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# Solid Phase Extraction and Flame Atomic Absorption Spectrometry for the Determination of Trace Lead

JIE YANG†, JINGJIAO XUE‡, JINGLI CAO‡, QIUFEN HU*‡,
PING NING† and GUANGYU YANG‡
*School of Chemistry and Biotechnology, Yunnan Nationalities*
*University, Kunming-650031, P.R. China*
*E-mail: huqiufena@yahoo.com.cn; huqiufena@163.com*

A reliable and rapid method for determination of lead using $C_{18}$ disc impregnated with 4-hydroxy-1-naphthal thiorhodanine (HNTR) and flame atomic absorption spectrometry is presented. The influence of aqueous phase pH, type of eluent, flow rates of sample solution and eluent, volume of eluent has been investigated. The method developed for determination of lead is good as seven replicate determinations provides a relative standard deviation (RSD) of 2.5-3.2 %. The selectivity of the proposed method was confirmed from the interference studies. The developed procedure was successfully applied for the determination of lead in tobacco, Chinese herb medicine and water.

**Key Words: Lead, 4-Hydroxy-1-naphthalthiorhodanine, Impregnated $C_{18}$ disc, Solid phase extraction, Flame atomic absorption spectrometry.**

## INTRODUCTION

Lead is one of the most ubiquitous elements in the environment and recognized as a major health risk to humans and animals[1,2]. The development of new methods for selective determination of lead in sub micro levels is received more and more attentions[3,4]. Flame atomic absorption spectrometry (FAAS) is a simple technique, commonly used for determination of lead in water, soil and plant samples[3-8]. However, the determination of traces of lead by flame atomic absorption spectrometry in such complex matrices is difficult due to its low sensitivity (0.1 mg $mL^{-1}$) and the interfering effects of matrix components. Hence, separation step is frequently necessary to improve the detection limit and sensitivity.

Solid phase extraction is an attractive separation-preconcentration technique for lead ions and various solid phase extraction materials have been successfully used for the preconcentration and separation of lead at trace levels[6,8-11]. However, solid phase extraction methods using columns with a narrow internal diameter limit the usable flow rates to a range of 1-10 mL $min^{-1}$ resulting in long time for enrichment

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†Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming-650031, P.R. China.

‡Key Laboratory of Tobacco Chemistry of Yunnan Province, Yunnan Academy of Tobacco Science, Kunming-650106, P.R. China.

from large sample volumes, while $C_{18}$ disc enable much higher flow rates[6,12,13]. In view of this, the extraction of lead with 4-hydroxy-1-naphthal thiorhodanine (HNTR) impregnated on $C_{18}$ disc and determination by flame atomic absorption spectrometry was systematically studied. This type of solid phase overcomes the limitations of solvent extraction, over use of large quantities of organic solvents while high specificity and selectivity of a liquid cation exchanger can be achieved by controlling the sorption and elution parameters.

## EXPERIMENTAL

ENVI-$C_{18}$ Disc (47 mm i.d.) was obtained from Beijing Kanglin Science and Technology Co. Ltd. The 4-hydroxy-1-naphthal thiorhodanine was synthesized according to our previous literature[14] and 4-hydroxy-1-naphthal thiorhodanine solution (1 %, m/v) was prepared by dissolving 1 g of the reagent in methanol. A stock standard solution of lead (1 mg/mL) was obtained from Chinese standard center and the working solution need was prepared by diluting this solution. Buffer solutions (pH 1-9) were made of mixture of acetic acid, boric acid and phosphoric acid plus sodium hydroxide in water. All solutions were prepared with double distilled water. Otherwise stated, analytical-grade acids and other chemicals were obtained from Merck (Darmstadt, Germany).

**Preparation of impregnated $C_{18}$ disc:** The 4-hydroxy-1-naphthal thiorhodanine impregnated $C_{18}$ disc was prepared as follows. After placing the membrane disc in the filtration apparatus, the disc was washed with 10 mL of HPLC grade methanol and double distilled water repeatedly by applying a slight vacuum. Then, a 3 mL of 1 % 4-hydroxy-1-naphthal thiorhodanine was introduced onto the disc so that the solution was spread on the whole disc surface. The solution was allowed to penetrate inside the membrane completely. The ethanol was evaporated and the impregnated $C_{18}$ disc was obtained.

