

Determination of trace lead in water samples by graphite furnace atomic absorption spectrometry after preconcentration with nanometer titanium dioxide immobilized on silica gel

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Abstract

Nanometer titanium dioxide immobilized on silica gel (immobilized nanometer TiO₂) was prepared by sol–gel method and characterized using X-ray diffraction (XRD) and scanning electron microscope (SEM). The adsorptive capability of immobilized nanometer TiO₂ for lead was assessed in this work using column method. It was found that lead can be quantitatively retained by immobilized nanometer TiO₂ in the pH range 4–7, then eluted completely with 1.0 mol L⁻¹ HCl. The adsorption capacity of immobilized nanometer TiO₂ for Pb was found to be 3.16 mg g⁻¹. A new method has been developed for the determination of trace lead based on preconcentration with a microcolumn packed with immobilized nanometer TiO₂ prior to its determination by graphite furnace atomic absorption spectrometry (GFAAS). The detection limit of this method for Pb was 9.5 ng L⁻¹ with an enrichment factor of 50, and the relative standard deviations (R.S.D.s) was 3.2% at the 10 ng mL⁻¹ Pb level. The method was validated using a certified reference material, and was applied for the determination of trace lead in water samples. © 2007 Elsevier B.V. All rights reserved.

Keywords: Immobilized nanometer titanium dioxide; Preconcentration; Lead; Graphite furnace atomic absorption spectrometry

1. Introduction

The field of nanocomposite materials has had the attention, imagination, and close scrutiny of scientists and engineers in recent years [1,2]. Nanomaterials are made of nanoparticles; the regime of nanoparticle is from 1 nm to almost 100 nm, falls between the classic fields of chemistry and solid-state physics. One of the specific properties of nanomaterials is that a high percent of the atoms of the nanoparticle is on the surface. The surface atoms are unsaturated and can therefore bind with other atoms, possess highly chemical activity. Nanoparticulate metal oxides exhibit intrinsic surface reactivity and high surface areas, and can strongly chemisorb many substances, such as acidic gases and polar organics [3]. Our previous studies show that nanometer TiO₂ material is a promising solid-phase extraction (SPE) adsorbent for metal ions [4–7].

Due to the fine grain size of nanometer TiO₂, when the suspension nanometer TiO₂ is used for adsorption of metal ions, it is easy to coagulate and loss of activity, and difficult to be recovered. These problems can be avoided by immobilizing nanometer TiO₂ on different substrates. Immobilized nanometer TiO₂ can be prepared by coating the support substrates with a TiO₂ sol by different techniques such as chemical vapor deposition [8], chemical spray pyrolysis [9], and sol–gel method [10]. Among the different techniques the sol–gel coating is the simplest, economical and has advantages such as TiO₂ is easily anchored on the substrates bearing the complicated shapes and large area substrates [11]. Immobilized nanometer TiO₂ has been widely applied as chemical sensors [12], electrochemical solar cells [13] and photocatalyst [14].

Lead is one of the most toxic metals, adversely affects the central and peripheral nervous systems and the kidney [15]. However, its unique properties make it to be used as industrial material in diverse fields, and released into the environment in considerable amounts. In 1991, the United States

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Environmental Protection Agency (USEPA) published a regulation to control lead in drinking water, which included an action level of 0.015 mg L^{-1} [16]. The World Health Organization (WHO) has released the guidelines for drinking water quality containing the guideline value of 0.01 mg L^{-1} for Pb [17]. Therefore, highly sensitive determination methods of trace lead in water samples ($<1 \text{ } \mu\text{g L}^{-1}$) need to be established.

Graphite furnace atomic absorption spectrometry (GFAAS) is a very attractive option for the determination of trace amounts of lead in water samples. However, the direct determination of trace amounts of lead in water samples with GFAAS is usually difficult due to the low level of lead in water samples is not compatible with the detection limit and major constituents such as organic compounds and inorganic salts cause matrix effects. Consequently, separation and preconcentration are often needed before GFAAS determination. The most widely used techniques for separation and preconcentration of trace lead include liquid–liquid extraction [18], cloud point extraction [19,20], solid-phase extraction [21–27], coprecipitation [28] and electrochemical deposition [29], etc. Recently, solid-phase extraction technique has become increasingly popular in compared with the classical liquid–liquid extraction method because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [30].

