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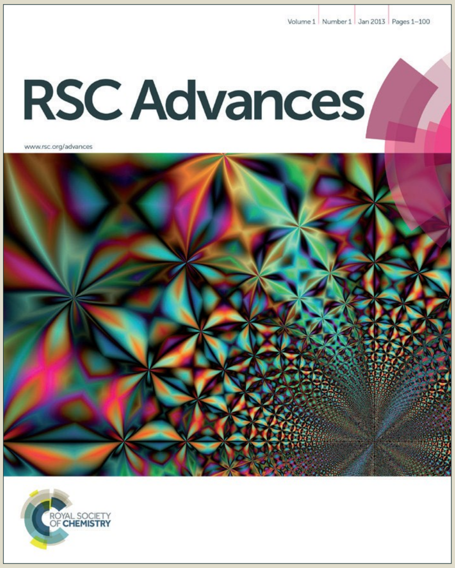

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An integrated system for field analysis of Cd(II) and Pb(II) via preconcentration using nano-TiO_2/cellulose paper composite and subsequent detection with a portable X-ray fluorescence spectrometer

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Abstract An integrative field analytical system was developed for the determination of Pb(II) and Cd(II). The system was based on the hyphenation of a preconcentration process with a portable X-ray fluorescence spectrometer. Preconcentration was accomplished with a composite consisting of TiO_2 and a cellulose film (TCP) which was prepared by immobilizing TiO_2 on cellulose filter paper. TCP is shown to be an adsorbent with high adsorption capacity, i.e., more than 254 μg per piece and 259 μg for Pb(II) and Cd(II), respectively. Under the optimum adsorption conditions, the best adsorption ratios of Pb(II) and Cd(II) were more than 95.5% and 94.4%, respectively. The preconcentration of Pb(II) and Cd(II) was not adversely affected by other metals ions and humic acid. Pb(II) and Cd(II) were then directly quantified by XRF. The calibration plots for both Pb(II) and Cd(II) were linear in the range from 1.0 to 50.0 μg L^{-1}. The detection limits (3σ; for n = 11) for Pb(II) and Cd(II) were 0.69 and 0.51μg L^{-1}, respectively, and the levels of quantification were 2.30 and 1.71 μg L^{-1}, respectively. The preconcentration factor was 10^3. Concentrations of Pb(II) and Cd(II) in drinking water and river waters were determined and found to be in agreement with ICP-MS assays.

Keywords TiO_2 immobilization; preconcentration; heavy metals; X-ray fluorescence; field analysis

1. Introduction

Lead and cadmium contamination in drinking water and natural water has raised public health and environmental safety concerns [1]. The drinking water standards are recommended by the World Health Organization, including 10 μg L^{-1} for Pb and 5 μg L^{-1} for Cd, respectively [2]. Hence, there is a great need to develop a simple, sensitive, selective and inexpensive method for field determination of Pb(II) and Cd(II) in water samples.

In order to determine the concentrations of Pb(II) and Cd(II) in water matrix, different instrumental methods have been developed, including atomic absorption spectrometry [3,4], inductively coupled plasma mass spectrometry [5], high performance liquid chromatography [6], and anodic stripping voltammetry [7]. However, the applications of these techniques are limited on field monitoring, because they usually require expensive and large instruments, expert operators, and sophisticated sample pretreatment, which limit their applications on field monitoring. The major advantages of X-ray fluorescence (XRF) are minimal sample preparation, rapid screen of large numbers of samples, and low cost [8-10]. Moreover, field-portable XRF analyzer is small enough to be used in the field [8-10]. However, XRF exhibites several limitations on aqueous samples, such as short linear range, matrix effects, and poor sensitivity [11]. The interferences for XRF can be attributed to spectral overlaps and/or the limited resolution of the analyzer [10]. XRF has been sparingly used for quantitative analysis, primarily due to LODs that are at best in the 1-10 ppm range for Pb(II) and Cd(II) [10]. Because metal concentrations in natural waters and drinking water standards are at the level of $\mu g\ L^{-1}$, the determination of Pb(II) and Cd(II) in water samples by XRF without preconcentration and elimination of interferences is not possible. Therefore, sample pretreatment using an appropriate adsorbent is a convenient step that makes this analysis possible [12,13].