A Perkin-Elmer model Aanalyst 600 atomic absorption spectrometer equipped with a model AS-800 autosampler (Norwalk, CT) and furnished with a lead hollow-cathode lamp was used. The instrument was adjusted according to the standard conditions: Lamp current 6 mA, wavelength 217 nm, air-acetylene flame (air flow rate 3.7 L $min^{-1}$, acetylene flow rate 1.1 L $min^{-1}$), spectral band width 0.5 nm. The pH of aqueous solutions was checked using a Beckman F-200 pH meter with a glass electrode.

**Procedure:** A 50-500 mL of Pb(II) solution, buffered at pH 3.8 (acetic acid-sodium acetate buffer, 0.01 mol $L^{-1}$), was passed through the disc at a flow rate of 50 mL $min^{-1}$. After finishing the sample solution, a volume of 2.5 mL of 0.25 mol $L^{-1}$ $HNO_3$ was passed through the disc in the reverse direction at a flow rate of 2.5 mL $min^{-1}$ to elute the Pb(II) ions. The eluant was afforded to flame atomic absorption spectrometry determination.

For water samples, the pH of the sample was adjusted to 3.8 and the solution was passed through the disc. Lead ions retained on the disc were eluted with 2.5 mL of 0.25 mol $L^{-1}$ $HNO_3$. The eluent was analyzed by the flame atomic absorption spectrometry.

For tobacco and Chinese herb medicine, the samples were dried at 60 ºC and pulverized to 80 mesh. An exact amount (0.500 g) of dried samples was placed into the 50 mL Teflon high-pressure microwave acid-digestion bomb. To which, 3 mL of concentrated nitric acid and 10 mL of 30 % hydrogen peroxide was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 10 min. The digest was evaporated to near dryness. The residue was dissolved with 25 mL of 1 % $HNO_3$ and the pH of the sample was adjusted to 3.8 with 5 % NaOH. Afterwards, the above preconcentration procedure was applied to the final solutions and the blank solution.

## RESULTS AND DISCUSSION

**Effect of aqueous phase pH and flow rate:** The influence of pH of sample solution on the preconcentration step of Pb(II) was studied. For this purpose, 500 mL of 0.05 mg $mL^{-1}$ Pb(II) at different pH values (1-7) was passed through the modified solid phase. Then the Pb(II) concentration in eluent solution was checked using flame atomic absorption spectrometry. The results showed that the suitable pH for adsorption of Pb(II) on the impregnated $C_{18}$ disc is around 2.8-6.2. Therefore, a buffer solution (acetic acid-sodium acetate, 0.01 mol $L^{-1}$) at pH 3.8 was used for the preconcentration step.

The effect of sample flow rate on the uptake of lead at pH 3.8 by the modified disc was studied. It was found that extraction of the metal ion was quantitative (96 ± 3 %) and reproducible up to a sample flow rate of 20-80 mL $min^{-1}$. The flow rate selected for all studies was 50 mL $min^{-1}$. Extraction of lead using this flow rate was rapid as compared to other reported solid phase extraction method.

For desorption of Pb(II) from the solid phase, different $HNO_3$ concentrations (2.5 mL) in the interval range of 0.1-1.0 mol $L^{-1}$ with flow rate of 2.5 mL $min^{-1}$ and with sample flow rate of 50 mL $min^{-1}$ were tested for the quantitative elution of the adsorbed Pb(II) ions from the disc. The results showed that 0.25 mol $L^{-1}$ $HNO_3$ was suitable to remove (95 ± 2.5) % of Pb(II) from the solid sorbent. In order to optimize the volume of 0.25 mol $L^{-1}$ $HNO_3$ solution, 200 mL of 0.2 mg $mL^{-1}$ Pb(II) was passed through the impregnated disc under the optimum conditions. Then the solid phases were washed with different volumes of 0.25 mol $L^{-1}$ $HNO_3$ (0.5-6.0 mL). The results showed that 2.5 mL of $HNO_3$ solution can elute Pb(II) from the disc completely. Therefore, 2.5 mL of $HNO_3$ was selected as eluant.

