


Article

Preconcentration of Pb with Aminosilanized Fe₃O₄ Nanopowders in Environmental Water Followed by Electrothermal Atomic Absorption Spectrometric Determination

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Abstract: A new preconcentration method to determine lead in environmental waters using the aminosilanized magnetite Fe₃O₄ powder sorbent has been developed. The preconcentration method was combined with electrothermal atomization atomic absorption spectrometry (ETAAS) and a graphite atomizer. Trace amount of sorbent (3 mg) could be applied into the preconcentration of Pb. According to the preconcentration, the detection limits were 14 and 19 pg·mL⁻¹ with bare and aminosilanized Fe₃O₄, respectively. The effect of interferent elements such as Al, Ca, Co, Fe, K, Mg, Na, Ni, and Zn (1000 ng·mL⁻¹ versus Pb 1 ng·mL⁻¹) on the preconcentration of Pb using bare magnetite was evaluated, and some elements (Al, Ni, and Zn) were found to interfere with the Pb preconcentration. The aminosilanized Fe₃O₄ sorbent was found to be effective in eliminating the severe interferences. The enrichment factors were 34 for the preconcentration with aminosilanized Fe₃O₄. The recovery of spiked Pb in the case of the sorbent with aminosilanized Fe₃O₄ was in the range of 75 to 110%. From the analytical data, the preconcentration technique was found to be useful for the determination of trace lead in environmental waters.

Keywords: aminosilanized Fe₃O₄; ETAAS; Pb; preconcentration; environmental sample

1. Introduction

In recent years, the contamination of aquatic systems with toxic heavy metals has become a serious problem. Some heavy metal elements are very toxic, even if at low concentrations, and these metals can accumulate in living bodies, resulting in several diseases and disorders [1]. In particular, Pb(II) is one of the most largely distributed elements in the environment, and it has been regarded as a hazardous heavy metal in the context of environmental risk. Therefore, the analysis and effective recovery of Pb(II) metal in water has been a crucial subject related to the quality of human life [2].

Several analytical techniques, such as electrochemical methods [3], atomic absorption spectrometry [4–6], inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [7], and inductively coupled plasma mass spectrometry (ICP-MS) [8], have been explored for the determination of lead. However, their sensitivity and selectivity are usually insufficient for the direct determination of ultra-trace lead levels in complex samples. To extract the target analyte metals from the sample matrix, and to determine an increase in the metal concentration, preconcentration and separation procedures such as solvent extraction [8], coprecipitation [9], cloud point extraction

(CPE) [10], solid-phase extraction (SPE) [11–13], and magnetic solid-phase extraction (MSPE) have been performed [14,15].

Nowadays, magnetic particles containing maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) are employed as excellent novel adsorbents, owing to their inimitable advantages relative to general micro-size adsorbents; they have strong supermagnetic characters that can match the need of rapid adsorption from large volume water samples by using strong external magnetic parts [16]. Recently, MSPE has been intensively used for environmental analysis at low concentrations. The handling of magnetic sorbents is much simpler in complex multiphase samples with an external magnetic field. Therefore, the advantages of MSPE include its simplicity, low cost, easy handling, and reusability [17].

Although magnetite has high adsorption capacities for metal ions, the adsorption of metals is not selective [18]. Therefore, several metal ions can be adsorbed on the magnetite surface. Consequently, competitive adsorption is obtained for the magnetite adsorbents, and the adsorption percentage is dependent on the difference in the affinities for metal ions on the magnetite surface.

3-Aminopropyl triethoxysilane (APTES) is selected to change the surface of inorganic materials. APTES contains more amino groups with free lone pairs of electrons on nitrogen atoms, indicating that these atoms are suitable sites for effective coordination with metal ions. Recently, Naghizadeh et al. [19] reported magnetic core/shell silica powders decorated with 3-[2-(2-aminoethylamino) ethylamino]propyl-trimethoxysilane (AAAPTS) for Bi and Pb determination by electrothermal atomization atomic absorption spectrometry (ETAAS). Sitko et al. [20] investigated aminosilane modified graphene oxide sheets for selective Pb preconcentration followed by ultrasensitive ETAAS determination. Li et al. [21] studied the adsorption of Pb in water with common reed ash-derived silica decorated with amino-silanes. Kheshtzar et al. [22] described the fabrication of a smart aminosilane modified- SnO_2 /porous silica composite for the purpose of better Pb removal efficiency and the inactivation of bacteria. However, there is little information on the determination of Pb by ETAAS combined with the preconcentration method using amino-silane modified magnetite.