Nanosized TiO_2 is an excellent preconcentration material because of its large surface area, high adsorption capacity and hypotoxicity [14-17]. However, nanosized TiO_2 powders frequently cause secondary pollutions and an extra microfiltration is necessary for the separation and recovery of TiO_2 powders after sample pretreatment. Nanosized TiO_2 can be immobilized on cellulose filter paper and form a TiO_2 cellulose composite film (TCP), which can offer better stability, feasible continuous operations, easy separation and recycle, and significant decrease of the operation costs [18].

In this work, a practical procedure was developed for the field determination of trace Pb(II) and Cd(II) in water samples by XRF after a preconcentration step. The sophisticated sample pretreatment (e.g., elution or digestion) was avoided and the risk of contamination and errors was reduced. TCP with different metal adsorption capacity was used for preconcentration of Pb(II) and Cd(II) and elimination of spectral overlaps on XRF and then the major obstacle of XRF was overcome.

2. Experimental

2.1 Apparatus and reagents

Both Pb(II) and Cd(II) on TCP were determined by energy dispersive XRF spectrometry using a Thermo Scientific Niton hand-held XRF analyser (XL3t 950, Niton, USA). The instrument was fitted with an X-ray tube with Ag anode target excitation source and a geometrically optimized large area drift detector, and data were transferred using Thermo Scientific Niton data transfer PC software. Inductively coupled plasma mass spectrometry (ICP-MS, 7500cx, Agilent, USA) was used as a comparative method for metal determination. The peristaltic pump (BT00-300T, Baoding Longer Peristaltic Pump Co., Ltd., China) was applied to propel water samples or standard solutions onto the circulating filtration system with TCP to enrich Pb(II) and Cd(II).

The standard solutions of Pb(II) and Cd(II) were prepared from stock standard solutions (GSB G 62071-90 and 62040-90, China, respectively). The certified reference water samples, GBW(E)080402 and GBW(E)080399 (NRCCRM, China) were used. Tetrabutyl titanate (TBOT), ethanol, acetic acid (HAc), HCl, NaOH and Tris(hydroxymethyl)aminomethane (Tris) were analytical grade (Sigma, USA). Cellulose filter paper (qualitative, Φ 7cm) was purchased from Xinhua Paper Industry (Hangzhou, China). River-derived humic acid was purchased from International Humic Substances Society (USA) and dissolved in 0.1 mol L^{-1} NaOH solution. The desired pH was adjusted by HCl or Tris. The plasticware for storing reagent solutions and standards as well as water samples were Teflon PFA (Nalgene, Nalge, USA) or low-density polyethylene

(Nalgene, Nalge, USA) bottles. All containers were soaked in 10% HCl solution at least 24 h before use.

2.2 Preconcentration and determination experiments

The preparation of TCP and a enrichment of Pb(II) and Cd(II) on TCP in a circulating filtration system were according to a literature procedure [18]. After adsorption, the concentration of residual metals was measured by ICP-MS and TCP was washed by water and dried immediately, then the metal contents on TCP were determined by XRF. The adsorption ratio of metals on TCP was given as follows: Adsorption ratio=$(C_0-C_t)/C_0$, where C_0 and C_t were the initial and final concentration of each metal in the solution, respectively.

2.3 Real samples analysis

The water samples, including drinking water and river water, were collected from Zhangzhou, Fujian province, China. The insoluble particles in water samples were excluded by filtration through a 0.22 μm pore (Millipore) cellulose acetate membrane. Adjusting the pH of the solution into 8.0, the filtrates were used for further preconcentration on TCP and determination by XRF. Meanwhile, the filtrates with 2.0 mL of concentrated HNO_3 and 1.0 mL of H_2O_2 (30%) were decomposed by microwaves under a pressure of 10 atm for 10 min. After being cooled naturally to room temperature, the decomposed solution was diluted to 25 mL and then used for metal determination by ICP-MS.

