Application of Nanometer Zirconium Oxide Immobilized on Silica Gel as a Solid Phase Extraction Sorbent for the Preconcentration of Pb in Water Samples Prior to Flame Atomic Absorption Spectrometry Determination

Binwu Yang^{*ab}, Liping Zhao^a, Yanfei Zhao^b, Jinxin Qin^a, Ningning Ren^a, Erlin Jie^a,
Qi Qin^a, Fuwen Zhao^a, and Fenglong Li^a

^a Department of Applied Chemistry, Yuncheng University

^b Analytical and Testing Center, Yuncheng University, Shanxi, P.R. China
No. 333 East Hedong Street, Yuncheng Shanxi 044000, P.R. China

INTRODUCTION

Lead (Pb) is one of the most toxic heavy elements to animals and humans, even at low concentrations. It is a neurotoxin and accumulates in the body, which can lead to behavioral abnormalities, slow mental development, and retardation (1). On the other hand, due to its unique properties, it is used as an industrial material in diverse fields and thus released into the environment in considerable amounts (2). Hence, accurate and sensitive determination of lead is an important part of analytical chemistry. Atomic absorption spectrometry (AAS) is a cost-effective and simple methodology used in many laboratories for the determination of heavy metals (3). However, the direct determination of metals in real samples, especially by flame AAS, is limited and difficult because of their low concentration levels and matrix interferences. For this reason, a chemical separation and preconcentration step is often required prior to analysis.

Solid phase extraction (SPE) has been used widely for trace metal enrichment and preconcentration. Its advantages include simplicity, speed, low cost, environmentally friendliness, and low consumption of organic solvents which results in high enrichment factors (4,5). In a SPE procedure, selection of the

ABSTRACT

A new method has been developed for the determination of Pb(II) based on the separation and preconcentration with a micro-column packed with nanometer ZrO₂, immobilized on silica gel (ZrO₂/SiO₂) prior to its determination by flame atomic absorption spectrometry. The optimum experimental parameters for preconcentration of Pb(II), such as pH, sample flow rate and volume, eluent and interfering ions, were investigated.

Lead was quantitatively retained by ZrO₂/SiO₂ in the pH range of 4–6, then eluted completely with 0.5 mol L⁻¹ HNO₃. The adsorption capacity for Pb(II) was 4.79 mg g⁻¹. The detection limit for Pb(II) was 5.2 µg L⁻¹ with an enrichment factor of 100. The relative standard deviation was 2.5% (n = 7, c = 1.0 µg mL⁻¹). The method was applied to the determination of trace amounts of Pb(II) in real samples with satisfactory results.

most appropriate sorbent is a key factor for obtaining high enrichment efficiency. Numerous substances have been used as SPE sorbents for the separation and preconcentration of metal ions, such as active carbon (6), chelating resin (7), modified silica gel (8), carbon nanotubes (9,10), and nanometer oxides (11–13). Among these, nanometer materials have gained interest due

to their specific properties. Compared with micrometer-sized particles, nanometer materials offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high extraction capacity, rapid extraction dynamics, and high extraction efficiency (14,15). The adsorption behavior of metal ions on nanometer TiO₂ (16,17) and Al₂O₃ has been studied (18,19). The results show that nano-materials are promising solid phase extraction adsorbents.

However, due to the fine grain size of nanometer oxides, they easily agglomerate, show loss of activity, and are difficult to recover. These problems can be avoided by immobilizing nanometer oxides on different substrates. Liu et al. (20) reported the synthesis of immobilizing nanometer TiO₂ on silica gel using the sol-gel method as the SPE sorbent for the determination of metal ions (2,21,22).

In this work, nanometer ZrO₂ immobilized on silica gel (ZrO₂/SiO₂) was prepared by the sol-gel method and characterized by X-ray diffraction (XRD) and FTIR spectra. The adsorptive potential of ZrO₂/SiO₂ for the preconcentration of trace Pb(II) was assessed using the column method. In this study, a new method is presented using a micro-column packed with ZrO₂/SiO₂ as sorbent for the preconcentration of trace lead prior to its determination by FAAS.

