

Determination of Trace Heavy Metal Ions by Flame Atomic Absorption Spectrometry after Preconcentration with Manual-Controlled Injection Nano-Calcium Titanate Enricher

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(Received: 11 October 2010;

Accepted: 20 July 2011)

AJC-10165

A new method has been developed for the determination of trace lead, cadmium, zinc, nickel and silver ions based on separation and preconcentration with a manual-controlled injection nano-calcium titanate enricher (MINTE) prior to their determination by flame atomic absorption spectrometry. The optimum experimental parameters for preconcentration of the heavy metals studied, such as pH, flow rate and volume, eluent and interfering ions, have been investigated. The results showed that all the heavy metals studied could be quantitatively retained by MINTE in the pH range of 5-9 and then eluted completely with 2 mol L⁻¹ HNO₃. The detection limits of this method for lead, cadmium, zinc, nickel and silver ions were 32, 5, 4.1, 9.4 and 7 ng L⁻¹, respectively. The method has been applied to the simultaneous determination of trace amounts of lead, cadmium, zinc, nickel and silver ions in water samples with satisfactory results.

Key Words: Nano-calcium titanate, Manual-controlled injection enricher, Pre-concentration, Heavy ion, Flame atomic absorption spectrometry.

INTRODUCTION

At present, determination methods of trace heavy metal in food, biological and environmental samples mainly included spectrophotometry, atomic absorption method and inductively-coupled plasma spectrometry (ICP)¹. However, it is difficult to directly determine extremely low concentrations of the required trace elements by these methods without pre-separation and enrichment. The limitations are associated not only with the insufficient sensitivity of these techniques but also with matrix interference. For this reason, preliminary separation and preconcentration of trace elements from matrix is often required. The most widely used techniques for the separation and preconcentration of trace elements include liquid-liquid extraction^{2,3}, ionic liquid preconcentration^{4,5}, coprecipitation^{6,7}, ion-exchange⁸, micelle-mediated extraction⁹, cloud point extraction¹⁰ and solid-phase extraction¹¹⁻¹⁸. Recently, with the development of nano-science and technology, nano-adsorption agents, as a new solid-phase extractant, have been successfully applied in separation and enrichment¹⁹⁻²⁶. Studies had ever used nano-barium strontium titanate in the adsorption of heavy metals in water for the first time²⁷⁻³². However, since nano-barium strontium titanate powder is too costly, this restricts its application in practice. Compared with nano-barium strontium titanate powder, nano-calcium titanate powder is low-cost for preparing sources and high ability of adsorption

for heavy metal ions³³. From the point of the separation and preconcentration procedures, people often use a batch adsorption method and centrifuge or the method based on the flow-injection (FI) system. These are discommodious and can not be operated on scene. On the other hand, although the static adsorption behaviour of nano-calcium titanate powder for lead and cadmium ion have been studied, up to now, no systematic data on the adsorption characteristics under dynamic condition has been investigated. The aim of this work is to prepare a manual-controlled injection nano-calcium titanate enricher (MINTE) which is convenient to enrichment on scene, study adsorption characteristics of some metal ions on this enricher under dynamic condition and optimize the conditions for the simultaneous preconcentration of trace heavy metal. A new method for enrichment and determination of trace lead, cadmium, zinc, nickel and silver ion in water sample was proposed.

EXPERIMENTAL

A TAS-990AFG atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.), equipped with hollow cathode lamps for lead, cadmium, zinc, nickel and silver as well as a deuterium lamp for background correction, was used. The operating conditions were adjusted according to the Manufacturer's recommendations. The pH values were measured with a PHS-3C acidometer (Shanghai REX Instrument

Factory, Shanghai, China) supplied with a combined electrode. Injector for medical purpose (50 mL), A self-made PTFE microcolumn (60 mm × 5 mm i.d.), fiber glass wool.

Standard solution and reagents: Stock solutions of Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Ag^{+} were prepared by dissolving each metal (purity > 99.99 %) in the minimum amount of 1 + 1 nitric acid separately and diluting the solution to 1000 mL with 1 % nitric acid. Working standard solutions were obtained by appropriate dilution of the stock solutions.

Nano-calcium titanate powder was prepared by a citric acid complex sol-gel method in our laboratory as previously described elsewhere³³.