3. Results and discussion

3.1 Characteristic of Nano-TiO_2/Cellulose Paper

The anatase TiO_2 possessed the highest chemisorption capacities among the crystal structures of anatase, rutile, mix crystal (Degussa P25) and amorphism, which could be attributed to its high surface energy, rough surface and unsaturated oxygen bond [19]. Therefore, anatase TiO_2 was immobilized onto cellulose filter paper. Fig. 1 showed representative SEM and EDX images (the previous report by us in Ref. 18) of the cellulose filter paper before and after the impregnation with TiO_2. Compared the changes in the morphology, the surface of filter paper became rough because of depositing a TiO_2 film (shown in **Figure 1a**, **1b and Figure 2**). This result was consistent with EDX images in Ref 1**6.** Cellulose filter paper with large numbers of -OH and -C-O-O- groups could easily combine with Ti ion on its cellulose surface. The interaction between cellulose and TiO_2 was strong enough to keep the stability of TCP during its application [20]. The crystal structure of TiO_2 in TCP was anatase and its average crystallite size was 6.0 nm, according to the calculation on the anatase (101) diraction peaks with the Debye−Scherrer formula **[18]**.

Figure 1

Figure 2

3.2 Optimization of method

To obtain the optimal conditions for the ppreconcentration of Pb(II) and Cd(II), the following parameters were optimized: (a) Sample pH value; (b) adsorption time; (c) dynamic adsorption; (d) adsorption capacity. Respective data and Figures were given in the Electronic Supporting Material. The following experimental conditions were found to give best results: (a) a sample pH value of 8.0 (**Figure S1**); (b) an adsorption time of 3 h (**Figure S2**); (d) a sample volume of 1.0 L (**Figure S3);** (d) a dynamic adsorption of the second-order equation (**Table S1**).

3.3 Adsorption Capacity of Nano-TiO_2/Cellulose Paper for Pb(II) and Cd(II)

The plots of adsorption capacity versus initial metal concentration were shown in **Figure 3**. Obviously, when initial concentrations of heavy metals were increased from 20.0 to 1000.0 μg L^{-1}, positive correlation between the amount of each metals (Pb(II) and Cd(II)) adsorbed by TCP and the equilibrium concentration of each metal in sample solution was obtained, and the adsorption rates of each metals were more than 90.0%. When metal concentration was 1000.0 μg L^{-1}, TCP did not reach its saturation adsorption for Pb(II) and Cd(II), so the adsorption capacity of TCP for Pb(II) and Cd(II) were more than 254 μg and 259 μg, respectively.

Figure 3

3.4 Evaluation of interference

As the real environmental water samples always contain various organics and inorganics, some potentially interfering ions were investigated

In order to investigate the preconcentration and determination of Pb(II) and Cd(II) from their binary mixtures with diverse interference ions, an aliquot of solutions (1.0 L) containing 20.0 μg L^{-1} of Pb(II) and Cd(II) and interference ions were treated according to our recommended procedure. The results indicated that no interference was observed when Na(I), K(I)(1500 fold), Ca(II), Mg(II) (250 fold), Cu(II), Ni(II), Zn(II) (150 fold), Mn(II), Cr(III), Al(III) (100 fold), Fe(III) (50 fold), nitrate ion, chlorid ion (1000 fold) were added. All the concentrations of these potentially interfering ions were higher than the quality standard of surface water (GB3838-2002, China).

Humic acids (HA) were presented widely in natural waters. They were organic macromolecules with a large number of carboxylic (-COOH) and phenolic (-OH) groups, which could combine heavy metals [21,22]. The influences of humic acids addition (0-20.0 mg·L^{-1}) on the adsorption ratio of Pb(II) and Cd(II) were so limited that they could be ignored (seen in **Figure 4**). HA had little effect on the surface properties of titanate although HA tended to affect competitive adsorption of Pb (II) and Cd (II) due to the formation of HA-metal coordination compounds [21,23], but the stability constant of the surface complex between metals and TiO_2 (anatase) was more than that of HA-Metal complexes [18]. The presence of HA could not affect the XRF signal of Pb(II) and Cd(II) at the concentration range of 3-21 mg L^{-1}.