^{*}Corresponding author.
E-mail: ybwufeng@163.com

EXPERIMENTAL

Instrumentation

A TAS-990 atomic absorption spectrophotometer (General Instruments Co. Ltd., Beijing, P.R. China), equipped with an air-acetylene burner, was used for the determination of lead. Background correction was performed with a deuterium lamp. A Pb hollow cathode lamp, operating at 283.3 nm, was used as the radiation source. The lamp current and slit width were set at 5.0 mA and 0.4 mm, respectively.

The FTIR spectra were obtained with a Bruker Tensor 27 FTIR instrument (Bruker, Germany). The X-ray diffraction (XRD) of the sample was examined on a Dandong Y-2000 X-ray diffractometer (Dandong, P.R. China) using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) at a scanning rate of $0.02^\circ \text{ s}^{-1}$ and a detection range from 20° to 80° .

The flow of the sample through the column was adjusted using a BT100-4 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, P.R. China). A homemade glass micro-column ($20 \text{ mm} \times 2.0 \text{ mm}$ i.d.) was packed with 50 mg of the solid sorbent. PTFE tubing with 0.5 mm i.d. was used for all connections. All pH measurements were carried out with a PHS-3 C digital pH meter, equipped with a

combined glass-calomel electrode (Shanghai Dapu, Shanghai, P.R. China).

Standard Solutions and Reagents

Stock standard solutions of Pb(II) ($1000 \mu\text{g mL}^{-1}$) were prepared by dissolving appropriate amounts of $\text{Pb}(\text{NO}_3)_2$ (A.R., The First Reagent Factory of Shanghai, P.R. China) in high purity deionized water. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Silica gel (80–100 mesh, Qingdao Ocean Chemical Factory, Qingdao, P.R. China) was boiled with (1 + 1) hydrochloric acid for 12 hours, then washed with doubly distilled water until all traces of chloride were eliminated. The cleaned silica gel was dried at 120°C for three hours. Zirconium tetrachloride was purchased from the Shanghai Reagent Factory (Shanghai, P.R. China). The certified reference materials (CRMs) GBW08505 Tea and GBW07601 Human Hair were purchased from the National Institute of Standards and Technology (Beijing, P.R. China). All other reagents were of analytical reagent grade or better. Doubly distilled water was used throughout.

Preparation of Immobilized Nanometer Zirconium Oxide Adsorbent

The $\text{ZrO}_2/\text{SiO}_2$ was synthesized as described by Ren et al. (23). In brief, a 2.0 g ZrOCl_2 was added to 40 mL of the mixture of doubly distilled water and ethanol (5:3 v/v) while stirring. Then, 5 g of cleaned silica gel was added to the solution and continuously stirred for two hours at ambient temperature. The pH was adjusted to 5.0 with 0.1 mol L^{-1} ammonia. The mixture was maintained at reflux at 70°C for four hours. The resulting material was washed with distilled water, then dried at 150°C for one hour, and subsequently calcined at 800°C

for 10 hours to obtain the immobilized nanometer zirconium oxide. In the following discussion, the samples are labeled $\text{ZrO}_2/\text{SiO}_2$.

Sample Preparation

The river water samples were collected from the Yellow River (Yuncheng, Shanxi, P.R. China) and the rain water from Yuncheng (Yuncheng, P.R. China). The tap water samples were obtained at our laboratory after allowing the water to flow for five minutes. The water samples were filtered through a $0.45 \mu\text{m}$ membrane filter, acidified to pH 2 with concentrated HNO_3 , and stored at 4°C in the refrigerator. Before use, the pH value was adjusted to 5.0 with ammonium hydroxide and HNO_3 solution. The CRMs GBW08505 Tea (1.0000 g) and GBW07601 Human Hair (0.5000 g) were accurately weighed into each PTFE beaker, 8 mL of concentrated HNO_3 was added, and the solution left standing overnight. Then, 2 mL of H_2O_2 was added to the samples and the solution heated to near dryness. The residue was dissolved in 0.1 mol L^{-1} HNO_3 and diluted to 50.0 mL with deionized water. A blank digest was prepared in the same way. Then the preconcentration procedure given below was applied to the final solution. The analyte in the final solution was determined by FAAS.

