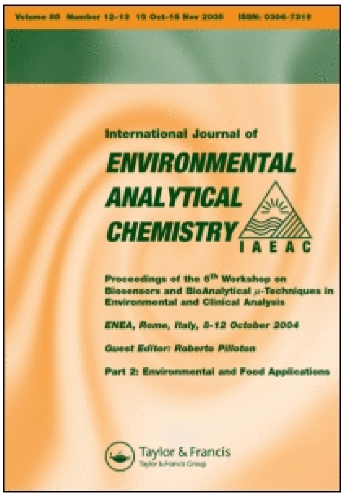

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A pre-enrichment procedure using diethyldithiocarbamate-modified TiO_2 nanoparticles for the analysis of biological and natural water samples by ICP-AES

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In this article, a new method that utilizes a diethyldithiocarbamate-modified nanometre TiO_2 (TiO_2–DDTC) as solid-phase extractant has been developed for simultaneous preconcentration of trace Cu(II), Pb(II), Zn(II), and Cd(II) prior to measurement by inductively coupled plasma atomic emission spectrometry (ICP-AES). The separation/preconcentration conditions of analytes, which include the effects of pH, sample flow rate and volume, elution conditions, and interfering ions on the recovery of the analytes, were investigated. At pH 5, the adsorption capacity of modified nanometre TiO_2–DDTC was found to be 6.2, 19, 4.7, and 6.0 mg/g for Cu(II), Pb(II), Zn(II), and Cd(II), respectively. According to the definition of IUPAC, the detection limits (3σ) of this method for Cu(II), Pb(II), Zn(II), and Cd(II) were 0.41, 1.7, 0.39, and 0.52 ng/mL, respectively. The proposed method achieved satisfied results when applied to the determinations of trace Cu(II), Pb(II), Zn(II), and Cd(II) in biological and natural water samples.

Keywords: DDTC-modified nanometre TiO_2; Trace elements; Preconcentration; ICP-AES

1. Introduction

In recent years, the toxicity and effects of trace elements to the danger of public health and environment have attracted increasing attention in the fields of pollution and nutrition. It has become necessary to develop an accurate and sensitive quantitative metal determination in environmental samples because of the environmental pollution from toxic metals. One of the most important objectives for analytical chemists is metal quantification at low concentration levels below ng/mL or ng/g. Despite recent progress in instrumental techniques and increases in the selectivity and sensitivity of analytical

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techniques, direct determination of trace elements in samples is still difficult. Therefore, preconcentration and selective separation of trace elements from biological and natural water samples are very important and need much more attention.

Currently, the most widely used techniques for preconcentration and separation of trace elements include liquid–liquid extraction [1], ion exchange [2], resin chelation [3], fibre chelation [4], solid-phase extraction [5, 6], and electrochemical deposition [7]. However, the solid-phase extraction (SPE) technique has become more popular than the traditional liquid–liquid extraction method [8]. The SPE has several major advantages: (1) a higher preconcentration factor, (2) simple operation, (3) rapid phase separation, (4) high selectivity, (5) lower cost and less time required, and (6) the ability to combine the technique with different modern detection techniques. The on-line column separation and preconcentration procedures, which are mainly based on the flow-injection (FI) system, have been increasingly utilized for atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry. This combination not only provides improvements in detection limits, but also reduces the interference caused by matrix. Numerous substances have been proposed and applied as solid-phase extractants, which include modified silica, alumina, magnesia, active carbon, cellulose, and micro-organisms.

Nowadays, nanometre material, a new solid material, has become more important owing to its special physical and chemical properties [9, 10]. Nanoparticles are clusters of atoms or molecules of metal and oxide, ranging in size from 1 nm to almost 100 nm, falling between single atoms or molecules and bulk materials. One of the properties of nanoparticles is that most of the atoms are on the surface. The surface atoms are unsaturated and therefore can bind other atoms that have a highly chemical activity.