In this work, nanometer TiO_2 immobilized on silica gel (immobilized nanometer TiO_2) was prepared by sol–gel method and characterized using X-ray diffraction (XRD) and scanning electron microscope (SEM). The potential of immobilized nanometer TiO_2 as sorbent for the preconcentration of trace lead was assessed using column method. A new method using immobilized nanometer TiO_2 as sorbent has been developed for the preconcentration of trace lead in water samples prior to its determination by GFAAS.

2. Experimental

2.1. Apparatus

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge Genereal 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 2.0 mA. The optimum operating parameters for GFAAS are given in Table 1. XRD pattern was obtained using Y-2000 diffractometer (Dandong Liaodong Radial Instrument Co. Ltd., Liaoning, China) with $\text{Cu K}\alpha$ radiation. SEM images were obtained on a SX-650 field emission scanning electron microscope (Hitachi, Japan). The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) was used in separation/preconcentration process. A self-made PTFE microcolumn ($20 \text{ mm} \times 3.0 \text{ mm i.d.}$), packed with

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)	20
Temperature program	
Drying	100 °C (Ramp 20 s, Hold 20 s)
Ashing	300 °C (Ramp 15 s, Hold 15 s)
Atomizing	1800 °C (Ramp 0 s, Hold 3 s)
Cleaning	2000 °C (Ramp 1 s, Hold 3 s)

immobilized nanometer TiO_2 , was used in the manifold for separation/preconcentration. A minimum length of PTFE tubing with an i.d. of 0.5 mm was used for all connection.

2.2. Standard solution and reagents

Stock standard solution ($1000 \text{ } \mu\text{g mL}^{-1}$) of lead was obtained from the National Institute of Standards (Beijing, PR China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Silica gel (40–60 mesh, Qingdao Ocean Chemical Factory, Qingdao, China) was boiled with (1+1) nitric acid for 3 h, then immersed in (1+1) hydrochloric acid for 24 h, finally washed with doubly distilled water until no chloride appeared in the washings. The cleaned silica gel was dried at 120 °C for 24 h. All reagents used were of the highest available purity and of at least analytical reagent grade. Doubly distilled water was used throughout. Titanium tetrabutoxide (Aldrich chemicals) was used without further purification. 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 6–7).

2.3. Preparation of immobilized nanometer TiO_2

Ten milliliter of titanium tetrabutoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) was added to 12.5 mL of ethanol. Then a mixture of doubly distilled water (0.5 mL), ethanol (12.5 mL) and conc. HCl (0.25 mL) was added slowly dropwise into the solution under stirring. The solution was kept stirring for 30 min at ambient temperature for hydrolysis and form sol–gel. The resulting TiO_2 sol can be used after aging for 12 h. Ten grams of silica gel was immersed into the viscous Ti-precursor sol for 10 min, then taken out and dried. This process was repeated three times. The coated silica gel was washed with doubly distilled water to remove the unimmobilized TiO_2 , then dried at 100 °C for 1 h and subsequently calcined in 450 °C for 2 h to obtain the immobilized nanometer TiO_2 .

2.4. Column preparation

Fifty milligram of immobilized nanometer TiO_2 was introduced into a PTFE microcolumn ($20 \text{ mm} \times 3.0 \text{ mm i.d.}$) plugged with a small portion of glass wool at both ends. Before use, 2.0 mol L^{-1} HCl solution and doubly distilled water were passed

