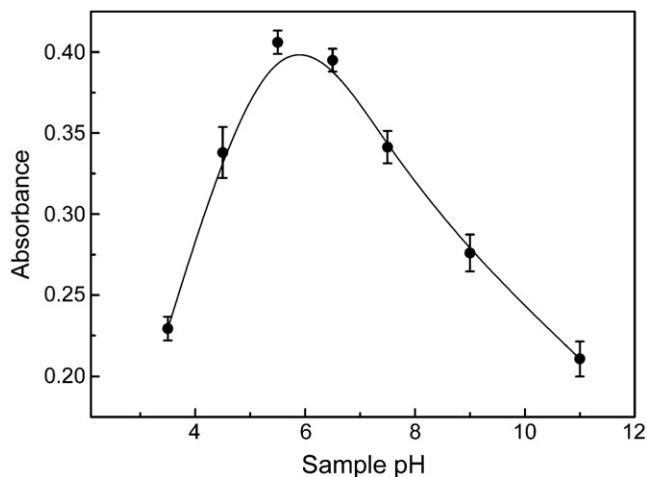


**Fig. 2.** Effect of different organic extraction solvents on Pb atomic absorbance after HF-SLME:  $4 \text{ ng mL}^{-1}$  Pb; stirring speed, 800 rpm; and extraction time, 20 min.

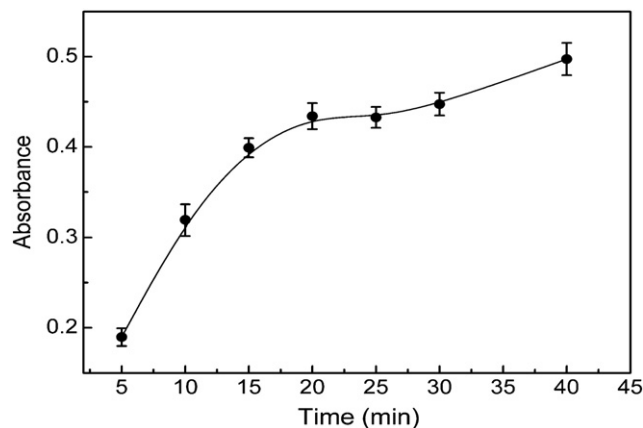
cheating reagent which can complex with many metal elements in a wide pH range. The sparingly soluble metal-PDC chelates can be extracted into a suitable organic solvent, which in this case is 1-octanol. The effect of pH on the extraction efficiency was shown in Fig. 3. The maximum of extraction efficiency was obtained at pH 5.5.

### 3.3. Effect of extraction time

To evaluate the effect of extraction time on the efficiency,  $1 \mu\text{g}$  Pb was spiked into 250 mL water sample to achieve a final Pb concentration of  $4 \text{ ng mL}^{-1}$ . Extractions were conducted for 5, 10, 15, 20, 25, 30 and 40 min at a stirring rate of 800 rpm. The HF-SLME is based on the partitioning of the analyte Pb-PDC between the aqueous phase and the organic phase 1-octanol. In order to minimize solvent loss and guarantee efficient extraction, extraction is often not allowed to proceed to equilibrium as it requires relatively long extraction time [3,14]. From Fig. 4, it can be seen that the lead atomic absorption signal increased with the increase of extraction time. After 20 min, the increasing trend for lead signal gradually leveled off. On the compromise of efficient extraction and time-saving, extraction time of 20 min was considered optimal.



**Fig. 3.** Effect of pH on Pb atomic absorbance after HF-SLME:  $4 \text{ ng mL}^{-1}$  Pb; stirring speed, 800 rpm; and extraction time, 20 min.



