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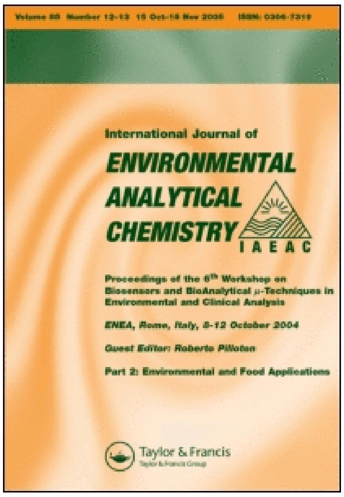

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NANOMETER-SIZE TITANIUM DIOXIDE SEPARATION/PRECONCENTRATION AND FAAS DETERMINATION OF TRACE Zn AND Cd IN WATER SAMPLE

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A new method using nanoparticle TiO_2 as solid-phase extractant coupled with FAAS was proposed for preconcentration and determination of trace Zn and Cd. The effects of pH, contact time, elution solution and interfering ions on the adsorption behavior of nanometer TiO_2 towards Zn and Cd were investigated. Under optimum conditions, nanometer TiO_2 possesses a significant capacity for the sorption of the metal ions studied. The limits of detection (3δ) of this method were $1.8\,\mathrm{ng\,mL^{-1}}$ of Zn and $3.0\,\mathrm{ng\,mL^{-1}}$ of Cd with an enrichment factor of 12.5, and relative standard deviations were 3.8% and 4.3% for Zn and Cd, respectively ($c = 0.5\,\mu\mathrm{g\,mL^{-1}}$, $n = 9$). The proposed method was validated by the analysis of water certified reference material.

Keywords: Nanometer TiO_2; Separation/preconcentration; FAAS; Zn; Cd

INTRODUCTION

In recent years, pollution of the environment by heavy metals including zinc and cadmium has received considerable attention. Zinc is an essential trace element for humans, plants and animals. It plays an important role in several biochemical processes and its compounds have bactericidal activity [1]. Zinc compounds have been employed in solutions as antiseptic and disinfectant agents. However, if it is in excess, this metal can also play an important role in several harmful effects in the human body, including disturbances in energy metabolism and increases in oxidative stress [2]. Cadmium can accumulate in living organisms and has a high toxic potential. Its wide technological use (in fertilizers, mining, pigments) and its production from burning oil and coal and incinerating waste bring about extensive anthropogenic contamination of soil, air, and water. Over the long term, drinking water containing cadmium concentrations higher than $0.005\,\mathrm{mg\,L^{-1}}$ can cause nausea, salivation, diarrhea, muscular cramps, renal degradation, lung insufficiency, bone lesions, cancer and hypertension in

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humans [3,4]. As a result, the determination of the concentrations of these metal ions in artificial and natural water resources is of current interest in order to have a check on the ecosystem.

Flame atomic absorption spectrometry (FAAS) has been widely used for determination of trace metal ions, because of the relatively simple and inexpensive equipment required. However, the direct determination of metal ions at trace levels by FAAS is limited, not only by insufficient sensitivity but also by matrix interference. For this reason, the preliminary separation and preconcentration of trace elements from the matrix is frequently necessary to improve the detection limit and selectivity for their determination by FAAS. The most widely used techniques for the separation and preconcentration of trace elements include liquid–liquid extraction [5], coprecipitation [6], ion-exchange [7,8], solid-phase extraction [9–13] and electrochemical deposition [14].

Recently, solid-phase extraction (SPE) techniques for the preconcentration of traces of heavy metal ions have become increasingly popular, compared with the traditional solvent-extraction methods because of the simple procedure, higher preconcentration factor, rapid phase separation and easy combination with different detection techniques [15,16]. The choice of solid-phase extractants is the decisive factor that affects analytical sensitivity and selectivity. The main requirements with respect to substances to be used as solid-phase extractants are as follows [17]: possibility of extracting a large number of elements over a wide pH range; fast and quantitative sorption and elution; high capacity, regenerability and accessibility. Numerous substances have been proposed and applied as solid-phase extractants, such as ion-exchange resins [18,19], chelating resins [20], modified silica [21,22] and alumina [23], magnesia [24], active carbon [25,26] and cellulose [27].

Nanometer material is a new functional material, which has gained importance owing to its special properties [28,29]. It is also known as ultrafine grained particle. Nanoparticles are defined as clusters of atoms or molecules of metal and oxide, ranging in size from 1 nm to 100 nm, falling between single atoms or molecules and bulk materials. One of their properties is that most of the atoms of a nanoparticle are on the surface. The surface atoms are unsaturated and can easily bind with other atoms, thus possessing high chemical activity. Consequently, nanometer materials can selectively adsorb metal ions, and have a very high adsorption capacity. As far as we know, up until now, there is little systematic data on the preconcentration characteristics of nanometer material in trace analysis and application [30].