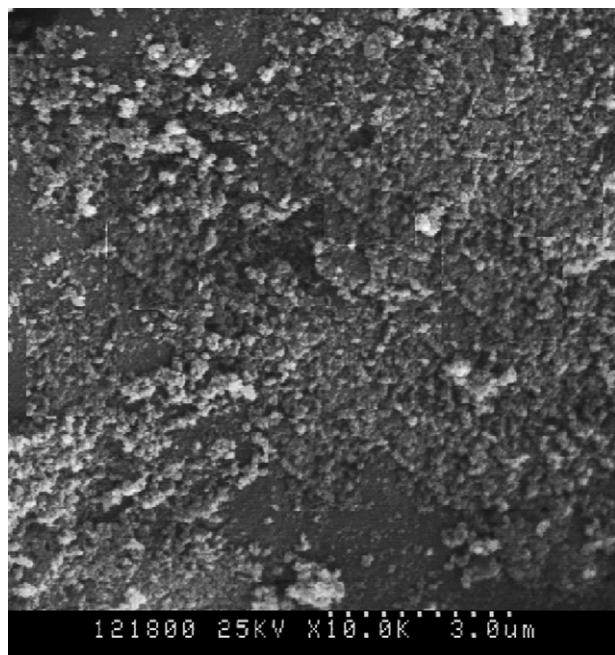


Fig. 1. SEM micrographs of immobilized nanometer TiO_2 .

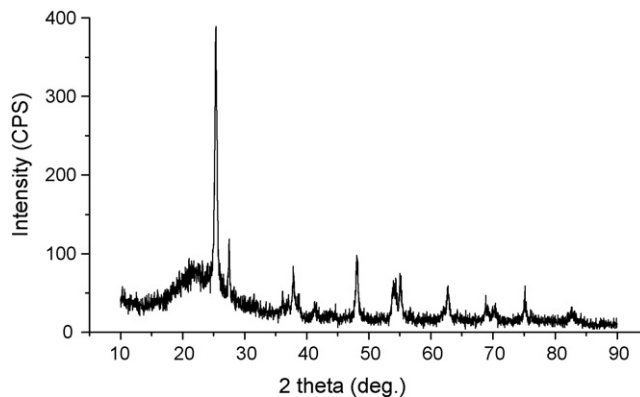


Fig. 2. XRD pattern of immobilized nanometer TiO_2 .

was determined by ICP-AES. The amount of TiO_2 coated was found to be 220 mg g^{-1} .

The TiO_2 coated onto the surface of silica gel was shown to be very stable to treatment with acid. No leaching of Ti(IV) from the surface was detected using 2.0 mol L^{-1} HCl.

3.2. Effect of pH on adsorption

The pH value plays an important role with respect to the adsorption of different ions on oxide surfaces. According to Morterra [32], the pH of solution influences the distribution of active sites on the surface of TiO_2 . At high pH, the OH^- on the surface provides the ability of binding cations. The decrease of pH leads to the neutralization of surface charge, and OH^- is displaced from the surface, so the adsorption of cations onto TiO_2 decreases quickly.

In order to evaluate the effect of pH on the adsorption of Pb, the sample solutions were adjusted to a pH range of 1–7 and processed according to the recommended procedure. The adsorption percentage was calculated based on a difference between the amount of Pb in the starting sample and the solution outflowing from the column. The results are shown in Fig. 3. It

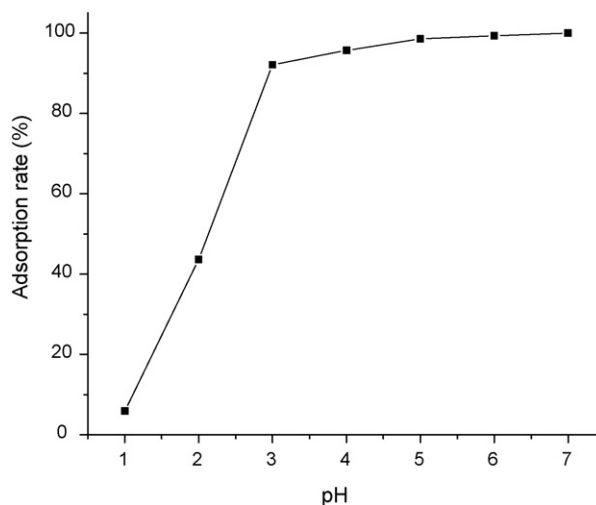


Fig. 3. Effect of pH on the adsorption of Pb ions on immobilized nanometer TiO_2 Pb: 10 ng mL^{-1} , sample volume: 20 mL .

through the column in order to clean and condition it. Then, the column was conditioned to the desired pH with buffer solution.