There have been reports in the literature on the preconcentration and separation of trace elements in sample solutions by means of nanometre TiO_2 material [11–16]. Nanometre TiO_2 is a promising material as a solid-phase extractant because of its large specific surface area, higher adsorption capacity, and low-temperature modification. However, some heavy-metal cations are poorly adsorbed on nanometre TiO_2 when the pH is below 6 [13, 14]. Although some metal cations can be adsorbed on nanometre TiO_2 when the pH is equal to or higher than 8, they are more likely to be precipitated under higher pHs. Therefore, nanometre TiO_2 was modified by DDTC in this work. Experimental results indicate that modified nanometre TiO_2 can enrich some heavy-metal cations when the pH is below 6. In addition, compared with nanometre TiO_2, modified nanometre TiO_2 offers a higher adsorption capacity and selectivity.

It is well known that DDTC is a well-characterized organic chelation ligand, which can form complex compounds with many metal ions under controlled pH conditions [17]. Many research studies have been conducted to find the most efficient way to immobilize DDTC on a number of different substrates through chemical modifications or physical adsorption procedures for the preconcentration of trace elements [18]. However, the use of modified nanometre TiO_2–DDTC as a solid-phase extractant for simultaneous preconcentration of trace amounts of Cu(II), Pb(II), Zn(II), and Cd(II) from biological and natural water samples has not yet been reported.

In this article, we report that DDTC was impregnated onto nanometre TiO_2 for the preconcentration of trace Cu(II), Pb(II), Zn(II), and Cd(II). The adsorption behaviour of analytes on nanometre TiO_2–DDTC is investigated in detail, and the experimental conditions for the separation and preconcentration process are discussed in detail.

The proposed method was applied to the determinations of trace Cu(II), Pb(II), Zn(II), and Cd(II) in biological and natural water samples by ICP-AES. Analytical precision and accuracy in the proposed method were achieved with satisfactory results, and the method was convenient to use.

2. Experimental

2.1 *Apparatus*

An IRIS Advantage ER/S inductively coupled plasma emission spectrometer (TJA, USA) was used for all metal determinations. The operation conditions and wavelengths are summarized in table 1.

The pH values were controlled with a pHs-10C digital pH meter (Xiaoshan Instrument Factory, China). Infrared spectra were recorded on a Nicolet NEXUS 670 FT–IR apparatus (USA). A YL-110 peristaltic pump (General Research Institute for Nonferrous Metals, Beijing) was used in the separation/preconcentration process. A home-made glass microcolumn (45 mm × 2.5 mm i.d.) was used. X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 instrument (Japan) with a CuKα X-ray source of 40 kV and 30 mA.

2.2 *Reagents and standard solutions*

Reagents of analytical and spectral purity were used for all experiments, and doubly distilled deionized water was used throughout. Diethyldithiocarbamate (DDTC) and sodium lauryl sulphate (SLS) were used in this work (The Third Reagent Factory, Shanghai, China).

Nanometre TiO_2 (nano-TiO_2) was synthesized from titanium sulphate according to a previously reported method [19]. Titanium sulphate (120.01 g) was carefully hydrolysed for 10 min at 100°C in 0.5 L of distilled deionized water, and then 120.12 g of carbamide and 2.45 g of sodium dodecyl benzene sulphonate were added to the solution. The solution was stirred for 3 h at 80°C by a magnetic stirrer. The precipitate was filtered, washed with distilled deionized water to neutral, and dried under vacuum at 100°C for 8 h. The powder obtained was ground in an agate mortar and calcined for 2 h at 500°C. The product was then extracted and stored (average diameter: 20 nm; specific surface area determined by the BET method: $90\,m^2/g$).

Table 1. ICP-AES operating conditions and wavelengths examined.

Parameter	
RF power (kW)	1.15
Carrier gas (Ar) flow rate (L/min)	0.6
Auxiliary gas (Ar) flow rate (L/min)	1.0
Coolant gas (Ar) flow rate (L/min)	14
Nebulizer flow (psi)	30
Pump rate (rpm)	100
Observation height (mm)	15
Integration time (s) on-axis	20
off-axis	5
Wavelength (nm)	Cu 324.754, Pb 216.999, Zn 202.548, Cd 228.802

Standard stock solution of Pb(II) and Cd(II) (1 mg/mL) were carefully prepared by dissolving spectral pure-grade chemicals $Pb(NO_3)_2$ and CdO (The First Reagent Factory, Shanghai, China). A standard stock solution of Cu(II) and Zn(II) (1 mg/mL) was prepared by dissolving the high-purity metal (The First Reagent Factory, Shanghai, China) in 0.1 M/L of nitric acid. The constituents were mixed and diluted in a standard solution containing 100 µg/mL of Pb(II) and 10 µg/mL of Cu(II), Zn(II), and Cd(II).