The aim of this work is to study the adsorption characteristics of Zn and Cd on nanometer TiO_2 under static conditions, optimize the conditions for separation/preconcentration of these elements and propose a new method using nanometer TiO_2 separation/preconcentration coupled with FAAS for the determination of trace Zn and Cd in water samples.

EXPERIMENTAL

Apparatus

A WFX-130 atomic absorption spectrophotometer (Beijing Second Optics, Beijing, P.R. China) equipped with a single-element hollow-cathode lamp and 10-cm air–acetylene burner was used for the determination of the metal ions under conditions as

TABLE I Optimal instrumental operating conditions

Element	*Wavelength* (nm)	*Lamp current* (mA)	*Slit width* (nm)	C_2H_2/*air* (L/min)
Zn	213.9	3	0.4	2/7
Cd	228.8	2.5	0.4	2/7

described in Table I. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd) supplied with a combined electrode. An 80-2 centrifuge (Changzhou Guohua Electric Appliance Co. Ltd, P.R. China) was used to centrifuge the solutions.

Standard Solutions and Reagents

Stock standard solutions of Zn and Cd at a concentration of $1000\,\mu g\,mL^{-1}$ were obtained from the National Institute of Standards (Beijing, P.R. China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. All reagents used were of analytical reagent grade. Doubly distilled water was used throughout. Nanometer TiO_2 (diameter from 10 nm to 50 nm and specific surface area, determined by the Brunauer–Emmett–Teller (BET) method of nitrogen adsorption at low temperature, $208\,m^2\,g^{-1}$) was provided by the Laboratory of Inorganic Chemistry, Department of Chemistry, Wuhan University. The synthesis method and properties of the nanometer TiO_2 have been described previously [31].

Procedure

To study metal ion preconcentration under static conditions, a portion of sample solution containing the studied ions was transferred to a 25-mL flask, the pH values were adjusted with 0.1 M HCl and 0.1M $NH_3 \cdot H_2O$, and the final volume was diluted to 25 mL. Then 20 mg of nanometer TiO_2 was added, and the solution was stirred vigorously for 10 min to facilitate adsorption of the metal ions. After centrifugation, the concentrations of the unsorbed ions in the liquid phase were determined directly by FAAS, and the amounts of the adsorbed ions were measured after elution with 0.1 M HNO_3.

RESULTS AND DISCUSSION

Effect of pH on Adsorption

The pH value has an important effect on the adsorption of different ions on oxide surfaces. According to Morterra [32], the pH of the solution influences the distribution of active sites on the surface of TiO_2, and the –OH on the surface provides the ability to bind cations. A decrease of pH leads to the neutralization of surface charge and overlay of the active sites, so the preconcentration of cations onto TiO_2 decreases quickly.

In order to evaluate the effect of pH, the pH values of sample solutions were adjusted wihin the range 1–10 with dilute HCl or $NH_3 \cdot H_2O$ and then the experiment procedure was followed. The effect of pH on recoveries of the studied ions is shown in Fig. 1. It can

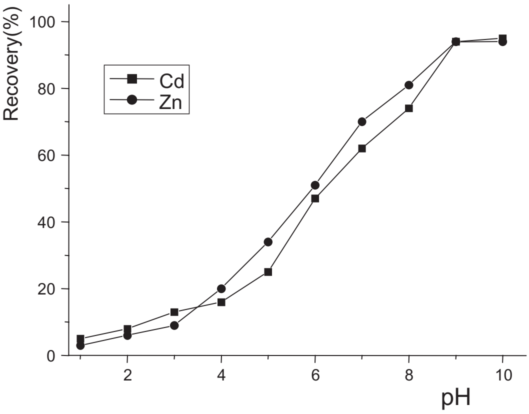

FIGURE 1 Effect of pH on the recovery (R%) of Zn and Cd following their sorption on nanometer TiO_2. Zn, Cd: 1.0 μg mL^{-1}, sample volume: 25 mL, nanometer TiO_2: 20 mg.

TABLE II Elution data (percentage recovery) for metal ions absorbed on nanometer TiO_2

Element	*HNO_3* (mol L^{-1})					
	0.01	*0.05*	*0.1*	*0.5*	*1*	*2*
Zn^{2+}	74.2	89.8	96.4	91.1	91.9	93.1
Cd^{2+}	78.0	83.9	97.2	98.9	93.7	95.0

Eluant volume: 2 mL.

be seen that the metal ions were absorbed poorly at $pH < 4$. Quantitative recovery (>90%) was found for Zn and Cd in the pH range 9–10, so a pH of 9.0 was selected as a compromise.