2.5. General procedure

A portion of aqueous sample solution containing Pb ion was prepared, and the pH value was adjusted to the desired value with corresponding buffer solution. The solution was passed through the column by using a peristaltic pump adjusted to the desired flow rate. Afterwards, the retained Pb ion was eluted with 1.0 mL of 1.0 mol L^{-1} HCl solution. The analyte in the eluent was determined by GFAAS. The column could be used repeatedly after regeneration with 2.0 mol L^{-1} HCl solution and distilled water, respectively.

3. Results and discussion

3.1. Characterization of immobilized nanometer TiO_2

The SEM image of immobilized nanometer TiO_2 is shown in Fig. 1. The SEM image shows dense microstructure and granular grain. The average grain size of immobilized nanometer TiO_2 is about 60 nm .

The crystal structure of immobilized nanometer TiO_2 was characterized using XRD. The diffraction pattern of XRD for 2θ diffraction angles from 10° to 90° was shown in Fig. 2. The sharp peaks at 25.27 , 37.84 and 48.07 can be attributed to anatase TiO_2 according to the standard pattern of anatase TiO_2 [31]. It can be concluded that immobilized nanometer TiO_2 existed as anatase structure.

The amount of TiO_2 coated was determined by treating the modified silica gel with the hot mixture of conc. H_2SO_4 and H_2O_2 (1 + 1). The solid was filtered and the Ti in the solution

Table 2
Eluent data (%) for Pb ion adsorbed on immobilized nanometer TiO₂

	Eluent (mol L ⁻¹)				
	0.5	1.0	2.0	3.0	4.0
HCl	84.8	94.2	95.3	96.6	95.4
HNO ₃	45.9	51.4	66.9	72.0	78.4

(Eluent volume 1.0 mL).

can be seen that quantitative adsorption (>95%) for Pb ion was obtained in the pH range of 4–7. So a pH of 5.0 was selected as the compromise condition.

3.3. Elution of the adsorbed Pb ions

It is found from Fig. 3 that the adsorption of Pb at pH < 2 could be negligible. For this reason, various concentrations HCl and HNO₃ were studied for the elution of retained Pb ion from the microcolumn at a flow rate of 0.5 mL min⁻¹. The elution efficiency (recovery) of Pb was calculated from the amount of Pb in the starting sample and the amount of Pb eluted from the column. The results obtained are given in Table 2. As can be seen, 1.0 mol L⁻¹ HCl was sufficient for quantitative recovery (>95%). The effect of eluent volume on the recovery of Pb was also studied by keeping the HCl concentration of 1.0 mol L⁻¹, it was found that quantitative recovery (>95%) could be obtained with 1.0 mL of 1.0 mol L⁻¹ HCl. Therefore, the volume of 1.0 mL eluent was used in the following experiments.

3.4. Effect of flow rate of sample solutions

The flow rate of sample solution affects the retention of Pb ion on the adsorbent and the duration of complete analysis. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions (pH, eluent, etc.). The flow rate was adjusted in a range of 0.5–2.5 mL min⁻¹. It was found that the retention of Pb ion was practically not changed up to a flow rate of 2.0 mL min⁻¹. The recovery of Pb decreased slightly when the flow rate is over 2.0 mL min⁻¹. Thus, a flow rate of 2.0 mL min⁻¹ was employed in this work.

3.5. Effect of the sample volume

In order to explore the possibility of enriching low concentrations of analyte from large volume, the effect of sample volume

Table 3
Tolerance limits for coexisting ions

Coexisting ions	Tolerance limit of ions (mg L ⁻¹)
Na ⁺ , K ⁺	5000
Ca ²⁺ , Mg ²⁺	1000
Al ³⁺ , Zn ²⁺	200
Fe ³⁺	50
SO ₄ ²⁻	5000
PO ₄ ³⁻	2000

on the recovery of Pb ion was also investigated. For this purpose, 25, 50, 100, 150 and 200 mL of sample solutions containing 1.0 µg of Pb were passed through the microcolumn at optimum flow rate. It was found that quantitative recovery (>95%) was obtained for Pb up to a sample volume of 50 mL. In this experiment, 50 mL of sample solution was adopted for the pre-concentration of Pb ion from water samples, the adsorbed Pb ion can be eluted with 1.0 mL 1.0 mol L⁻¹ HCl, so an enrichment factor of 50 is achieved by this method.

