

Solid Phase Extraction Trace Lead using Amberlite XAD-2000 Resins prior to Determination by Flame Atomic Absorption Spectrometry

LI Qingbin^{1,2+}, CAO Yunli¹ and CHENG Yonghua¹

¹ School of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan, 467000, Henan, China

² Laboratory of Special Ceramics and Powder Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

Abstract. A method for the determination of the trace lead(II) in aqueous by flame atomic absorption spectrometry with solid phase extraction using Amberlite XAD-2000 resins was proposed. Resins life and the effects of various parameters such as pH, type and concentration of eluent, volume of eluent and sample, flow rate of sample and eluent, coexisting ingredients were studied. Under the optimum conditions, the capacity of the adsorbent for lead was 7.2 mg g⁻¹ and the recovery from the resin was 92%. The preconcentration factor was calculated as 100. The detection limit by three sigma was 3.0 µg L⁻¹(n=10). The presented procedure was applied to the determination of trace lead in tap, phreatic and river water with successfully results.

Keywords: lead, trace, Amberlite XAD-2000, solid phase extraction, flame atomic absorption spectrometry.

1. Introduction

Lead is an unquestionable toxicity which can cause various diseases in humans and animals^[1, 2]. Therefore, the determination of trace lead is a very important part of environment protection, food safety, sewage disposal, and so on. Flame atomic absorption spectrometry(FAAS) is a relatively simple and available technique for lead determination, but it often suffers from its low sensitivity^[3, 4]. Preconcentration, such as ion-exchange^[5], co-deposition^[6] and extraction^[7, 8], is absolutely necessary for lead determination by FAAS. However, these traditional enrichment methods lead to secondary pollution or need long time. In recently years, solid phase extraction (SPE)^[9] is paid much attention to for its simplicity, high efficiency and ability of extracting quantitatively. More and more researchers^[10-12] preconcentrate heavy metals in aqueous by this way.

Due to their porosity, void ratio, uniformity, high surface area and good sorption to non-polar compounds^[13], Amberlite XAD resins are nice supports for columns used in SPE. Amberlite XAD-2000, as a kind of Amberlite XAD resins, is seldom reported in literatures.

This paper proposed a method to determine lead by FAAS after SPE trace lead in aqueous using Amberlite XAD-2000.

2. Experimental

2.1. Regents and Solutions

GBW 08619 (1 000mg L⁻¹) and GBW 08608 were produced by Chemistry Department of national institute of Metrology. GBW (E) 080040 was a product of the Second Institute of Oceanography. Nitric acid,

⁺ Corresponding author. Tel.: + 86 375 2657698; fax: +86 375 2077298.
E-mail address: lqbUSTB@163.COM.

hydrochloric acid, sulphuric acid, acetone and ethanol are guaranteed reagents. Other chemicals are analytical reagents. The solution of 8-hydroxyquinoline (8-HQ) was prepared by dissolving 0.1 g 8-HQ in 100 mL ethanol. Na₂SO₄-NaHSO₄ buffer (pH 2), HAC-NH₄Ac buffer (pH 4-6), NH₃-NH₄Cl buffer (pH 8-10) and NaOH-Na₂HPO₄ buffer (pH 12) were made by us. All solutions were prepared in distilled water. Amberlite XAD-2000 resins (180-250 µm) were washed orderly by 4.0 mol L⁻¹ HCl, distilled water, 1.0 mol L⁻¹ NaOH and 10 mL methanol and then dried naturally.

2.2. Instruments

A WFX-1F2B atomic absorption spectrometer with deuterium background corrector was used in this study. An air-acetylene flame and ISIS flow injection equipment were used too. The FAAS worked at 217.0 nm wavelength, 0.8 nm slit, 7.0 mA lamp current and 1.5/10.5 combustion-supporting ratio. The measure mode was apex with D lamp correcting baseline. A PHS-3CT pH meter with a combined glass electrode was employed for pH measurements. All glassware were dip in 5% HNO₃ and washed by distilled water before use.

2.3. Column Preparation

Amberlite XAD-2000 resins were screened for 180-250 µm, weighed 250 mg, filled to a glass mini column (Φ10 mm × 100 mm) with a coarse sintered-glassed disc and stopcock at the bottom. Then, the resin in the column was washed with 1.0 mol L⁻¹ NaOH, distilled water, 1.0 mol L⁻¹ HNO₃, distilled water, acetone, distilled water in turn. After each use, the resin was washed thoroughly by distilled water, 1.0 mol L⁻¹ HNO₃ and distilled water. Then the resin was soaked in distilled water for next use. Before preconcentration, it was conditioned to the studied pH by passing a buffer solution having the same pH as that of sample solution through the column.