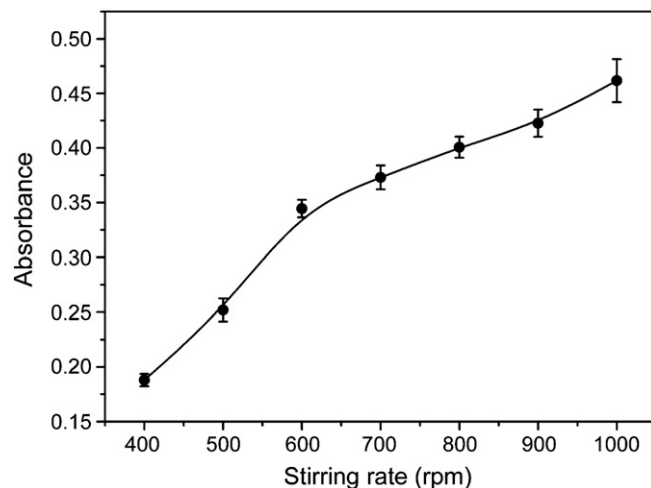
**Fig. 4.** Effect of extraction time on Pb atomic absorbance after HF-SLME:  $4 \text{ ng mL}^{-1}$  Pb; stirring speed, 800 rpm; and pH 5.5.

### 3.4. Effect of stirring rate

Magnetic stirring can accelerate the diffusion of the analyte and reduce the time to reach dynamic equilibrium in HF-SLME [11]. The organic solvent used as the acceptor solution in this study was injected into the lumen of the hydrophobic hollow fiber membrane, so it could tolerate relatively high stirring speeds. As shown in Fig. 5, the extraction efficiency increased with stirring speed. However, higher stirring speed could generate excessive air bubbles which adhered to the hollow fiber surface, leading to poor precision and possible experimental failure. Besides, the membrane on hollow fiber surface was prone to be lost at the higher stirring speed. Therefore, a stirring speed of 800 rpm was selected for use.

### 3.5. Effect of chelating reagent concentration

The chelating concentration was very important to the extraction efficiency and subsequent W-coil ET-AAS determination. Thus, the influence of APDC concentration on absorbance was also investigated. The results showed that the lead atomic absorbance increased with the increase of APDC concentration from 0.0002% to 0.001% (m/v) and then leveled off up to the concentration of 0.01% (m/v). Apparently, 0.01% (m/v) APDC should be sufficient for selective extraction of the target analyte from aqueous solution into 1-octanol.



**Fig. 5.** Effect of stirring rate on Pb atomic absorbance after HF-SLME:  $4 \text{ ng mL}^{-1}$  Pb; pH 5.5; and extraction time, 20 min.

### 3.6. Optimization of W-coil ET-AAS parameters

#### 3.6.1. Pyrolysis current

In order to remove complicated organic matrix, a relative higher pyrolysis current was needed. When the current was lower than 3.4 A, much higher spectral background interferences appeared. However, when the current was higher than 3.6 A, the absorbance was seriously reduced because of lead loss. Therefore, the pyrolysis current of 3.5 A was selected for use in this experiment.

#### 3.6.2. Atomization current

Atomization current was evaluated in the range of 6.9–9.1 A. No chemical modifiers were used in this study, and there was no obvious matrix interference found during the atomization. Since high temperature may decrease the lifetime of W-coil and a lower atomization current could not afford efficient atomization, an atomization current of 8.6 A was used for the measurement of lead atomic absorbance.

#### 3.6.3. Flow rate of $H_2$

The mixture of Ar and  $H_2$  was used as the working gas of W-coil ET-AAS. The flow rate of mixture gas was at  $1\text{ L min}^{-1}$ . The flow rate of  $H_2$  was evaluated in the range of  $0.16\text{--}0.26\text{ L min}^{-1}$ . When the flow rate was higher than  $0.24\text{ L min}^{-1}$ , the Pb absorbance significantly decreased. For sensitivity and safety consideration, a flow rate of  $H_2$  at  $0.22\text{ L min}^{-1}$  was used in this work.