2.3 *Sample preparation*

Qinghai lake water was collected from Qinghai Lake, Qinghai, China. Yellow River water was collected from Yellow River, Lanzhou, China. All water samples were filtered through a 0.45 µm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China) and acidified to a pH of about 1 with concentrated HCl prior to storage for use [20]. The pH value was adjusted to 5 with 0.1 M/L of HCl or 0.1 M/L of $NH_3 \cdot H_2O$ and stored in polyethylene bottles prior to use.

Pig liver was purchased from Binhe market, Lanzhou, China. Balsam pear leaves were obtained from Anning village, Lanzhou, China. Pig liver and balsam pear leaves were dried in an oven at 80°C to constant weight. One gram of pig liver or balsam pear leaves sample was weighed and transferred to a digestion tube, and then 5 mL of concentrated HNO_3 was added. The tube was left at room temperature for one night, then placed in a digester block and heated slowly until the temperature reached 165°C. This temperature was maintained until the evolution of brown fumes ceased. After the tube was cooled down, 1.3 mL of perchloric acid was added. Then, the temperature was raised to 210°C until the evolution of white fumes began. The volume was adjusted to 100 mL with doubly distilled deionized water after the tube had cooled down [21].

2.4 *Modification process*

Surface modification of TiO_2 nanoparticles was performed in a beaker with a total volume of 250 mL. To maintain a relatively constant ionic force, 3 mL of 1 M/L KNO_3 was dropped into 100 mL of 0.001 M/L HCl containing 20 g of TiO_2 under ultrasonic action to reduce the aggregation of TiO_2 nanoparticles. The pH of the solution was adjusted to 5 using either 0.1 M/L of HNO_3 or 0.1 M/L of $NH_3 \cdot H_2O$, and then an appropriate amount of sodium lauryl sulphate (SLS) was added, making a final SLS concentration of 7.5 mM/L. The solution was stirred for 1 h by a magnetic stirrer. Two grams of DDTC were then added into the solution with constant stirring. The process in which DDTC was impregnated on nanometre TiO_2 was completed after 1 h at 60°C. The reaction mixture was then filtered under vacuum. The obtained sediment was washed with doubly distilled deionized water and dried at 60°C for 2 h under vacuum to obtain a fine white powder.

2.5 *Recommended procedure*

2.5.1 Static method. A portion of standard or sample solution containing Cu(II), Pb(II), Zn(II), and Cd(II) was transferred into a 10 mL beaker, and the pH values were adjusted to the desired value with 0.1 M/L of HNO_3 or 0.1 M/L of $NH_3 \cdot H_2O$.

Then, the volume was adjusted to 10 mL with doubly distilled deionized water. Twenty milligrams of TiO_2–DDTC were added, and the mixture was shaken vigorously for 30 min to facilitate adsorption of the metal ions onto the TiO_2–DDTC. After the solution was centrifuged, the concentrations of the metal ions in the solution were directly determined by ICP-AES.

2.5.2 Column preparation. First, a homogenous mixture of 20 mg of TiO_2–DDTC and 50 mg of glass beads (40–60 mesh, The First Regent Factory, Shanghai, China) were filled into a glass microcolumn (45 mm × 2.5 mm i.d.), plugged with a small portion of glass wool at both ends. Before use, HNO_3 solution, pH 5, and doubly distilled deionized water were sequentially passed through the column to equilibrate, clean, and neutralize it. Portions of aqueous standard or sample solutions containing Cu(II), Pb(II), Zn(II), and Cd(II) were prepared, and the pH values were adjusted to the desired pH with 0.10 M/L of HNO_3 and $NH_3 \cdot H_2O$. Each solution was passed through the column at a flow rate of 1.0 mL/min using a peristaltic pump. Afterwards, the metal ions retained on microcolumn were eluted with 1.5 mL of 0.10 M/L HCl solution. The analytes in the elution were determined by ICP-AES.