The present work deals mainly with the preconcentration of Pb in environmental waters using aminosilane modified iron oxide magnetite followed by ETAAS determination. The trace amount of sorbent (3 mg) for sorption was applied into the preconcentration. The developed technique has the advantages of simplicity, rapid results, and low cost.

2. Materials and Methods

2.1. Materials

Magnetic iron oxide powders (Fe_3O_4 , diameter: 50–100 nm, surface area: $>60 \text{ m}^2\cdot\text{g}^{-1}$) were purchased from Sigma-Aldrich. The aminosilane chemical, (3-aminopropyl) triethoxysilane (APTES, 99%), was obtained from Shin-Etsu Chemical Co., Ltd. The lead stock solution ($1 \text{ mg}\cdot\text{mL}^{-1}$ of Pb) was purchased from FUJIFILM Wako Pure Chemical Corp. All of the chemical reagents, which were analytical grade, were used without further purification.

2.2. Preparation of Aminosilane Modified Fe_3O_4 Magnetite

The aminosilane modified Fe_3O_4 was fabricated by the surface functionalization method. First, the suspension of 1.0 g of magnetite Fe_3O_4 in 300 mL ethanol was sonicated for 1 h. After the addition of APTES (10 mL), the mixture was heated at 70°C for 4 h using a hot stirrer. The resulting solid product was magnetically collected, and washed with ethanol and water for the removal of residual APTES. Finally, the prepared aminosilane modified Fe_3O_4 was dried at 60°C under vacuum for 12 h.

2.3. Characterization

The X-ray diffraction (XRD, RIGAKU Ultima IV, sample horizontal type) with powder type was employed so as to record the diffraction patterns of samples using $\text{Cu K}\alpha$ radiation. A Hitachi S-4000 scanning electron microscope (SEM) was employed to observe the morphologies of the samples.

The Fourier transform infrared (FT-IR) spectrum was observed with a PerkinElmer Spectrum 100 with the universal attenuated total reflection (ATR) accessory. A pH/DO METER D-55 (HORIBA) was used for pH measurement.

2.4. Magnetic Solid-Phase Extraction Procedure

The initial pH of the solution (100 mL) was adjusted to 5 using $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ and $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaOH}$. Then, $100 \text{ }\mu\text{L}$ of the sorbent suspension ($30 \text{ mg}\cdot\text{mL}^{-1}$) was added into the sample solution, and the sorbent nanopowders were dispersed by magnetic stirring for 5 min. Next, the magnetic sorbent was magnetically removed from the sample solution using a powerful magnet. After the decantation of the supernatant solution, the obtained sorbent was washed with 1.0 mL of $0.3 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ solution so as to desorb the Pb ions under ultrasonic irradiation using an ultrasonic cleaner (SIBATA SCIENTIFIC TECHNOLOGY Ltd., SUP-10, 100 W). The Pb-concentrated solution was obtained by the removal of sorbents with a powerful magnet. The measurement for lead determination was performed with an AA-7000 (SHIMAZU) equipped with an electrothermal graphite atomizer, an autosampler, and D_2 lamp background correction. A Pb hollow cathode lamp was employed for the absorbance measurements at a wavelength of 283.3 nm. Argon was used as a sheathing gas, and the internal Ar gas flow in the graphite atomizer was interrupted in the atomization step. The furnace temperature program is presented in Table S1 in the Supplementary Material. The calibration curves were prepared by performing all of the preconcentration procedures using the standard Pb solution. The analytical data were the average values obtained with more than three samples.

