

Determination of trace lead in water samples by continuous flow microextraction combined with graphite furnace atomic absorption spectrometry

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Abstract

A new method of continuous flow microextraction (CFME) combined with graphite furnace atomic absorption spectrometry (GFAAS) was proposed for the determination of trace lead in water samples. A drop of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) dissolved in benzene is injected into a glass chamber by a microsyringe and held at the outlet tip of a PTFE connecting tube, the sample solution flows right through the tube and the glass chamber, the solvent drop interacts continuously with the sample solution, and the analyte was extracted into the drop and concentrated. After extracting for a period of time, the drop was retracted into the microsyringe and directly injected into graphite furnace for determination of Pb. Several factors affecting the extraction efficiency, such as solution pH, sample flow rate, drop volume and extraction time, were optimized. Under the optimized conditions, a concentration factor of 45 was achieved, and the detection limits for Pb were 12 pg mL^{-1} . The relative standard deviation for six replicate analyses of 10 ng mL^{-1} Pb was 6.8%. The proposed method was applied to determine of trace Pb in water samples with satisfactory results.

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1. Introduction

In recent years, the pollution of the environment by heavy metals has received considerable attention. Lead is one of the most toxic elements and has accumulative effect. It distributed widely in the environment and produces several diseases [1]. It has been ranked as environmental priority pollutant in many countries. Therefore it is important to monitor the levels of lead in environments.

Several analytical techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), polarographic analysis and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of lead with sufficient sensitivity for most of applications. However, the determination of

trace lead in aqueous samples is difficult due to various factors, particularly its low concentration and matrix effect. In order to achieve accurate and reliable results, an efficient separation and preconcentration procedure is required. The most widely used techniques for the separation and preconcentration of trace lead include co-precipitation [2], liquid–liquid extraction (LLE) [3,4], solid-phase extraction (SPE) [5–7], cloud point extraction (CPE) [8], etc. LLE is one of the widely used preconcentration and matrix isolation techniques in the determination of metal ions. Although it offers high reproducibility and high sample capacity, it is considered to be a time and labor-consuming procedure, has the tendency for emulsion formation and poor potential for automation, and uses large amount of hazardous and costly organic solvents.

More recently, efforts have been placed on miniaturizing the LLE extraction procedure by greatly reducing the solvent to aqueous phase ratio, leading to the development of liquid-phase microextraction (LPME) methodology [9,10]. LPME is based on the distribution effect of the analytes between a drop of extraction solvent at the tip of a microsyringe needle and

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aqueous sample solution. The solvent drop is first exposed to the sample solution and target analyte is then transferred from the sample matrix into the drop. After extracting for a prescribed period of time, the drop is retracted back into the microsyringe and transferred to the instrumentation for further analysis. LPME uses inexpensive apparatus and virtually eliminates solvent consuming, and it combines extraction, preconcentration and sample introduction in one step. Since the method was first introduced by Liu and Dasgupta in 1996 [11], the applications of LPME have received much attention. Several different models of LPME have been developed, such as single drop microextraction (SDME) [12], dynamic LPME [13], headspace LPME [14] and hollow fiber-based LPME [15], etc., and the method has been successfully applied for the determination of organic pollutants and drugs in environmental and biological samples [16–20]. However, the application of LPME in the separation and preconcentration of metal ions has rarely been found in literature [21,22].

Continuous flow microextraction (CFME) is a novel LPME method, which was first reported by Liu and Lee [23]. In this method, the extraction solvent drop is injected into a glass chamber by a conventional microsyringe and held at the outlet tip of a PTFE connecting tube, the sample solution flows right through the tube and the extraction glass chamber to the waste, the solvent drop interacts continuously with the sample solution and extraction proceeds simultaneously. Because the drop of solvent fully and continuously makes contact with the sample solution, this method could gain higher concentration factor. Hu et al. [24,25] made minor modification of the method, and combined it with low temperature electrothermal vaporization ICP-AES/MS for the determination of trace elements.

The aim of this work is to combine CFME with GFAAS and develop a new method for the determination of trace lead in water samples. The chelating reagent 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP), which forms complexes with more than 40 metal ions and has found numerous applications in trace element separation and preconcentration by solvent extraction [26,27], solid-phase extraction [28,29] and cloud point extraction [30], was dissolved in benzene and used as extraction solvent. Factors affecting the extraction efficiency, such as solution pH, sample flow rate, drop volume and extraction time, were studied and optimized.