### 3.7. Interference evaluation

When HF-SLME is applied to real sample analysis, potential interferences from co-existing species should be taken into account. A series of potential interfering metal ions was selected for evaluation of the robustness of the proposed method, including  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Hg^{2+}$ ,  $Fe^{3+}$  and  $Co^{2+}$ . A series of solutions of  $4\text{ ng mL}^{-1}$  Pb containing the above metal ions at different concentrations was respectively prepared and determined by W-coil ET-AAS after extraction. As can be seen from Table 2, the macro constituents ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) had no significant influence on Pb extraction and determination. Some transition metal ions may interfere with the Pb extraction, because they can form complex with APDC. Fortunately, in real water samples, the common concentration levels for these transition metal ions are often low, and potential interferences can be ignored.

### 3.8. Analytical performance

Under the optimal experimental conditions, analytical figures of merit (the enrichment factor, the linear dynamic range and correlation coefficient, the limit of detection (LOD), and the precision) were evaluated. The calibration curves were linear in the range of  $0.5\text{--}10\text{ ng mL}^{-1}$  Pb ( $R^2 > 0.998$ ). A limit of detection of  $0.2\text{ ng mL}^{-1}$  was obtained for lead, which was far better than the instrumental LOD ( $72\text{ ng mL}^{-1}$ ) without the extraction procedure. The enrichment factor was defined as the ratio of the slope of the calibration curves with and

**Table 2**

Effect of co-existing metal ions on the extraction and determination of Pb ( $4\text{ ng mL}^{-1}$ ).

Co-existing metal ions	[M]/[Pb]	Recovery (% , $n = 3$ )
$K^+$	$1.0 \times 10^7$	94
$Na^+$	$1.0 \times 10^6$	105
$Ca^{2+}$	$2.5 \times 10^4$	107
$Mg^{2+}$	7500	99
$Zn^{2+}$	200	106
$Cu^{2+}$	200	101
$Hg^{2+}$	50	94
$Fe^{3+}$	20	96
$Co^{2+}$	20	93

**Table 3**

Analytical results for Pb in water samples.

Samples	Added ( $\text{ng mL}^{-1}$ )	Found <sup>a</sup> ( $\text{ng mL}^{-1}$ )	Recovery (%)
River water	0	–	–
	1.00	$1.05 \pm 0.07$	105
	2.00	$2.18 \pm 0.12$	109
Tap water	0	–	–
	1.00	$0.99 \pm 0.05$	99
	2.00	$2.13 \pm 0.14$	107
Pond water	0	–	–
	1.00	$1.03 \pm 0.08$	103
	2.00	$1.92 \pm 0.13$	96

<sup>a</sup> Mean and standard deviation for three determinations.

without extraction, and an enrichment factor of 499 was achieved. The relative standard deviation calculated from five replicate measurements for Pb at  $4\text{ ng mL}^{-1}$  was 5.6%.

In order to validate the accuracy of the proposed method, five water samples were collected and subjected to Pb analysis. Two certified reference samples (GBW (E) 080398 and GSBZ (E) 50009-88) with certified values for Pb of  $500 \pm 2\text{ ng mL}^{-1}$  and  $1480 \pm 70\text{ ng mL}^{-1}$ , respectively, were analyzed. The determined values after proper dilution,  $517 \pm 3\text{ ng mL}^{-1}$  and  $1400 \pm 50\text{ ng mL}^{-1}$ , respectively, were in good agreement with the certified values. Other three water samples were collected and filtered through a  $0.45\text{ }\mu\text{m}$  filter membrane. Then APDC was added and pH was adjusted to 5.5 with the buffer solution. The analytical results were shown in Table 3, with spike-recoveries in the range of 96–109%.

### 4. Conclusion

In this work, HF-SLME was successfully coupled with portable W-coil ET-AAS for the determination of trace lead in water samples. Under the optimized experimental conditions, an enrichment factor of 499 was obtained. The present method showed the merit of high enrichment factor, simplicity, sensitivity, selectivity and no need for chemical modifiers. This is a potential on-site method by using a portable instrument in many cases.

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