3. Results and discussion

3.1 *Modification mechanism of DDTC on SLS-coated nano-TiO_2*

The studies on TiO_2 surface modification conducted using organic agents were aimed at altering its surface character in the hydrophilic–hydrophobic system. Nano-TiO_2 under normal pH conditions in water is hydrophilic and hence does not have large adsorption capacities for hydrophobic organic compounds. Modification of nano-TiO_2 particles can be achieved by bringing the particles into contact with a low pH solution and an anionic surfactant. Surfactants can be used to enhance the adsorption tendency of metal oxides towards organic compounds [22–24]. The pH of the solution influences the surface charge of oxides. The pH at which point the surface has zero charge is called 'pHpzc', which is 6.2 for nano-TiO_2 [25].

Coulombic interactions are the primary forces responsible for adsorption at low surfactant concentrations in the process of modifying titanium dioxide. As the surfactant concentration increases gradually, this surface aggregation of SLS molecules formed hemi-micelles [24]. With the formation of the hemi-micelle on the nano-TiO_2 surface, the hydrophilic characteristics of nano-TiO_2 surface are transformed into hydrophobic characteristics. Owing to the hydrophobic interaction between the hydrophobic groups in DDTC and the exposed hydrocarbon tails in the hemi-micelles, DDTC adsorbs on hydrophobic titanium dioxide. Because of orientation of the hydrophilic groups of DDTC to the aqueous [26], adsorption of metal ions on modified TiO_2–DDTC surface becomes easier.

3.2 *FT–IR spectra*

Fourier transform–infrared spectra were obtained from DDTC, nano-TiO_2, and modified TiO_2–DDTC. According to the literature [27], the main characteristic peaks of DDTC are assigned as follows: γ NH ($3365.85\,cm^{-1}$), γ CH_3– ($2977.621\,cm^{-1}$),

γ CH$_2$– (2927.43 cm^{-1}), γ C=S (1203.06, 1129.52, and 1067.35 a cm^{-1}), γ C–N–C (909.80 cm^{-1}), γ S=C–N (1477.43 and 1455.49 cm^{-1} similar to the acylamide II bond), γ S=C–N (1413.67, 1297.61, and 1261.99/cm^{-1} similar to the acylamide I bond), γ S=C–N (986.19 cm^{-1} similar to acylamide III bond), γ S=C–N (843.32, and 732.85 cm^{-1} similar to the acylamide IV bond) (where γ is the stretching vibration). The main characteristic peaks of modified TiO$_2$-DDTC are 3423.01, 2922.60, 2852.95, 1627.94, 1460.51, 1383.09, 1126.23, 1060.84, and 517.29 cm^{-1}, respectively. However, some peaks shift slightly, and the intensity of the peaks changes distinctly. Besides, FT–IR spectra reveal that the maximum absorption peak of TiO$_2$ (465.72 cm^{-1}) occurs in modified TiO$_2$–DDTC. These results indicate that a strong interaction exists at the interface of DDTC and nano-TiO$_2$.

3.3 *X-ray diffraction patterns*

X-ray diffraction patterns were obtained from nano-TiO$_2$, DDTC and modified TiO$_2$–DDTC. This reveals that DDTC also has some degree of crystallinity. The higher diffraction peaks appear in the region of $2\theta = 2$–$55°$, where the maximum is around 2° for DDTC. Nano-TiO$_2$ has a classical anatase structure, and the strongest diffraction peak appears at $2\theta = 25°$ [28]. The diffraction pattern of modified TiO$_2$–DDTC is the same as that of untreated nano-TiO$_2$. This result means that DDTC deposited on the surface of TiO$_2$ nanoparticles has no effect on the crystallization performance of nano-TiO$_2$.