2. Experimental

2.1. Apparatus

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, PR China) with a deuterium background correction and a GFH990 graphite furnace atomizer system was used. All measurements were performed using integrated absorbance (peak area). Hollow-cathode lamps for Pb were operated at 2 mA. The optimum operating parameters for GFAAS are given in Table 1. CFME Extraction was performed in a homemade glass chamber (~0.2 mL). A 2232 microperpex peristaltic pump (Pharmacia LKB, Sweden) and a 10 μ L GC microsyringe (Shanghai, PR

Table 1
Operating parameters for GFAAS

Parameters	
Lamp current (mA)	2.0
Wavelength (nm)	283.3
Slit (nm)	0.4
Ar flow rate (mL min^{-1})	200 (stopped during atomizing)
Sample volume (μL)	5
Temperature program	
Drying	120 °C (ramp 18 s, hold 10 s)
Ashing	800 °C (ramp 10 s, hold 10 s)
Atomizing	1800 °C (ramp 0 s, hold 4 s)
Cleaning	2400 °C (ramp 1 s, hold 3 s)

China) were used for the sample solution delivery and extraction solvent introduction. A minimum length of PTFE tube (i.d. 0.5 mm) was used for all connections. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, PR China) supplied with a combined electrode.

2.2. Reagents and solutions

Stock standard solution of Pb at a concentration of 1000 $\mu\text{g mL}^{-1}$ was obtained from the National Institute of Standards (Beijing, PR China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. A 0.05 mol L^{-1} solution of PMBP was prepared by dissolving appropriate amounts of this reagent in benzene from the commercially available product. All other reagents were of analytical reagent grade or better. Doubly distilled water was used throughout the entire study. The following buffers were used to control the pH of the solutions: hydrochloric acid–glycine (pH 1–3), sodium acetate–acetic acid (pH 3–6), ammonium acetate–ammonia (pH 6–8). The pipettes and vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with doubly distilled water.

2.3. Procedures

The continuous-flow microextraction system used in this work is similar to that used in ref. [23] with minor modification (Fig. 1). The injector in the system of ref. [23] was omitted. A 10 μL GC microsyringe was used to introduce and withdraw the extraction solvent drop directly, and inject the post-extraction solvent drop into graphite furnace for the determination of Pb by GFAAS.

The CFME consists of four steps: (1) the aqueous sample was pumped continuously, vertically upward at a constant flow rate into the bulb glass extraction chamber (~0.2 mL) via the connecting PTFE tubing; (2) after the chamber has been filled with the sample solution, the required volume of PMBP solvent was introduced into the extraction chamber by the microsyringe, and forms a drop which remains at the tip of the microsyringe above the PTFE tube outlet in extraction chamber; (3) as the solvent drop was immersed in the sample solution, the analyte was extracted into the solvent drop from the sample solution,

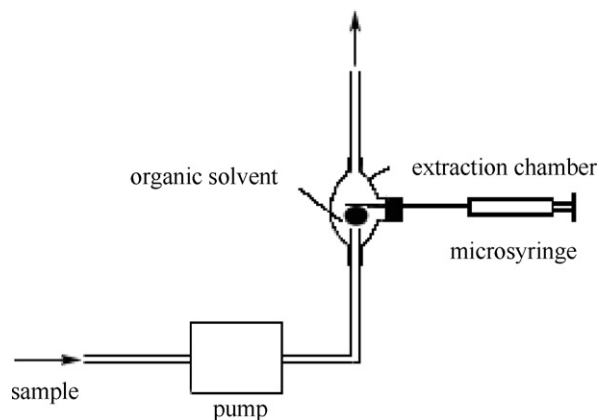


Fig. 1. Assembly of continuous-flow microextraction system.

with the sample solution being continuously ejected from the PTFE tubing into the chamber; (4) after extracting for a prescribed period of time, the solvent drop was retracted into the microsyringe and injected into the graphite furnace for analysis.

Calibration was performed against aqueous standards submitted to the same CFME procedure. A blank submitted to the same procedure described above was measured parallel to the samples and calibration solutions.

3. Results and discussion

3.1. Pyrolysis and atomization curves

The purpose of the pyrolysis step is to remove as much of the matrix as possible prior to atomization. This decreases the possibility of chemical interference and reduces the magnitude of the background signal. In order to avoid losing the lead during the pyrolysis step, the optimal pyrolysis temperature is necessary. Pyrolysis and atomization curves were established using 20 ng mL^{-1} Pb(II) solutions submitted to the CFME procedure. Fig. 2 shows the pyrolysis and atomization curves for Pb(II). The optimal pyrolysis and atomization temperatures are 800 and