Micro-column Preparation

A 50 mg amount of $\text{ZrO}_2/\text{SiO}_2$ was filled into a self-made glass micro-column ($20 \times 2.0 \text{ mm}$ i.d.), plugged with a small portion of glass wool at both ends. Before use, 0.5 mol L^{-1} HNO_3 solution and doubly distilled water were passed through the column in order to clean and condition it. Then, the column was conditioned to the desired pH with a buffer solution.

TABLE I
Instrumental Operating
Conditions for
Lead Determination by FAAS

Parameters	
Instrumentation	TAS-990 AAS
Wavelength	283.3 nm
Slit Width	0.4 mm
Lamp	Hollow cathode
Current	5.0 mA
Flame	Air- C_2H_2

Analytical Procedure

Aqueous sample solutions (10 mL) containing the Pb analyte were prepared, and the pH was adjusted to the value of 5. The solution was passed through the $\text{ZrO}_2/\text{SiO}_2$ column using a peristaltic pump at a flow rate of 1.5 mL min^{-1} . Afterwards, the Pb(II) retained on the micro-column was eluted with 1.5 mL of 0.5 mol L^{-1} HNO_3 solution. The analyte in the effluent was determined by FAAS. A blank solution was also run under the same conditions without adding the analyte. The recovery was calculated based on the ratio of the amount of analyte in the eluent and the starting sample.

RESULTS AND DISCUSSION

$\text{ZrO}_2/\text{SiO}_2$ Characterization

The crystal structure of immobilized nanometer ZrO_2 was characterized using X-ray diffraction (XRD). The diffraction pattern of XRD for 2θ diffraction angles from 20° to 80° is shown in Figure 1. The sharp peaks at 30.19° , 35.34° , 50.36° , and 60.02° can be attributed to ZrO_2 crystallites according to the standard pattern of ZrO_2 crystallites (JCPDS File No. 03-640). FTIR spectra are helpful to further understand the formation of the $\text{ZrO}_2/\text{SiO}_2$ composite. Figure 2 shows the FTIR spectra of the nanocomposite. A broad band was observed at the low frequency region (around 500 cm^{-1}) of the composite, which can be ascribed to the Zr-O and Zr-O-Zr vibrations.

Effect of pH on Adsorption of Pb(II)

The effect of pH on the adsorption of Pb(II) on the $\text{ZrO}_2/\text{SiO}_2$ sorbent was investigated according to the analytical procedure described above. The recovery was calculated based on the ratio of the amount of lead in the eluent and the starting sample. As can be seen in Figure 3, the sorption of Pb(II) on the sor-

bent increases with an increase in pH, and quantitative recovery ($> 90\%$) was obtained at a pH range of 4–6. For all further experiments, the pH of 5 was chosen for preconcentration of Pb(II).

Effect of Eluent Concentration and Volume

Elution of the adsorbed lead was achieved by using an appropriate eluent solution capable of effectively stripping it from the sorbent and bringing it into the solution. Thus, various concentrations of HNO_3 were studied for the desorption of the retained lead from the micro-column at the flow rate of 1 mL min^{-1} . The results in Figure 4 show that 0.5 mol L^{-1} HNO_3 was sufficient for the recovery of lead. The effect of eluent volume on the recovery of lead was also studied by keeping the HNO_3 concentration at 0.5 mol L^{-1} .

Fig. 1. X-ray diffraction pattern of $\text{ZrO}_2/\text{SiO}_2$.

Fig. 2. FTIR spectra of $\text{ZrO}_2/\text{SiO}_2$.

It was found that quantitative recovery was obtained with 1.5 mL eluent volume. Therefore, 1.5 mL of 0.5 mol L^{-1} nitric acid was used in the following experiments.

Effect of Sample Flow Rate

The flow rate of the sample solution affects retention of the Pb ion on the adsorbent and the duration of the complete analysis. Therefore, the effect of the sample flow rate was examined under optimum conditions. The flow rate was adjusted ranging from 0.5 – 3.0 mL min^{-1} . Figure 5 shows that quantitative recovery of lead was obtained at the flow rate ranging from 0.5 – 1.5 mL min^{-1} . However, the lead recovery decreased at a flow rate above 1.5 mL min^{-1} . Hence, the flow rate of 1.5 mL min^{-1} was employed in this work for the preconcentration of lead in a 10-mL water sample.