For the optimization and interference studies, the preconcentration method using a Pb standard solution (1 or $0.3 \text{ ng}\cdot\text{mL}^{-1}$) was performed in the same manner as described above.

3. Results and Discussion

3.1. Acquisition of Base Data

First, in order to obtain the base data for the preconcentration of lead, the sorption of lead in the solution by the magnetite Fe_3O_4 was investigated. Therefore, the effect of the solution pH, sorption time (stirring time), ultrasonic irradiation, and sorbent amount on the enrichment factor for lead with magnetite Fe_3O_4 was explored. The enrichment factor is defined as the Pb concentration in the final solution after the preconcentration divided by the initial Pb concentration in the solution before the preconcentration.

The pH of the solution seems to become one of the predominant factors for the sorption of metal ions. The influence of pH on the enrichment factor was studied, in the range between 3 and 8, while keeping the other parameters constant. The solution was magnetically stirred during the sorption process. The effect of pH on the sorption of Pb ions is shown in Figure 1. These results show that the enrichment factor increased with increasing the pH value from 3 to 5, and the maximum value was observed at pH 5. When the pH was further increased from 5 to 8, the enrichment factor decreased. In the range of pH 1–7, the dominant lead chemical species are Pb^{2+} . However, the protons in acid solution can protonate binding points of the chelating molecules onto the magnetite Fe_3O_4 surface. It was reported in a previous study [23] that the point of zero charge for magnetite Fe_3O_4 is pH of 7.9. The positive charges generated on the magnetite Fe_3O_4 result in electrostatic repulsion. However, because the lead species of PbOH^+ appear from pH 6, the electrostatic repulsion becomes more weak upon increasing the pH from 3 to 5. On the other hand, the lead ions start to form a precipitate at pH 8–11, depending on the initial metal concentration. Therefore, the ion exchange mechanism may be responsible for the sorption of Pb ion onto the magnetite Fe_3O_4 . Consequently, pH 5 was selected as the optimal pH for all subsequent experiments.

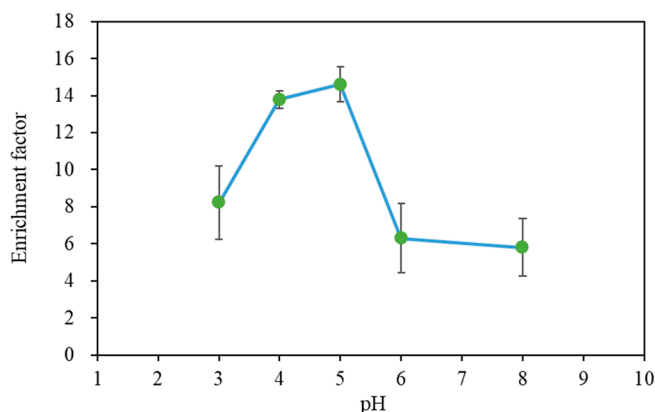


Figure 1. Effect of pH on the enrichment factor for Pb with magnetite Fe_3O_4 . Sample: Pb $1 \text{ ng}\cdot\text{mL}^{-1}$, 100 mL; sorption time (magnetic stirring time): 30 min; magnetic stirring desorption: $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ 1 mL.

The effect of the sorbent amount on the enrichment factors was investigated. The results are shown in Figure S1. With increasing the amount up to 3 mg, the enrichment efficiencies increased, after which the efficiencies reached a plateau. Hence, the sorbent amount of 3 mg was used as the optimal amount.

The stirring time can affect the efficiency of the preconcentration of Pb. Hence, the magnetic stirring time (5 to 30 min) for the solution was investigated for the sorption of Pb onto magnetite Fe_3O_4 nanopowders (Figure 2). The results show that the enrichment factor became almost constant from 5 to 30 min sorption time. It can be pointed out that the sorption process is very quick for the preconcentration of Pb ion. Therefore, the magnetic stirring time (sorption time) of 5 min was employed in all subsequent experiments.

Next, the effect of ultrasonic desorption on the enrichment factor of Pb was studied. The enrichment factor (23.1 times) obtained with ultrasonic irradiation during the desorption was better relative to that obtained with magnetic stirring (15.6 times). As a consequence, ultrasonic irradiation was selected for the desorption process.