3.4 *Effect of the pH on enrichment recovery*

According to the recommended procedure (static method), eight aliquots of 1 mL mixed standard solution containing 100 µg/mL Pb(II) and 10 µg/mL Cu(II), Zn(II), and Cd(II) ions were pipetted and diluted to 10 mL with doubly distilled deionized water. The solutions were enriched at pH 1–8 and then analysed. The results of the effect of pH on the recoveries of the metal ions were shown in figure 1. It can be seen that a quantitative recovery (>95%) was found for Cu(II), Zn(II), and Cd(II) in the pH range of 4–8. For Pb(II), the highest recovery was obtained in the pH range of 3–8. To avoid hydrolysing at higher pH and to determine these elements simultaneously, pH 5 was selected as the enrichment acidity for further study. However, untreated nano-TiO$_2$ micro-column does not adsorb Cu(II), Pb(II), Zn(II), and Cd(II) at pH 5.

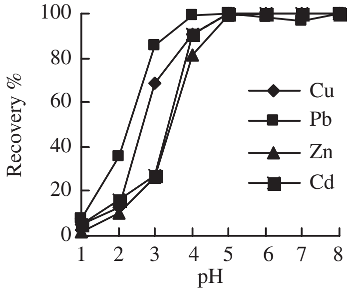

Figure 1. Effect of pH on analyte recovery; Cu(II), Zn(II), Cd(II): 1.0 µg/mL; Pb(II): 10.0 µg/mL.

These experiments show that nanometre TiO_2–DDTC offers a higher selectivity for Cu(II), Pb(II), Zn(II), and Cd(II) adsorption than untreated nano-TiO_2 does.

In addition, Co(II) and Ni(II) ions were not enriched by the nanometre TiO_2–DDTC at pH 5. Cr(III), In(III), Ga(III), Al(III), Fe(III), and Hg(II) could be adsorbed by nanometre TiO_2–DDTC about 40–60% at pH 5, but they do not interfere with enrichment and determination of Cu(II), Pb(II), Zn(II), and Cd(II).

3.5 *Effect of elution condition on recovery*

Since the adsorption of cations at $pH < 2$ is negligible, one would expect elution to be favoured in acidic solutions. Therefore, various concentrations of HCl and HNO_3 were studied for the desorption of retained Cu(II), Pb(II), Zn(II), and Cd(II) that follow the above procedure (dynamic method). The results are shown in table 2. As can be seen, 0.10 M/L HCl was sufficient for complete elution. It was found that quantitative recoveries (>95%) with 1.5 mL of 0.10 M/L HCl as eluent could be obtained. Therefore, 1.5 mL of 0.10 M/L HCl was used as eluent in the following experiments.

3.6 *Effect of the flow rate of the sample solution*

As the retention of elements on adsorbent depends upon the flow rate of the sample solution, its effect was examined under optimum conditions (pH, eluent, etc.) by passing 10 mL of sample solution through the microcolumn with a peristaltic pump. The flow rates were adjusted in the range of 0.5–3.0 mL/min. As shown in figure 2, quantitative recoveries of the metal ions will decrease with a further increase in flow rate over 1.5 mL/min. Thus, a flow rate of 1.0 mL/min was selected in this work.

3.7 *Effect of the sample volume*

To explore the possibility of enriching low concentrations of analytes from large volumes, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, 20, 50, 100, 150, and 200 mL of sample solutions containing 1.0 µg of Cu, Zn, and Cd, and 10.0 µg of Pb, respectively, were passed through the microcolumn with the optimum flow rate. As shown in figure 3, quantitative recoveries (>95%) were obtained for sample volumes of ≤ 50 mL for all metal ions.

Table 2. Elution recovery (%) for Cu(II), Pb(II), Zn(II), and Cd(II) adsorbed on nanometre TiO_2–DDTC.

Eluent[a] (M/L) HCl	Cu(II)	Pb(II)	Zn(II)	Cd(II)	Eluent[a] (M/L) HNO_3	Cu(II)	Pb(II)	Zn(II)	Cd(II)
	Recovery (%)						Recovery (%)		
0.01	77	79	72	74	0.01	70	75	69	71
0.05	83	88	83	81	0.05	81	86	79	82
0.10	97	99	99	99	0.10	93	97	96	90
0.25	96	98	97	98	0.25	95	99	98	92
0.50	93	99	96	98	0.50	94	99	97	91
1.0	92	98	97	98	1.0	94	97	96	91
2.0	92	98	97	98	2.0	92	97	96	90

[a] Eluent volume: 1.5 mL.