Elution

Figure 1 shows that the adsorption of cations at pH <2 could be negligible. For this reason, various concentrations HNO_3 were studied for the desorption of adsorbed substances. The results obtained are given in Table II. It can be seen that 0.1 M HNO_3 was sufficient for complete elution. The effect of eluant volume on the recovery of analytes was also studied while keeping the HNO_3 concentration as 0.1 M. The results show that quantitative recoveries (>90%) could be obtained with 2.0 mL of 0.1 M HNO_3. Therefore, a volume of 2.0 mL eluant was used, and an enrichment factor of 12.5 could be achieved.

Sorption Kinetics

Because rapid adsorption is of great importance in analytical application, the sorption kinetics of nanometer TiO_2 towards Zn and Cd was studied at pH 9.0. 20 mg nanometer TiO_2 was stirred with 25 mL of solution containing 10 μg mL^{-1} Zn and Cd at 25°C for 5, 10, 15, 20 and 30 min. The concentration of metal ions in the supernatant solution was determined by FAAS, and the amount of metal ions sorbed on nanometer TiO_2 was calculated by checking the mass balance. It was observed that by the tenth minute, the degree of sorption (R%), which represents the percentage of ions adsorbed, is higher than 90% for all the metal ions studied, indicating that sorption of metal ions on nanometer TiO_2 at the optimum pH is fairly fast.

Static Adsorption Capacities (Q_s)

To determine metal ion static adsorption capacity, a 50-mg portion of nanometer TiO_2 was shaken with 25 mL of an aqueous solution containing 1000 μg of the corresponding metal ion under the optimal pH condition for sorption (pH 9.0). After the distribution equilibrium had been reached, the concentration of the metal ion in solution was determined by FAAS, and the adsorption capacity for metal ion was calculated. The adsorption capacity of nanometer TiO_2 for Zn and Cd was found to be 15.3 and 7.9 mg g^{-1}, respectively

Interference Effects

The effects of common coexisting ions on the adsorption of the studied elements on nanometer TiO_2 were investigated. In these experiments, solutions of 1.0 μg mL^{-1} of Zn^{2+} and Cd^{2+} containing the added interfering ions were treated according to the recommended procedure. The element contents in the effluents were determined in order to calculate the recovery of the studied elements. The tolerance of the coexisting ions, defined as the largest amount for which the recovery remains above 90%, are given in Table III. From the results obtained, it can be concluded that the presence of common cations and anions has no significant influence on the studied element adsorption under the selected conditions.

Analytical Performance of the Method

The precision of the method, evaluated as the relative standard deviation (RSD), obtained after analyzing a series of nine replicates for 5.0 μg Zn(II) and Cd(II) in 25 mL of model solutions was 3.8% and 4.3%, respectively.

The limits of detection (LOD) of the proposed method for the determination of the investigated elements were studied under the optimal experimental conditions. The detection limits based on three times the standard deviations of the blank for Zn and Cd were found to be 1.8 ng mL^{-1} and 3.0 ng mL^{-1}, respectively.

TABLE III Tolerance limits for coexisting ions in the adsorption of the studied elements

Coexisting ion	*Tolerance limit of ions* (mg L^{-1})
Na^+, K^+	5000
Ca^{2+}, Mg^{2+}	2000
Al^{3+}	1000
Fe^{3+}	100
SiO_4^{2-}, SO_4^{2-}	5000
PO_4^{3-},	2000

The concentration of Zn^{2+} and Cd^{2+} ions is 1.0 μg mL^{-1}.

TABLE IV Analytical results for metal ions in standard water sample ($n = 5$)

Element	*Found* (μg mL^{-1})	*Certified* (μg mL^{-1})
Zn	0.381 ± 0.024	0.360 ± 0.011
Cd	0.157 ± 0.010	0.160 ± 0.003

Application to a Water Sample

The contents of the studied elements in environmental water reference material (ERM, GSBZ50009-8, P.R. China) were determined by the method proposed. The results are shown in Table IV. As can be seen, the results are in good agreement with the certified values.

CONCLUSION

In this study, a selective and sensitive method for the determination of trace Zn and Cd was developed. This procedure combines the simplicity and rapidity of the FAAS measurements with the use of nanometer TiO_2 as sorbent for preconcentration. Zn and Cd can be retained quantitatively on nanometer TiO_2 in the pH range 9–10, then eluted with 0.1 M HNO_3. An enrichment factor of 12.5 was achieved, and the detection limits for Zn and Cd were 1.8 ng mL^{-1} and 3.0 ng mL^{-1}, respectively. The determination of Zn and Cd in water samples with the proposed method shows good reproducibility and accuracy.

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