2.4. Sample Disposal and Preconcentration

Water samples were acidified with nitric acid, filtrated by a nitrocellulose membrane with 0.45 µm pores. The pH was adjusted according to the method given above with buffer. Then the column was injected 5.0 mL 8-HQ solutions at speed of 10.0 mL min⁻¹, injected 50 mL lead aqueous (with 50 µg Pb (II)) or 1 000 mL real water sample. After two minutes without drop dripping, the column was washed by 5.0 mL buffers three times to remove dissociative lead ions. The adsorbed lead ions were eluted with 7.5 mL 2.0 mol L⁻¹ HNO₃ in acetone solutions. The eluate was heated at about 40°C until near to dryness. The remainder was irrigated with 10.0 mL 1.0 mol L⁻¹ HNO₃ and transferred to 10.0 mL volumetric flask. This solution was determined the lead by FAAS.

3. Results and Discussion

3.1. Effect of pH

Studies^[14-16] about SPE have shown than the pH plays an important role in the preconcentration procedure. In order to estimate the influence of pH on recoveries, solutions were adjusted to a pH range of 2-12 and processed as the procedure given above. Results had shown that the maximum recovery was obtained at pH 10.0 and the recoveries were above 90% when the pH was in the range of 7.0-10.0. Thus, the pH of the sample solutions was adjusted at 10.0 on the subsequent works or not adjusted in real works if it was between 7.0 and 10.0.

3.2. Selection of Elution Reagent and its Concentration

The other important parameters that affected the recovery are the elution reagent and its concentration. As can be seen from Tab. 1, retention of lead on the column was considerably low under acid conditions. In this work, the different concentrations of nitric acid and hydrochloric acid in acetone, ethanol and water were used as eluent. According to the obtained experimental results as table 1, the solution of 2.0 mol L⁻¹ HNO₃ in acetone was chosen as eluent.

Tab. 1: Effect of eluent type and concentration on recovery

| Eluent type | Recovery(%) |
|-------------|-------------|
|-------------|-------------|

| | |
|---|----|
| 1.0 mol L ⁻¹ HCl in acetone | 91 |
| 0.5 mol L ⁻¹ HNO ₃ in acetone | 95 |
| 1.0 mol L ⁻¹ HNO ₃ in acetone | 96 |
| 2.0 mol L ⁻¹ HNO ₃ in acetone | 97 |
| 4.0 mol L ⁻¹ HNO ₃ in acetone | 93 |
| 1.0 mol L ⁻¹ HNO ₃ in ethanol | 79 |
| 1.0 mol L ⁻¹ HCl in ethanol | 79 |
| 1.0 mol L ⁻¹ HCl | 85 |
| 4.0 mol L ⁻¹ HCl | 83 |
| 1.0 mol L ⁻¹ HNO ₃ | 86 |
| 4.0 mol L ⁻¹ HNO ₃ | 71 |

3.3. Flow Rate of the Eluent and Sample

It is necessary to require the preconcentration procedure in short time. So the best way to shorten time of this process is increasing flow rate of the eluent and sample. But the successfully adsorption and desorption procedures all need indispensable times. The effect of eluent's flow rate on recovery was studied with the range of 1.0-35.0 mL min⁻¹. Under 10.0 mL min⁻¹, leads were efficiently eluted from the column. So, an eluent's flow rate of 10.0 mL min⁻¹ was selected.

In real analysis process, the sample volume is so huge that sample's complete adsorption spends a large proportion of preconcentration times. In this work, 50.0 mL solution was loaded on the column at different flow rates from 1.0 to 35.0 mL min⁻¹. The results shown that the recoveries seldom changed when the flow rate was in the range of 1.0-17.5 mL min⁻¹ and the recoveries decreased quickly when the flow rate was above 17.5 mL min⁻¹. Therefore, we selected 10.0 mL min⁻¹ as sample's flow rate on the subsequent works.

3.4. Volume of the Eluent and Sample

The volume of the eluent affected recovery of lead evidently. We have studied the recoveries changed with the eluent's volume was within the range of 2.5-20.0 mL. The results are given in Tab. 2. Thus, the eluent's volume was 7.5 mL on the follows works.

Tab. 2: Effect of eluent's volume on the recovery

| | | | | | | |
|----------------------|-----|-----|-----|------|------|------|
| Eluent's volume (mL) | 2.5 | 5.0 | 7.5 | 10.0 | 15.0 | 20.0 |
| Recovery (%) | 78 | 89 | 93 | 93 | 94 | 93 |

Breakthrough volume is a main parameter for obtaining high preconcentration factors. In order to achieve a high enrichment factor for sample with trace lead, the effect of the sample volume on the recovery was studied by passing through 50-1500 mL sample containing 50 µg Pb(II) through the column. The results showed that quantitative extraction of lead ions (>90%) were obtained up to 1000 mL sample. The recovery decreased when the sample volume was above 1000 mL. Thus the sample volume was selected as 1000 mL and the preconcentration factor was calculated as 100.