3.6. Adsorption capacity

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. To determine the adsorption capacity, 25 mL of Pb ion solution at 20 µg mL⁻¹ was adjusted to the appropriate pH, then preconcentrated and eluted according to the recommended procedure. The amount of Pb ion adsorbed was determined by GFAAS. The adsorption capacity of immobilized nanometer TiO₂ for Pb was found to be 3.16 mg g⁻¹.

3.7. Column reuse

The stability and potential regeneration of the column were investigated. The column can be reused after regenerated with 10 mL of 2.0 mol L⁻¹ HCl and 20 mL distilled water, respectively, and stable up to at least 20 adsorption–elution cycles without obvious decrease in the recoveries for the studied ions.

3.8. Effects of coexisting ions

The effects of common coexisting ions on the adsorption of Pb ion on immobilized nanometer TiO₂ were investigated. In

Table 4
Comparison of the characteristic data between typical published methods with the proposed method in this work

Adsorbent	Detection method	Enrichment factor	Detection limit	Reference
Chelex-100	FAAS	70	0.5 µg L ⁻¹	[21]
Fullerene	TFF-AAS	100	2.4 µg L ⁻¹	[22]
PTFE fiber	FAAS	49	0.26 µg L ⁻¹	[23]
Diaion HP-2MG	FAAS	20	3.7 µg L ⁻¹	[24]
Chromosorb-106	FAAS	250	0.32 µg L ⁻¹	[25]
Epoxy resin	FAAS	50	1.2 µg L ⁻¹	[26]
Alumina	FAAS	240	0.73 µg L ⁻¹	[27]
Immobilized nanometer TiO ₂	GFAAS	50	9.5 ng L ⁻¹	This work

Table 5
Determination of Pb (ng mL⁻¹) in natural water samples (n = 5)

Samples	Added	Found	Recovery (%)
Tap water	0	1.92 ± 0.03	–
	2.0	3.84 ± 0.15	96
	4.0	5.84 ± 0.19	98
Lake water	0	2.40 ± 0.08	–
	2.0	4.48 ± 0.17	104
	4.0	6.32 ± 0.22	98

Sample volume: 50 mL.

these experiments, solutions of 10 ng mL⁻¹ of Pb containing the added interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Pb less than 90%, were given in Table 3. It can be seen that the presence of major cations and anions has no obvious influence on the adsorption of Pb ion under the selected conditions.

3.9. Detection limits and precision

The calibration curve for lead, based on optimal conditions, was linear with a correlation coefficient of 0.9997 (A (absorbance) = 0.0121 C (μg L⁻¹) + 0.00457) in the range of 0.5–100 μg L⁻¹. The detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of seven replicate measurements of blank solution using the preconcentration method, was found to be 9.5 ng L⁻¹ for Pb. The precision of this method (R.S.D.s), examined by eleven replicate measurements of 0.5 μg Pb²⁺ in 50 mL of model solutions, was about 3.2%.

Table 4 compares the characteristic data of the present method with those reported in literatures. Generally, the present method requires lower acid concentration and volume for efficient analyte elution, and gave better precision. The enrichment factor obtained by the present method is comparable to those reported method, and the detection limit is better than them.

3.10. Analytical application

In order to establish the validity of the proposed procedure, the method has been applied to the determination of lead in environmental water reference material (GSBZ50009-88, China). The determined value (1.33 ± 0.05 μg mL⁻¹, n = 5) was not significantly different from the certified value (1.36 ± 0.07 μg mL⁻¹).

The proposed method was applied to the determination of Pb in tap water and lake water sample. Lake water sample was collected from East Lake, Wuhan, PR China, and tap water sample was freshly collected from our laboratory, after allowing the water to flow for 5 min. All water samples were filtered through a 0.45 μm 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 are shown in Table 5. The results indicated that the recoveries were reasonable for trace analysis, in a range of 96–104%.

4. Conclusions

It can be concluded from the results that immobilized nanometer TiO₂ is an effective sorbent for trace amounts of lead and can be used for its preconcentration from the dilute aqueous solutions. The proposed solid phase extraction procedure based on immobilized nanometer TiO₂ showed enough sensitivity for trace lead determinations in diverse kind of samples. The precision and accuracy were satisfactory. The method can be successfully applied to the separation, preconcentration and determination of lead in real samples.

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