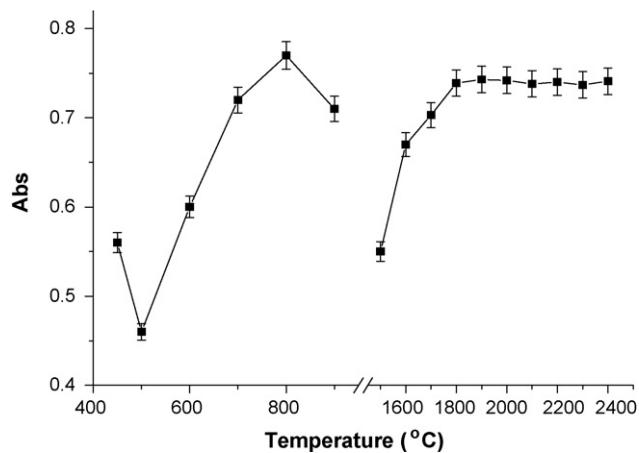


Fig. 2. Pyrolysis curve and atomization curve for CFME of Pb. CFME conditions: pH of sample 6.0, flow rate 0.5 mL min^{-1} , solvent drop volume $5 \mu\text{L}$, extraction time 15 min.

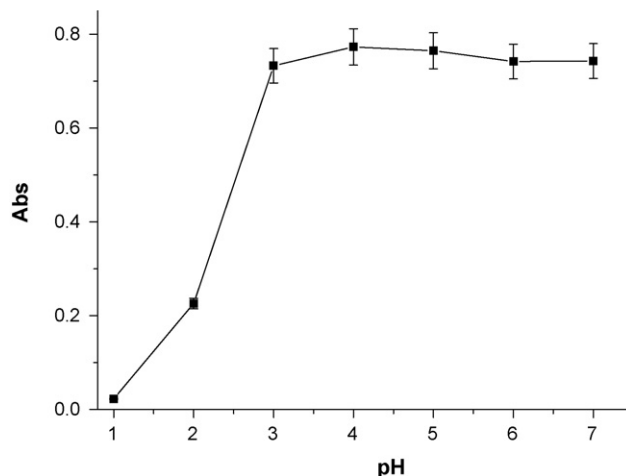


Fig. 3. Effect of pH on the CFME extraction of Pb.

$1800 \text{ }^\circ\text{C}$ for Pb(II). No modifier was used because considerable analyte stabilization is provided by the medium itself.

3.2. Effect of pH

The pH plays a unique role on metal–chelate formation and subsequent extraction, so the effect of pH on the CFME extraction of lead was studied and the results were shown in Fig. 3. It can be seen that the absorbance of Pb is almost constant when the pH exceeds 3. Accordingly, the original pH of natural water (pH 6.3–7.1) was selected for the subsequent work and the real water samples analysis.

3.3. Flow rate of sample solution

In CFME, the flow rate of sample solution could affect extraction dynamics remarkably since the thickness of the interfacial layer surrounding the drop will vary with the change of flow rate, which will affect the mass transfer of analytes in both phases involved in extraction. The effect of sample flow rate was evaluated with the change of flow rate from 0.05 to 0.8 mL min^{-1} and the results were shown in the Fig. 4. As can be seen, the

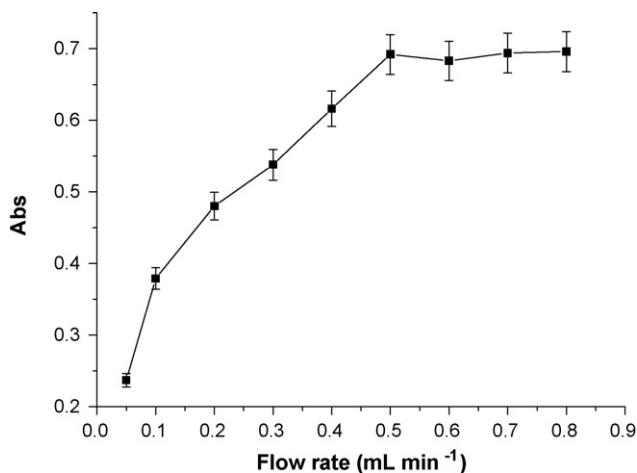


Fig. 4. Effect of flow rate of sample solution on the CFME extraction of Pb.

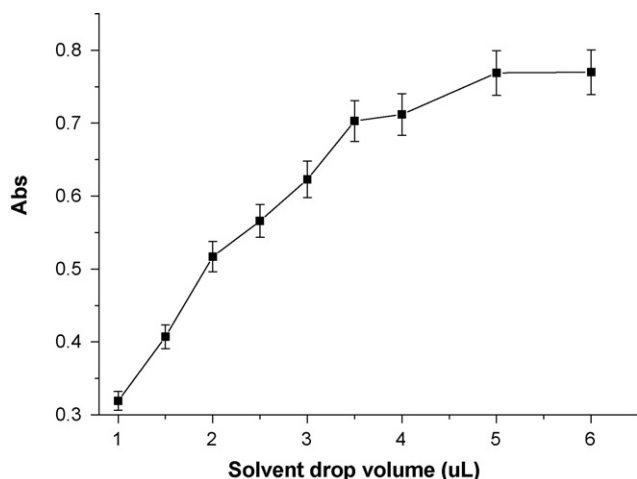


Fig. 5. Effect of solvent drop volume on the CFME extraction of Pb.