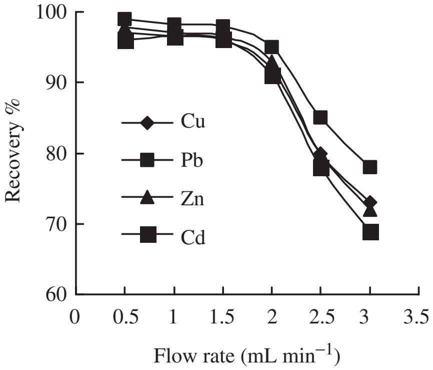

Figure 2. Effect of flow rate on analyte recovery; pH 5; Cu(II), Zn(II), and Cd(II): 1.0 μg/mL; Pb(II): 10.0 μg/mL; sample volume, 10 mL.

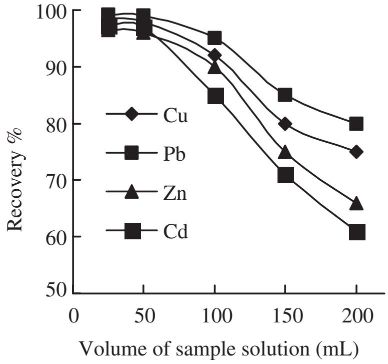

Figure 3. Effect of sample volume on analyte recovery; pH 5; Cu(II), Zn(II) and Cd(II): 1.0 μg; Pb(II): 10.0 μg.

Therefore, 50 mL of sample solution was adopted for the preconcentration of analytes from sample solutions.

3.8 *Adsorption capacities*

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively concentrate the analytes from a given solution. The capacity study was adopted from the paper recommended by Maquieira *et al*. [29]. Ten-millilitre aliquots of a series of concentrations (10–500 μg/mL) were adjusted to the appropriate pH, and the recommended procedure (static method) described above was applied. A breakthrough curve was gained by plotting the concentration (μg/mL) vs. the micrograms of Cu(II), Pb(II), Zn(II), and Cd(II) adsorbed per gram. From the breakthrough curve, the adsorption of modified nanometre TiO_2–DDTC for Cu(II), Pb(II), Zn(II), and Cd(II) was found to be 6.2, 18.6, 4.7, and 6.0 mg/g at pH 5, respectively. However, Cu(II), Pb(II), Zn(II), and Cd(II) ions were poorly adsorbed on untreated nano-TiO_2 at pH 5. The result also shows that the capacity of modified nanometre TiO_2–DDTC is significantly higher than that of silica (usually used as an extractant) [25, 30].

3.9 *Effects of coexisting ions*

The effects of common coexisting ions on the adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) in nanometre TiO_2–DDTC were investigated. In these experiments, solutions of 10.0 μg/mL of Pb(II), 1.0 μg/mL of Cu(II), Zn(II), and Cd(II) that contain the added interfering ion were analysed according to the recommended procedure (Column preparation). The tolerance of the coexisting ions, defined as the largest amount making the recoveries of Cu(II), Pb(II), Zn(II) and Cd(II) less than 90%, were Na^+, K^+, 1500 mg/L; Ca^{2+}, Mg^{2+}, 300 mg/L; Mn^{2+}, Ni^{2+}, 10 mg/L; Fe^{3+}, Ba^{2+}, 5 mg/L. The tolerance of the coexisting ions is given in table 3. It can be seen that the presence of major cations has no obvious influence on the determination under the selected conditions.

3.10 *Analytical precision and detection limits*

Under the selected conditions, eight portions of mixed standard solutions were enriched and analysed simultaneously following the recommended procedure. The results (table 4) show that the relative standard deviations (RSDs) of the method were lower than 6.0%, indicating that the method has good precision for the analysis of trace chromium and lead ions from solution samples. According to the definition of IUPAC, the detection limits (3σ) of this method for Cu(II), Pb(II), Zn(II), and Cd(II) are 0.41, 1.68, 0.39, and 0.52 ng/mL, respectively; the RSDs are 3.4%, 5.6%, 3.7%, and 4.8%, respectively ($n = 11$, $C = 50$ ng/mL).