The effect of flow rate of $HNO_3$ (0.25 mol $L^{-1}$) on desorption efficiency of Pb(II) ions from the disc was also checked in the range of 1-5 mL $min^{-1}$. The results showed that the recovery of lead was maximized when using elution rates up to 2.0-3.5 mL $min^{-1}$. Therefore, 2.5 mL $min^{-1}$ was selected.

**Capacity of the impregnated disc:** The capacity of the impregnated $C_{18}$ disc for adsorption of Pb(II) was checked by passing 200 mL of Pb(II) solution containing 0.05-10.00 μg $mL^{-1}$ Pb(II) through the disc. The lead was stripped off the disc with

2.5 mL 0.25 mol $L^{-1}$ $HNO_3$ and measured by flame atomic absorption spectrometry. Under the condition of lead recovery $\geq 95$ %, the adsorption capacity was calculated to be 0.82 mg $g^{-1}$. The disc has adequate capacity to enrich the lead in real sample.

**Reusability of impregnated disc:** Reusability of the impregnated disc was checked using the same disc for sorption-desorption of Pb(II) ions for 30 times the reusability was tested. The maximum change in the performance (sorption capacity) of the solid phase after the repeated use was less than 2.8 %, indicating that its repeated use is feasible as leaching of the dye from the disc matrix is insignificant. No change in the sorption capacity of the impregnated $C_{18}$ disc was noticed after storing it for 2 months.

**Calibration graphs and detection limits:** Under the flame atomic absorption spectrometry analysis conditions, regression equations of Pb(II) was established based on the standard samples injected and their absorption signals. The results shown that the linearity range for lead was obeyed in the range of 0.05-5.00 mg $mL^{-1}$ and the linear regression equation obtained was: $A = 0.00237 + 0.0462\ C$ (mg $mL^{-1}$), $r = 0.9995$.

The results showed that the limit of quantitative preconcentration was 0.5 μg $L^{-1}$ Pb(II) with a preconcentration factor of 200 (500 mL of sample solution was passed the disc). Recoveries from further diluted solutions or larger sample volume were not quantitative (the recovery of lead < 95 %). The limit of detection values based on three times the standard deviations of the blank was equal to 0.12 μg $L^{-1}$ Pb(II).

**Interference study:** The influence of matrix ions in water samples on the separation and recovery of Pb(II) ions was also investigated by passing different amounts of potential interfering ions plus 0.1 mg $mL^{-1}$ Pb(II). The results showed that 5000-fold of alkaline and alkaline-earth ions, chloride, nitrate, hydrogen carbonate, carbonate and sulphate, 1000-fold Zn(II), Al(III), Fe(II), Ni(II), Pd(II), V(III), 500-fold Mn(II), Cu(II), Hg(II), Mo(VI), Co(II), Cr(III), Ag(I), 100-fold Cd(II), Hg(II) did not interfere. The results confirm that the modified solid phase is highly selective for Pb(II) and interferences did not occur.

**Application to real samples:** The method was applied to the determination of lead in tobacco, Chinese herb medicine and water. The results (deducted the reagents blank) were given in Table-1. A standard method using ICP-MS had also been used as reference method and the result were also shown in Table-1.

TABLE-1
DETERMINATION RESULTS OF THE TOBACCO, WATER AND CHINESE HERB MEDICINE SAMPLES

| Samples | ICP-MS Method | This method | RSD % (n = 7) | Recovery (%) (n = 5) |
|---|---|---|---|---|
| Kunming tap water | 0.188 (μg/L) | 0.201 (μg/L) | 3.2 | 86-94 |
| Lake water | 0.963 (μg/L) | 0.942 (μg/L) | 2.9 | 91-97 |
| Tobacco leaf | 1.260 (μg/g) | 1.180 (μg/g) | 2.5 | 94-103 |
| Chinese herb medicine (*Polygonum cuspidatum*) | 0.475 (μg/g) | 0.468 (μg/g) | 3.2 | 93-104 |

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