All reagents used were of spectra or highest purity reagent grade. Doubly quartz sub-boiling distilled water was used throughout.

Manual-controlled injection enricher preparation: Manual-controlled injection nano-calcium titanate enricher (MINTE) is made of a injector for medical purpose (50 mL) and a PTFE microcolumn (60 mm × 5 mm i.d.) packed with nanometer calcium titanate supported by fiber glass wool.

A total of 500 mg of nanometer CaTiO_3 powder was imposed on a glass fiber filter by dipping it into a CaTiO_3 powder water suspension for 10 min and then calcinating at 120 °C for 1 h. After that, this glass fiber was rolled into columned and was filled into the PTFE microcolumn plugged with a small portion of glasswool at both end. Before use, 50 mL of 2 mol L^{-1} HNO_3 solution was passed through the column in order to clean and washed it to neutral with water. The schematic illustration of MINTE is shown in Fig. 1.

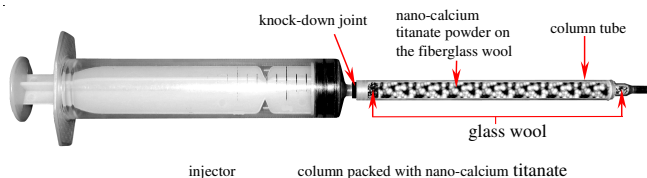


Fig. 1. Schematic illustration of MINTE

General procedure: A portion of aqueous sample solution containing Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Ag^{+} were prepared and the pH value was adjusted to the desired value with HNO_3 and ammonia. The solution was passed through the column by using the injector for medical purpose adjusted to the desired flow rate, then the 20 mL water was passed through the column to washing. Afterwards, indraft 2.0 mol L^{-1} HNO_3 solution into injector, passing through the column with desired flow rate, collected the eluent in a colorimetric cylinder, the eluent was directly inhaled into the atomic absorption spectrometer in which the content of heavy metal ions were determined under selected working conditions. Then the absorption capacity and enrichment factor were calculated.

RESULTS AND DISCUSSION

Effect of pH on adsorption: The pH value plays an important role with respect to the adsorption of different ions on titanate surfaces. The pH of solution influences the distribution of active sites on the surface of titanate and the -OH on the surface provides the ability of binding cation. The decrease

of pH leads to the neutralization of surface charge and overlay of the active sites, so the adsorption of cation onto nano-calcium titanate decreases quickly.

In order to evaluate the effect of pH, 50 mL sample solutions containing 10 mg L^{-1} of Pb, 2.0 mg L^{-1} of Cd, Zn, Ni and Ag was prepared. The pH values of sample solutions were adjusted to a range of 0.5-9.0 with HNO_3 or $\text{NH}_3\cdot\text{H}_2\text{O}$, respectively. The results of the effect of pH on the adsorption percentage of studied ions are shown in Fig. 2.

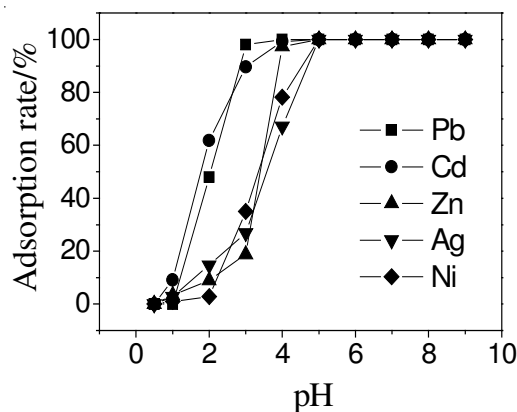


Fig. 2. Effect of pH on the adsorption of the studied metal ions on MINTE, Pb^{2+} : 10 mg L^{-1} ; Cd^{2+} , Zn^{2+} , Ni^{2+} and Ag^{+} : 2 mg L^{-1} , respectively

It could be seen that the adsorption capacity of the analytes increased with the increase of pH. The percentage adsorption (> 95 %) was found for Pb at the pH range of 3-9. Cd and Zn at the pH range of 4-9. For Ag and Ni, the highest percentage adsorption was obtained in the pH range of 5-9. In order to preconcentration all studied ions simultaneously, a pH of 6.0 was selected as the compromise condition.