3.5. Effect of Coexisting Ingredients

In real samples, the trace lead always coexists with other ingredients. In order to studies the effect of these matrix ions, the recoveries were tested after adding possible salts to 1.0 mg L⁻¹ lead solutions. As can be seen from Tab. 3, the recoveries were still more than 90% when foreign ions was added, Also, no interference was detected on the recovery of lead ions when coexisting ions were 2.5 mg L⁻¹ of Al(III), Bi(III), Cr(III), Sb(III), Sn(IV), Se(IV), V(V) ions in solutions. This result demonstrates that the proposed method can be applied perfectly for lead determination in sea water samples.

Tab. 3: Effect of salts on the recovery

| Ions | Salt | Conc(mg L ⁻¹) | Recovery(%) |
|---------|----------|---------------------------|-------------|
| Ca (II) | Chloride | 1 000 | 93 |
| K (I) | Chloride | 1 000 | 90 |
| Mg(II) | Chloride | 1 000 | 91 |
| Na (I) | Chloride | 10 000 | 92 |
| Ca (II) | Nitrate | 1 000 | 93 |

| | | | |
|--------------------|---------|--------|----|
| K (I) | Nitrate | 1 000 | 91 |
| Mg(II) | Nitrate | 1 000 | 93 |
| Na (I) | Nitrate | 10 000 | 92 |
| Mixed ^a | - | 2.5 | 91 |

^a 2.5 mg L⁻¹ of Al(III), Bi(III), Cr(III), Sb(III), Sn(IV), Se(IV), V(V) ions.

250 µg other heavy metal was individually added to 50 mL solution (50 µg lead) and enriched by given method. The results are described in Tab. 4. The results showed that the recovery of lead in trace was not affected by the metals with high concentration.

Tab. 4: Effect of heavy metal ions on the recovery

| Intruder | Cd(II) | Co(II) | Cu(II) | Fe(II) | Mn(II) | Ni(II) | Zn(II) | mixed ions ^a |
|-------------|----------|----------|----------|----------|----------|----------|----------|-------------------------|
| Recovery(%) | 92 | 92 | 90 | 91 | 90 | 93 | 91 | 90 |

^a mixed ions: 250 µg of Cu(II), Fe(II), Mn(II), Zn(II) ions.

3.6. Lifetime and Adsorption Capacity of Resins

The adsorption capacity is the maximum lead taken up by 1.0 g of resin and given by milligram of lead per gram resin. In this study, 50 -10 000 µg Pb(II) was loaded on the 250 mg resins. After that, Langmuir isotherms were plotted. According to the gradient and intercept of Langmuir isotherm, the adsorption capacity of Amberlite XAD-2000 resin to lead was calculated as 7.2 mg g⁻¹. Under the selected conditions, 250 mg resins can be used 150 -200 times in this study.

3.7. Analytical performance and application of the method for real water sample

With the optimized parameters described above, the determination procedure was applied to GBW 08608, GBW(E) 080040 and real water sample of tap, phreatic and river water. The results reflect the suitability of the method for determination of lead in trace level and are listed in Tab. 5.

Tab. 5: Analytical performance and application of the method for real water sample

| Sample | Certified value (µg L ⁻¹) | Measured value (µg L ⁻¹) | RSD (%, n=3) | Adding value (µg L ⁻¹) | Measured value (µg L ⁻¹) | Recovery (%) |
|----------------|--|---|-----------------|---------------------------------------|---|-----------------|
| GBW 08608 | 50 ± 1 | 47.60 | 2.8 | 20.00 | 63.12 | 93 |
| GBW(E) 080040 | 10.0 ± 0.6 | 9.51 | 2.9 | 5.00 | 13.57 | 94 |
| Tap water | - | - | - | 5.00 | 4.66 | - |
| Phreatic water | - | 3.55 | 2.4 | 5.00 | 7.98 | 93 |
| River water | - | 5.10 | 2.4 | 5.00 | 9.42 | 93 |

4. Conclusions

This SPE using Amberlite XAD-2000 resins is a simple, economic, sensitive and accurate technique to enrich trace lead in aqueous prior to determine. In optimum conditions, the recovery was as high as 94% and the preconcentration factor was calculated as 100. The adsorption capacity was 7.2 mg g⁻¹. The support of SPE, 250 mg resins, can be used 150 -200 times. Moreover, with the anti-interfering ability to coexisting ingredients, this method is economic and possible to determine the lead in aqueous in environment even can be used to analyze the sea water sample.

5. References

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