The effect of the type and concentration of eluent (desorption agent) on the enrichment factor of Pb(II) was investigated (Figure 3). Nitric acid with $1.0 \text{ mol}\cdot\text{L}^{-1}$ was optimal. As the acid concentration increases, the enrichment factor may increase. However, a high acid concentration can cause damage to the graphite furnace. Hence, 1 mL of $0.3 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ was used in subsequent experiments.

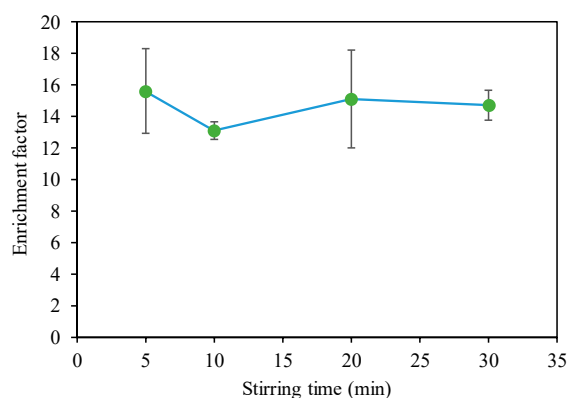


Figure 2. Effect of the magnetic stirring time (sorption time) on the enrichment factor for Pb with magnetite Fe_3O_4 . Sample: Pb $1 \text{ ng}\cdot\text{mL}^{-1}$, 100 mL; pH: 5; magnetic stirring desorption: $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ 1 mL.

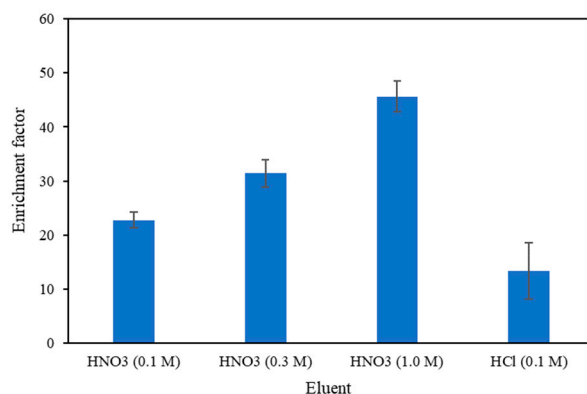


Figure 3. Effect of the desorption agent on the enrichment factor for Pb with magnetite Fe_3O_4 . Sample: Pb $1 \text{ ng}\cdot\text{mL}^{-1}$, 100 mL; pH: 5; sorption time (magnetic stirring time): 5 min; desorption: ultrasound; eluent volume: 1 mL.

3.2. Characterization of Aminosilanized Magnetite Fe_3O_4

So as to confirm the surface morphology and conditions for aminosilanized Fe_3O_4 , the morphology was characterized by SEM images, XRD, and FT-IR. The SEM images at different magnifications show that the diameter of the magnetic particles was around 50 to 150 nm, as shown in Figure 4. The particle size distribution for aminosilanized Fe_3O_4 is illustrated in Figure S2. The crystalline structure of the nanoparticles was identified with XRD (Figure 5). The diffraction peaks at $2\theta = 30.1, 35.5, 43.1, 53.4, 56.9, 62.6,$ and 73.9 corresponded to the (2 2 0), (3 1 1), (4 0 0), (4 2 0), (5 1 1), (4 4 0), and (5 3 3) planes of the cubic inverse spinel structure lattice of the magnetite (Fe_3O_4). The results are in accord with the standard XRD pattern of Fe_3O_4 (JCPDS Card No.82-1533). The same sets of characteristic peaks were also obtained for aminosilanized Fe_3O_4 , indicating the good stability of the crystalline phase of Fe_3O_4 . The results suggest that the modification of amino silanization could scarcely cause changes in the phase of Fe_3O_4 . The aminosilanized Fe_3O_4 was evaluated by FT-IR analysis, as shown in Figure S3 in the Supplementary Material.