Fig. 3. Effect of pH on the adsorption of Pb(II) on $\text{ZrO}_2/\text{SiO}_2$, Pb(II): $1 \mu\text{g mL}^{-1}$, sample volume: 10 mL.

Fig. 4. Effect of HNO_3 concentration on the recovery of lead, Pb(II): $1 \mu\text{g mL}^{-1}$, sample volume: 10 mL.

Effect of Sample Volume

Sample volume is one of the most important parameters for obtaining high preconcentration factors. For this purpose, 25, 50, 150, 200, and 250 mL of sample solutions containing 10 µg of Pb(II) were passed through the micro-column at the optimum flow rate. It was found that quantitative recovery was obtained for Pb(II) up to a sample volume of 150 mL. Above 150 mL, the recovery of Pb(II) decreased. The preconcentration factor was 100 for all sample solutions since the final elution volume was kept at 1.5 mL.

Adsorption Capacity

The adsorption capacity is an important factor because it determines how much sorbent is required to remove a specific amount of metal ions from the solution quantitatively. To determine the adsorption capacity, 20 mL aliquots of a series of concentrations (5–50 µg mL⁻¹) were adjusted to the appropriate pH, then preconcentrated and eluted according to the recommended procedure. The amount of lead adsorbed at each concentration level was determined by FAAS. The adsorption capacity of ZrO₂/SiO₂ for Pb(II) was found to be 4.79 mg g⁻¹.

Fig. 5. Effect of flow rate on lead recovery, Pb(II): 1 µg mL⁻¹, sample volume: 10 mL.

Effect of Coexisting Ions

The effect of common coexisting ions on the adsorption of lead on immobilized nanometer ZrO₂/SiO₂ was investigated. In this experiment, solutions of 1 µg mL⁻¹ lead containing the added interfering ions were treated according to the recommended procedure. The tolerance of the coexisting ions, defined as the maximum concentration found to cause a change in signal by less than 10% compared with the signal for the analyte alone, were K⁺ and Na⁺: 5.0 mg mL⁻¹; Ca²⁺ and Mg²⁺: 5.0 mg mL⁻¹; Ni²⁺ and Co²⁺: 1.0 mg mL⁻¹. It can be seen that under the selected conditions, the presence of common coexisting ions did not interfere with the retention of lead.

TABLE II
Determination of Pb(II) in Water Samples Using Proposed Methodology (n=3) (mean±S.D.)

Sample	Added (µg mL ⁻¹)	Found (µg mL ⁻¹)	Recovery (%)
Yellow River Water	0	0	-
	1.0	1.05 ± 0.05	105
	2.0	1.95 ± 0.11	97.5
Rain Water	0	0	-
	1.0	1.02 ± 0.08	102
	2.0	1.98 ± 0.18	99
Tap Water	0	0	-
	1.0	1.08 ± 0.13	108
	2.0	2.0 ± 0.13	96.2

Detection Limits and Precision

According to IUPAC definition, the detection limit of the instrument is calculated based on three times the standard deviation of 11 runs of the blank solution. The instrumental detection limit for Pb(II) was 0.52 µg mL⁻¹. Given the 100-fold enrichment factor, the detection limit of the method was found to be 5.2 µg L⁻¹ for Pb(II). Seven replicate determinations of lead in the final solution gave a relative standard deviation (R.S.D.) of 2.5% for Pb(II).

Analytical Application

The proposed method was applied to the determination of lead in tap water, rain water, and Yellow River water samples, and the recoveries of the lead spikes were also studied. The results given in Table II show that the recoveries of the spiked samples ranged from 96.2–108.0%. In order to establish the validity of the proposed procedure, the method was applied to the determination of lead in the CRMs. As can be seen from Table III, the analytical values are in agreement with the certified values.