Effect of flow rate of sample solution on the adsorption: The flow rate of sample solution affects the retention of metal ions on the adsorbent and the duration of analysis. 50 mL of sample solutions containing 10 mg L^{-1} of Pb, 2 mg L^{-1} of Cd, Zn, Ni and Ag was prepared, respectively. Operated according to the general procedure, the effect of flow rate of sample solution on the adsorption of metal ions was examined through adjusting the speed of driving stopper.

It was found that percentage adsorption (> 95 %) of all studied heavy metal ions were obtained at flow rates ≤ 6 mL min^{-1} . However, the adsorption rate of the metal ions will decrease with further increasing flow rate when it was over 6 mL min^{-1} , due to a decrease in the adsorption kinetics at a high flow rate. Thus, a flow rate not over 6 mL min^{-1} was employed in this work.

Elution of the adsorbed metal ions: It was found from Fig. 2 that the adsorption of cations at pH < 1 could be negligible. For this reason, various concentrations and volumes of nitric acid were studied for elution of retained metal ions from the MINTE at a flow rate about 2 mL min^{-1} and the eluent volume was set to 5 mL. It was found that a concentration of 1 mol L^{-1} nitric acid at least was required to obtain quantitative elution. Therefore, 2 mol L^{-1} HNO_3 was chosen for complete elution.

The effect of elution volume on recovery of the studied ions was investigated. The results showed that 2 mL of elution

solution containing 2 mol L⁻¹ HNO₃ sufficient to recover analytes quantitatively when elution flow rate with in 3 mL min⁻¹. Thus, elution volume of 2 mL was employed in this work.

Effect of the sample volume: In order to explore the possibility of enriching low concentrations of analytes from large volumes, the effect of sample volume on the retention of heavy metal ions was also investigated. For this purpose, 25, 50, 100, 250 and 500 mL of sample solution containing 1 µg of Pb, 0.20 µg of Cd, Zn, Ni and Ag, respectively, were passed through the MINTE under optimum conditions. As shown in Table-1, quantitative recoveries (> 95 %) were obtained for sample volumes up to 500 mL for Pb and Ni, 250 mL for Cd, Zn and Ag. The adsorbed analytes can be eluted with 2.0 mL 2.0 mol L⁻¹ HNO₃, so the enrichment factor achieved by this method is 250 for Pb and Ni, 125 for Cd, Zn and Ag. In this experiment, 250 mL of sample solution was adopted for the preconcentration of analytes from water sample.

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, 100 mL of each metal ions solution at 50 mg L⁻¹ was adjusted to the appropriate pH, then preconcentrated and eluted according to the recommended procedure. The amount of metal ions adsorbed was determined. The adsorption capacity of MINTE for Pb²⁺, Cd²⁺, Zn²⁺, Ni²⁺ and Ag⁺ were found to be 5.0, 1.58, 4.34, 2.86 and 3.03 mg, respectively.

Column reuse: The stability and potential regeneration of the manual-controlled injection nano-calcium titanate

enricher were investigated. The MINTE could be reused after regenerated with 10 mL 2.0 mol L⁻¹ HNO₃ and 50 mL distilled water, respectively and was relatively stable up to 50 runs without obviously decrease in the recoveries for the studied ions.

Detection limits and precision: According to the definition of IUPAC, the detection limits (evaluated as the concentration corresponding to three times the standard deviation of 11 runs of the blank solution) of this method for Pb²⁺, Cd²⁺, Zn²⁺, Ni²⁺ and Ag⁺ were 32, 5, 4.1, 9.4 and 7 ng L⁻¹ with an enrichment factor of 125, respectively. Relative standard deviations (RSD) were 2.68, 3.71, 1.35, 1.32 and 2.08 %, respectively (n = 6, C_{Pb} = 50 µg L⁻¹, C_{Cd} = C_{Zn} = C_{Ag} = C_{Ni} = 5 µg L⁻¹ and the sample volume was 50 mL) (Table-1).

Effects of coexisting ions: Various interference ions, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Mn²⁺, Cr⁶⁺, Cu²⁺, Al³⁺, Mn²⁺, Co²⁺ and Fe³⁺, were added into 50 mL volumetric flask containing 2.5 µg of Pb²⁺, 0.25 µg of Cd²⁺, Zn²⁺, Ni²⁺ and Ag⁺. The recovery of heavy metal ions were determined according to experimental method with the error controlled within ± 5 %. The results showed that in the presence of 1000 mg L⁻¹ Na⁺, K⁺, 500 mg L⁻¹ Mg²⁺, Ca²⁺, Mn²⁺, Cr⁶⁺, 200 mg L⁻¹ Cu²⁺, 100 mg L⁻¹ Mn²⁺ and 50 mg L⁻¹ Al³⁺, Co²⁺ and Fe³⁺. The recoveries of the analytes were still above 95 %. It can be seen that the presence of major cations had no obvious influence on the recovery under the selected conditions.