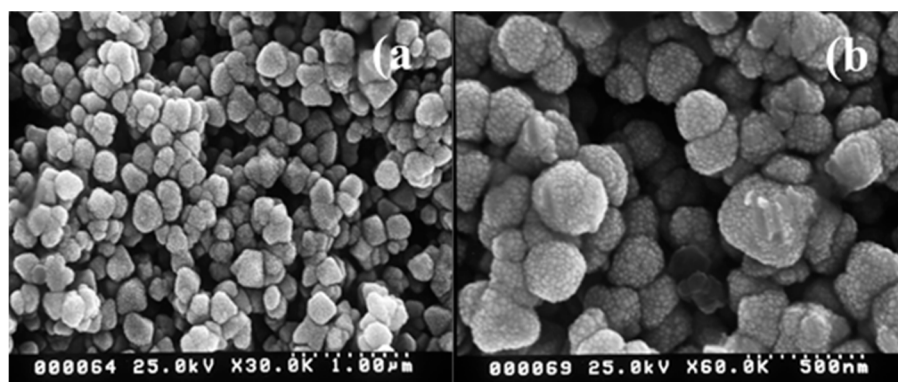


Figure 4. SEM images of aminosilanized Fe_3O_4 with magnifications of (a) 30,000 \times and (b) 60,000 \times .

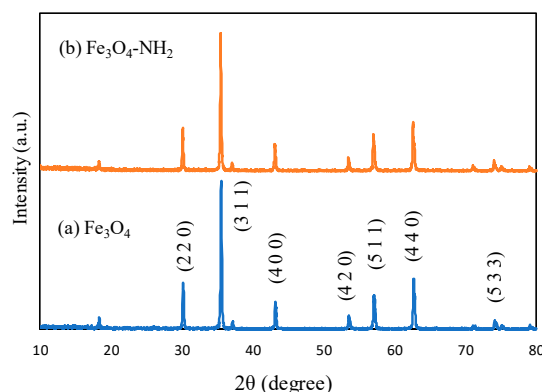


Figure 5. X-ray diffraction (XRD) pattern of (a) bare Fe_3O_4 and (b) aminosilanzed Fe_3O_4 .

3.3. Effect of Coexisting Elements

Interference problems with coexisting elements on the determination of Pb in environmental samples by ETAAS have been described [24]. For the interference study of Pb, elements contained in the environmental samples, such as Al, Ca, Co, Fe, K, Mg, Na, Ni, and Zn ($1000 \text{ ng}\cdot\text{mL}^{-1}$ for Pb $1 \text{ ng}\cdot\text{mL}^{-1}$), were selected. First, the effect of these matrix elements on the preconcentration of Pb was studied with magnetite Fe_3O_4 . The results are shown in Figure 6. Some elements, such as Al, Ni, and Zn, affected the enrichment factor for Pb. When the matrix element concentrations were reduced down to approximately 100 fold for Pb, only small interference was perceivable.

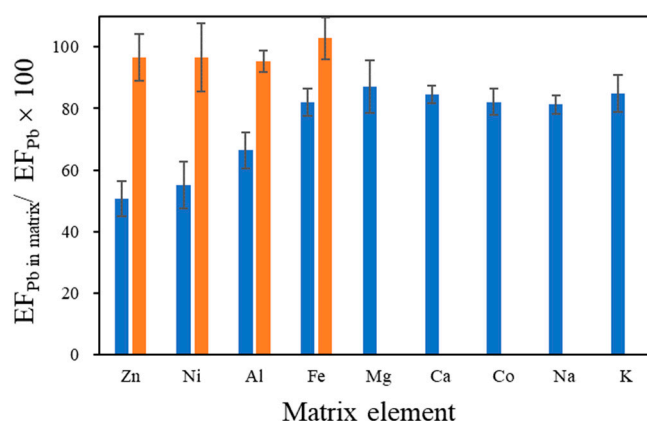


Figure 6. Interference by coexisting elements on the preconcentration of Pb with bare Fe_3O_4 . Sample: Pb $1 \text{ ng}\cdot\text{mL}^{-1}$, 100 mL ; matrix element; $1000 \text{ ng}\cdot\text{mL}^{-1}$ for all elements (blue) and $100 \text{ ng}\cdot\text{mL}^{-1}$ for Al, Ni and Zn (orange); pH: 5; sorption time (magnetic stirring time): 5 min; ultrasonic desorption agent: 1 mL of $0.3 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$.