CONCLUSION

In this work, the adsorption behavior of Pb(II) on ZrO₂/SiO₂ was investigated. The method is based on the separation and preconcentration of Pb(II) using a micro-column packed with nanometer ZrO₂, immobilized on silica gel (ZrO₂/SiO₂) prior to its flame atomic absorption spectrometry determination in real water samples. The results show good

TABLE III
Determination of Lead in Certified Reference Materials (n=3)

Sample	Measured (µg g ⁻¹)	Certified (µg g ⁻¹)	Recovery (%)
GBW08505 Tea	1.18 ± 0.24	1.09 ± 0.10	92.4
GBW07601 Human Hair	8.8 ± 1.1	8.5 ± 0.82	96.6

precision and accuracy, with a Pb(II) detection limit of $5.2 \mu\text{g L}^{-1}$ and an enrichment factor of 100. The recoveries for the different samples were more than 90%. The method is simple, rapid, cost-effective, and sensitive for the preconcentration and determination of trace amounts of Pb(II) in real samples.

ACKNOWLEDGMENT

This work was supported by the open experimentation program of Yuncheng University.

Received August 6, 2011.

REFERENCES

1. X.J. Liu and Z. F. Fan, *At. Spectrosc.* 28, 215 (2007).
2. R. Liu and P. Liang, *J. Hazard. Mater.* 152, 166 (2008).
3. M. Tuzen, K.O. Saygi, and M. Soylak, *J. Hazard. Mater.* 152, 632 (2008).
4. J.S. Suleiman, B. Hu, C.Z. Huang, and N. Zhang, *J. Hazard. Mater.* 157, 410 (2008).
5. X.H. Shang and X.P. Yan, *J. Anal. At. Spectrom.* 22, 1284 (2007).
6. Z.H. Li, X.J. Chang, Z. Hu, X.P. Huang, X.J. Zou, Q. Wu, and R. Niem, *J. Hazard. Mater.* 166, 133 (2009).
7. M. Tuzen, O.D. Uluozlu, C. Usta, and M. Soylak, *Anal. Chim. Acta* 581, 241 (2007).
8. F.Z. Xie, X.C. Lin, X.P. Wu, and Z. H. Xie, *Talanta* 74, 836 (2008).
9. L.P. Zhao, Q.J. Gong, H. Sun, B.W. Yang, and Y.D. Zhu, *At. Spectrosc.* 31, 201 (2010).
10. M. Savio, B. Parodi, L.D. Martinez, P. Smichowski, and R.A. Gil, *Talanta* 85, 245 (2011).
11. C.Z. Huang, Z.C. Jiang, and B. Hu, *Talanta* 73, 274 (2007).
12. Q.X. Zhou, X.N. Zhao, and J.P. Xiao, *Talanta* 77, 1774 (2009).
13. L. Zhang, M. Zhang, X.J. Guo, X.Y. Liu, P.L. Kang, and X. Chen, *Talanta* 83, 344 (2010).
14. M. Faraji, Y. Yamini, and M. Rezaee, *Talanta* 81, 831 (2010).
15. M. Faraji, Y. Yamini, A. Saleha, M. Rezaee, M. Ghambariana, and R. Hassania, *Anal. Chim. Acta* 659, 172 (2010).
16. P. Liang, Y. C. Qin, B. Hu, T. Y. Peng and Z. C. Jiang, *Anal. Chim. Acta* 440, 207 (2001).
17. P. Liang, T.Q. Shi, H.B. Lu, Z.C. Jiang, and B. Hu, *Spectrochim. Acta Part B* 58, 1709 (2003).
18. G. Chang, Z.C. Jiang, T.Y. Peng, and B. Hu, *Acta Chim. Sinica* 61, 100 (2003).
19. M. Ezoddin, F. Shemirani, K. Abdi, M.K. Saghezchi, and M.R. Jamali, *J. Hazard. Mater.* 178, 900 (2010).
20. Y. Liu, P. Liang, and L. Guo, *Talanta* 68, 25 (2005).
21. P. Liang and R. Liu, *Anal. Chim. Acta* 602, 32 (2007).
22. R. Liu and P. Liang, *Anal. Chim. Acta* 604, 114 (2007).
23. Y.Z. Ren, Z.F. Fan, and J.Y. Wang, *Microchim. Acta* 158, 227 (2007).