absorbance of Pb increased with the increase of sample flow rate to 0.5 mL min^{-1} because the thickness of the interfacial layer decreased with the increase of flow rate and more analyte was extracted into the solvent drop. However, a plateau in absorbance was observed for the analyte after the flow rate exceeded 0.5 mL min^{-1} . This is possibly due to the linear velocity of the sample solution being too high at higher flow rates to allow establishment of extraction equilibrium in the interfacial layer of both phases. Therefore, a flow rate of 0.5 mL min^{-1} was used for the subsequent work.

3.4. Solvent drop volume

In LPME, the volume of extraction solvent has great affection on the extraction efficiency. The influence of solvent drop volume on extraction efficiency of Pb was investigated with an extraction time of 10 min at a sample flow rate of 0.5 mL min^{-1} , and the result is shown in Fig. 5. As can be seen, absorbance of Pb increased with the increase of organic solvent volume. In the other hand, when the volume exceeded $5.0 \mu\text{L}$, the drop became too unstable to suspend at the needle tip. So, a drop volume of $5.0 \mu\text{L}$ was selected for subsequent experiments.

3.5. Extraction time

The effect of extraction time on the extraction efficiency was investigated in the range of 2–20 min with a solvent drop volume $5.0 \mu\text{L}$ at a constant flow rate of 0.5 mL min^{-1} . The absorbance of Pb increased with extraction time, long extraction time could lead to high preconcentration factor. However, long extraction time may also result in organic drop dissolution and poor precision. On base of these facts, an extraction time of 15 min was selected for the subsequent experiments.

3.6. Interferences

The potential interference in the present method has been investigated. The interference is due to the competition of other heavy metal ions for the chelating agent and their subsequent

Table 2
Tolerance limits of coexisting ions

Coexisting ions	Foreign ion to analyte ratio
$\text{K}^+, \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$	10000
$\text{Al}^{3+}, \text{Ba}^{2+}$	1000
$\text{Cu}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$	100
$\text{Cd}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$	50
$\text{Cr}^{3+}, \text{Fe}^{3+}$	10

co-extraction with lead. The tolerable limit is taken as a relative error $\leq \pm 5\%$. The tolerable concentration ratio of foreign ions to 10 ng mL^{-1} Pb was studied and shown in Table 2. Large amounts of alkaline and alkaline earth metal ions have no interferences with the microextraction of Pb under the selected conditions because of their very low stability constants of PMBP complexes.

3.7. Evaluation of method performance

For the purpose of quantitative analysis, a calibration curve for Pb with concentrations ranging over four orders was obtained by spiking the standards directly into distilling water and extracted under the optimal conditions. Linearity was observed over the range of $0\text{--}60 \text{ ng mL}^{-1}$ with a correlation coefficient (R^2) of 0.9994. The limit of detection (LOD), based on a signal-to noise ratio (S/N) of 3, was 12 pg mL^{-1} . The precision of this method was determined by analyzing standard solution at 10 ng mL^{-1} of Pb for six times in continuous, and the relative standard deviation (R.S.D.%) was 6.8%. The concentration factor (CF), defined as the ratio of the peak area of the analyte attained after and before extraction, was 45. Compared with the SDME method [21], the LOD is similar, and a better precision was obtained by the proposed method.

3.8. Real water samples analysis

In order to demonstrate the performance of the proposed method, tap water from our laboratory and natural water from east Lake of Wuhan were analyzed for the Pb presence. All water samples were filtered through a $0.45 \mu\text{m}$ membrane filter and analyzed as soon as possible after sampling. In addition, the recovery experiments of different amounts of Pb were carried out, and the results were shown in Table 3. The results indicated that the recoveries were reasonable for trace analysis, in a range of 97–103%.

Table 3
Determination of lead in real water samples

Samples	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Tap water	0	nd	
	5	4.9	98
	10	12.4	102
Lake water	0	5.2	
	5	10.5	103
	10	14.9	97

nd: not detected.

4. Conclusion

A new method, CFME coupled with GFAAS was developed for the determination of Pb in water samples at low ng mL^{-1} levels. The various parameters that affect the efficiency of CFME were optimized. Besides of general advantages of simple, virtually solvent-free, low costs, this method proved to be stable, reliable and accurate. The optimized procedure revealed satisfactory precision with R.S.D. of 6.8% and the limit of detection was 12 pg mL^{-1} . As discussed above, the potential of this microextraction technique in trace element analysis is tremendous.

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