Because more severe interferences could be observed in the presence of coexisting element concentration was large (about 1000 fold), the aminosilanzed Fe_3O_4 was applied into the sorbent for the preconcentration of Pb. The results are illustrated in Figure 7. The enrichment factor with aminosilanzed Fe_3O_4 (24 times) was smaller relative to that obtained with the bare magnetite version (33 times). However, all of the elements were found to barely affect the preconcentration of Pb in the aqueous solution. Consequently, it could be speculated that the effect of many interfering metals with large concentrations ($>3.3 \times 10^3$ fold) could be eliminated by using the aminosilanzed magnetite Fe_3O_4 as the sorbent.

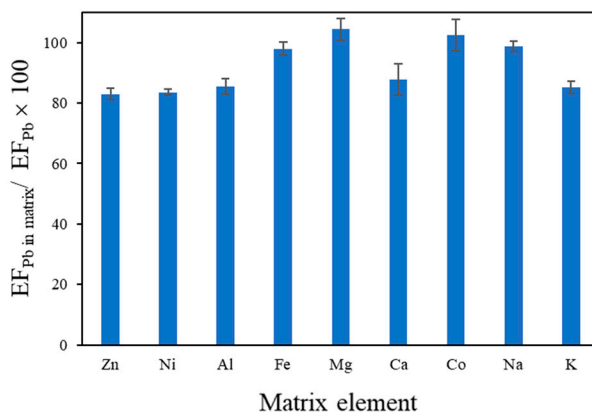


Figure 7. Interference by coexisting elements on the preconcentration of Pb with aminosilanzed Fe₃O₄. Sample: Pb 0.3 ng·mL⁻¹, 100 mL; matrix element; 1000 ng·mL⁻¹ for all elements; pH: 5; sorption time (magnetic stirring time): 5 min; ultrasonic desorption agent: 1 mL of 0.3 mol·L⁻¹ HNO₃.

3.4. Analytical Performance

The analytical performances, such as the enrichment factor, detection limit, and dynamic (linear) range (DR), were investigated with bare and aminosilanzed Fe₃O₄ as the sorbent. The enrichment factor was 34 for the preconcentration with aminosilanzed Fe₃O₄. The detection limits, which are defined as 3Sd(blank)/m, where Sd is the standard deviation of the blank measurement and m is the slope of the calibration curve, were 14 and 19 pg·mL⁻¹ with bare and aminosilanzed Fe₃O₄, respectively. The obtained dynamic ranges were 2.5 ng·mL⁻¹ and 3 ng·mL⁻¹ with bare and aminosilanzed Fe₃O₄, respectively. Although the value obtained with aminosilanzed Fe₃O₄ was inferior compared with the detection limit obtained with the bare version, the effect of the matrix elements with the aminosilanzed Fe₃O₄ preconcentration was negligible, constituting a significant advantage. In the present work, the optimum conditions for aminosilanzed Fe₃O₄ were scarcely changed relative to those of the bare version because the detection limits were similar. However, a thorough exploration of suitable conditions for aminosilanzed magnetite was not performed.

Also, reproducibility in the case of the preconcentration of Pb with aminosilanzed Fe₃O₄ was investigated. The relative standard deviation (RSD) in the case of the aqueous 0.3 ng·mL⁻¹ Pb solution was only 12% for six preconcentration treatments. Since the desorption could be fully completed by using the eluent of 1 M HNO₃, the sorption efficiency was estimated as about 45%. The capacity of Pb was evaluated to be 0.3 mg·g⁻¹ (sorbent).