3.11 *Analysis of real samples*

The proposed method (dynamical method) has been applied to the determinations of trace Cu(II), Pb(II), Zn(II), and Cd(II) in biological and natural water samples. The analytical results of biological samples in table 5 are in agreement with

Table 3. Tolerance limits for coexisting ions in the adsorption of the studied elements.

Coexisting ions	Na^+, K^+	Ca^{2+}, Mg^{2+}	Mn^{2+}, Ni^{2+}	Fe^{3+}, Ba^{2+}
Tolerance limits of ions (mg/L)	1500	300	10	5

Table 4. Analytical precision.

Ion concentration (μg/L) times	Recovery (%)								Average	RSD (%)
	1	2	3	4	5	6	7	8		
Cu^{2+}(10)	98	94	100	97	103	102	99	94	98.4 ± 3.3	3.4
Pb^{2+}(100)	98	91	94	102	92	97	90	105	96.1 ± 5.4	5.6
Zn^{2+}(10)	95	99	92	103	98	99	98	93	97.1 ± 3.6	3.7
Cd^{2+}(10)	98	102	96	99	90	94	103	92	96.8 ± 4.6	4.8

Table 5. Analytical results of biological samples.

Ion	Found by the proposed method (μg/g)[a]	Found by the ET-AAS method (μg/g)[a]
Pig liver		
Cu	21.48 ± 0.05	21.90 ± 0.11
Pb	9.34 ± 0.07	9.69 ± 0.09
Zn	16.50 ± 0.13	16.85 ± 0.08
Cd	0.43 ± 0.09	0.45 ± 0.10
Balsam pear leaves		
Cu	14.66 ± 0.09	14.88 ± 0.08
Pb	30.99 ± 0.12	31.79 ± 0.11
Zn	3.38 ± 0.06	3.45 ± 0.09
Cd	1.22 ± 0.09	1.26 ± 0.13

[a]Average values for three determinations.

Table 6. Analytical results of natural water samples.

Ion	Added (μg/L)	Found (μg/L)	Recovery (%)
Qinghai lake water			
Cu	0	2.21 ± 0.11	–
	5.0	7.06 ± 0.21	97
	10.0	12.28 ± 0.36	100.7
Pb	0	9.88 ± 0.21	–
	5.0	14.69 ± 0.37	96.2
	10.0	19.66 ± 0.45	97.8
Zn	0	5.78 ± 0.16	–
	5.0	10.56 ± 0.31	95.6
	10.0	15.69 ± 0.46	99.1
Cd	0	0.30 ± 0.03	–
	5.0	5.21 ± 0.09	98.2
	10.0	9.91 ± 0.16	96.1
Yellow river water			
Cu	0	–	–
	5.0	5.01 ± 0.21	96
	10.0	9.99 ± 0.15	97.8
Pb	0	4.76 ± 0.09	–
	5.0	9.85 ± 0.19	101.8
	10.0	14.52 ± 0.36	97.6
Zn	0	1.28 ± 0.22	–
	5.0	6.10 ± 0.18	96.4
	10.0	11.30 ± 0.35	100.2
Cd	0	–	–
	5.0	4.96 ± 0.11	98.6
	10.0	9.72 ± 0.32	96.9

[a]Average values for three determinations; –: not detected.

the electrothermal atomic absorption spectrometry method. In the analysis of natural water samples, the standard addition method was used. The analytical results are listed in table 6. The results indicated that the recoveries were reasonable for trace analysis in a range of 96–102%.

4. Conclusion

In this study, a simple, rapid, accurate, selective, and reliable method for the determination of trace levels of Cu(II), Pb(II), Zn(II), and Cd(II) was developed using nanometre TiO_2–DDTC as a solid-phase extractant. The preparation of nanometre TiO_2–DDTC is relatively simple and rapid. This newly developed method has been successfully applied to analyse of trace Cu(II), Pb(II), Zn(II), and Cd(II) in biological and natural water samples. The precision and accuracy of the method are satisfactory.

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