Analysis application: River water sample collected from Hun He river (Shenyang, China), was filtered through a 0.45 µm membrane filter (Shanghai Xin-ya Purge Instrument Factory, Shanghai, China). The pH value was adjusted to 6

TABLE-1
PRECONCENTRATION AND RECOVERIES OF METAL IONS

Volume of the solution (mL)	Quantity in eluent (µg)					Recovery (%)					Enrichment factor
	Pb ²⁺	Cd ²⁺	Zn ²⁺	Ni ²⁺	Ag ²⁺	Pb ²⁺	Cd ²⁺	Zn ²⁺	Ni ²⁺	Ag ²⁺	
25	1.049	0.197	0.193	0.196	0.198	104.9	98.5	96.5	98.0	99.0	12.5
50	1.004	0.206	0.205	0.192	0.197	100.4	103.0	102.5	96.2	98.5	25
100	0.998	0.194	0.197	0.196	0.190	99.8	97.0	98.5	98.0	95.0	50
250	1.034	0.192	0.196	0.195	0.194	103.4	96.0	98.0	97.6	97.0	125
500	0.952	0.188	0.186	0.193	0.181	95.2	94.0	93.0	96.6	90.5	250

TABLE-2
DETERMINATION OF HEAVY METAL IONS IN WATER SAMPLES

Element	River water			Tap water		
	Added (µg L ⁻¹)	Founded (µg L ⁻¹)	Recovery (%)	Added (µg L ⁻¹)	Founded (µg L ⁻¹)	Recovery (%)
Pb ²⁺	0.00	4.90	—	0.00	1.70	—
	5.00	9.82	98.2	2.00	3.80	105.0
	10.00	15.38	104.7	5.00	6.78	101.6
Cd ²⁺	0.00	1.08	—	0.00	n.d.a	—
	5.00	6.12	100.8	2.00	1.94	97.0
	10.00	10.59	95.1	5.00	4.76	95.2
Zn ²⁺	0.00	8.72	—	0.00	2.34	—
	5.00	13.69	99.4	2.00	4.31	98.0
	10.00	18.28	95.6	5.00	7.07	94.6
Ni ²⁺	0.00	1.07	—	0.00	0.71	—
	5.00	6.12	101.0	2.00	2.64	96.5
	10.00	10.81	97.4	5.00	5.70	99.8
Ag ²⁺	0.00	1.15	—	0.00	n.d.a	—
	5.00	6.06	98.2	2.00	1.91	95.5
	10.00	10.38	92.3	5.00	4.69	93.8

a.d.a.: Not detected.

with HNO₃ and ammonia, according to the 2.4 general procedure. Metal ions was adsorbed on the nano-calcium titanate enricher at locale. Then it was brought lab to elute and determinate the Pb²⁺, Cd²⁺, Zn²⁺, Ni²⁺ and Ag⁺ with FAAS, respectively. Tap water sample was collected from water supply of Shenyang city and was inhaled into the injector to concentration and analyzed immediately. Meanwhile, the recovery tests were also conducted. The results were given in Table-2. The results indicated that the recoveries were reasonable for trace analysis, in a range of 92.3-105.0 %.

Conclusion

It could be concluded from the results that manual-controlled injection nano-calcium titanate enricher (MINTE) was prepared successfully and it was an effective sorbent for trace amounts of lead, cadmium, zinc, nickel and silver ions and could be used for their preconcentration from various aqueous solutions. The proposed method based on preconcentration with MINTE and determination by FAAS showed enough sensitivity for those trace heavy metal ions in water determinations. The precision and accuracy were satisfactory. The method was successfully applied to the preconcentration and determination of lead, cadmium, zinc, nickel and silver ions in water samples with fast using, reproducible, simple and low cost. The developed method was very suitable for rapid adsorption of heavy metal ions from large volume of sample solution at locale.

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