3.5. Comparison with Other Techniques

A figure of merit for the developed method was compared to other techniques described for the preconcentration of Pb in environmental samples (Table 1). The developed method has the advantages of (1) easy magnetic separation, (2) a trace amount of sorbent (3 mg), and (3) free interference. As seen from the data in this table, the outstanding features of the developed extraction technique could be comparable to or better than previously reported preconcentration methods.

3.6. Determination of Pb in Environmental Samples

The developed preconcentration techniques were applied to the determination of Pb in environmental water samples. The analyzed samples were spiked with 100–500 pg·mL⁻¹ Pb to evaluate the recovery in the spiked samples. The analytical results obtained from the samples are presented in Table 2. The recovery range for the spiked samples was 75 to 110%. The relative standard deviations (RSDs) were better than 14% for three replicate analyses.

Table 1. Comparison of the present method with the other methods.

Method	Sample Volume (mL)	Detection Limit (pg·mL ⁻¹)	Reference
SPE	100	110	[25]
HF-LLSMET	20	7	[26]
MC-ICPOES	3	1130	[27]
MSPE-ETAAS	25	3.7	[19]
GO-ETAAS	50	12	[20]
Fe ₃ O ₄ -ETAAS	50	0.8	[28]
Fe ₃ O ₄ /HKUST-FAAS	200	800	[29]
This work	100	14	

SPE: solid phase extraction. HF-LLSMET: Hollow fiber liquid-liquid solid micro extraction. MC-ICPOES: Microcolumn ICP optical emission spectrometry. MSPE-ETAAS: Magnetic solid-phase extraction-ETAAS. GO-ETAAS: Aminosilanized Graphene oxide adsorption preconcentration-ETAAS. Fe₃O₄-ETAAS: Fe₃O₄ nanoparticle adsorption preconcentration-ETAAS. Fe₃O₄-FAAS: Functionalized magnetite nanoparticles-FAAS.

Table 2. Determination of Pb in the environmental samples (n = 3).

Sorbent	Sample	Concentration of Pb (ng·mL ⁻¹)		
		Add	Found	Recovery (%)
Fe ₃ O ₄	Tap water	-	n.d.	
		0.3	0.33 ± 0.01	110
	Mineral water	-	n.d.	
		0.3	0.32 ± 0.01	106
	Ground water	-	n.d.	
		0.3	0.33 ± 0.01	110
NH ₂ -Fe ₃ O ₄	Mineral water	-	n.d.	
		0.1	0.075 ± 0.010	75
		0.5	0.50 ± 0.03	101

n.d.: not detected.

4. Conclusions

Fe₃O₄ was successfully coated with 3-aminopropyltriethoxysilane as an organic shell via a simple one-pot method. Characterization methods including SEM, XRD, and FT-IR revealed that the structure of Fe₃O₄ was hardly changed after the amino-functionalization. The figures of merit for the present sorbents include some advantages such as the need for only a trace sorbent amount, fast sorption, and easy separation after the sorption reaction by an external magnet. In combination with ETAAS, the preconcentration technique with aminosilanized Fe₃O₄ sorbent can be useful for the determination of lead in environmental water samples. Therefore, aminosilanized Fe₃O₄ can be regarded as a potential candidate for a highly efficient and renewable sorbent for Pb.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2305-7084/3/3/74/s1>, Table S1: Furnace heating program for electrothermal atomic absorption spectrometry, Figure S1. Effect of sorbent amount on the enrichment factor for Pb with magnetite Fe₃O₄. Sample: Pb 1 ng·mL⁻¹, 100 mL; pH: 5; magnetic stirring desorption: 0.1 mol·L⁻¹ HNO₃ 1 mL. Figure S2: FT-IR spectra of (a) bare Fe₃O₄ and (b) aminosilanized Fe₃O₄ (Fe₃O₄-NH₂).

Author Contributions: T.K. and S.K. conceived and designed the experiments. T.K. performed the experiments and wrote the paper. I.T., M.F., and H.K. analyzed the results and advised the project.

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Notes: All experiments were conducted at Mie University. Any opinions, findings, conclusions, or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

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