Figure 4

3.5 Methods performance and analysis of real samples

According to the above mentioned procedure, a series of experiments were conducted to obtain the calibration graph, precision and detection limit for the determination of Pb (II) and Cd (II). The analytical curves consisted of seven points and good correlation coefficients were shown in **Figure 5**. The calibration curves presented linear behavior in the concentration range from 1.0 to 100 μg L^{-1}, for Pb (II) and Cd (II), the curves could be described as M=0.920C-1.992 (R^2=0.997, n=6), and M=1.055C-1.998 (R^2=0.998, n=6), respectively, where M was the amount of metals on TCP, and C was the elemental concentration in the water sample. The detection limits (based on 3σ of the blank determinations, n=11) were 0.69 and 0.51 μg L^{-1} for Pb (II) and Cd (II), respectively, and the levels of quantification were 2.30 and 1.71 μg L^{-1}, respectively. Meanwhile, the certified reference water samples, GBW(E)080401 (certified Cd concentration: 0.10 mg L^{-1}) and GBW(E)080398 (certified Pb concentration: 0.50 mg L^{-1}) were used to validate the above mentioned procedure, and the relative standard error (n=5) were 4.1% and 4.4% for Pb (II) and Cd (II), respectively. As shown in **Table 1**, compared the characteristic data of present method with those reported in Ref. 27-29, the detection limits was notably improved. Though the mehods in Ref. 24-26 had lower detection limits, they were not suitable for field monitoring because of their large instruments, expert operators, and sophisticated sample pretreatment.

Figure 5

Table 1

The real water samples were collected from drinking water and Jiulong River in Zhangzhou, Fujian province, China. The concnetration of Pb (II) and Cd (II) in water samples was determined by our procedure. The comparisons between our method and ICP-MS method were summarized in **Table 2** and **Table 3**. The results of this method The results were in agreement with ICP-MS determinations.

Table 2

Table 3

4. Conclusion

In this study, an integration of TCP and field-portable XRF for the preconcentration and field determination of Pb (II) and Cd (II) in natural water was studied. This method showed high adsorption capacity, inexpensive, simple pretreatment and detection for Pb (II) and Cd (II) without the interference of coexisted metals and humic substances, i.e., the major obstacle of XRF was overcome.

Acknowledgement

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Table 1 Comparison of the published methods with the developed method in this work

Table 2 Determination of Cd(II) by this method and ICP-MS

Table 3 Determination of Pb(II) by this method and ICP-MS

Table 1 Comparison of the published methods with the developed method in this work

Methods	Materials	Linear range (μg L^{-1})		Detection limit (μg L^{-1})		Ref.
		Cd(II)	Pd(II)	Cd(II)	Pd(II)	
Flame atomic absorption spectrometry	Halloysite nanotubes / Fe_3O_4	0.5-50	-	0.27	-	24
Flame atomic absorption spectrometry	3-aminopropyltriethoxysilane-2,4-bis(3,5-dimethylpyrazol)-triazine /Fe_3O_4 nanoparticle	1-100	3-100	0.01	0.7	25
Electrothermal atomic absorption spectrometry	graphene / the zeolite clinoptilolite	0.24-10.3	0.011-0.48	0.004	0.07	26
Fluorescence spectrometry	2,2-dipicolylamine	0-1124	0-2072	4.0	8.1	27
Electrochemical sensor	graphene/polyaniline/polystyrene nanoporous fibe	10-500	10-500	4.43	3.30	28
X-ray fluorescence spectrometry	multiwalled carbon nanotubes	0-50	0-50	1.0	2.1	29
X-ray fluorescence spectrometry	Nano-TiO_2/cellulose paper	1.0-50	1.0-50	0.69	0.51	This work

Table 2 Determination of Cd(II) by this method and ICP-MS

Water samples	Add (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	Found by ICP-MS (μg L^{-1})
Drinking water	0	0.65±0.07	-	0.70
	1.0	1.58±0.21	93.0	1.61
	2.0	2.58±0.14	96.5	2.72
Jiulongjiang water	0	0.91±0.09	-	0.86
	1.0	1.86±0.22	95.0	1.79
	2.0	2.80±0.16	94.5	2..89

232 **Table 3** Determination of Pb(II) by this method and ICP-MS

Water samples	Add (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	Found by ICP-MS (μg L^{-1})
Drinking water	0	-	-	0.07
	1.0	1.09±0.19	109.0	1.11
	2.0	1.95±0.13	97.5	2.09
Jiulongjiang water	0	-	-	0.29
	1.0	1.16±0.16	116.0	1.32
	2.0	1.88±0.13	94.0	2.43

Figure Captions

Figure 1 SEM images of cellulose filter paper (a) and TiO_2/cellulose paper (b)

Figure 2 EDX images of cellulose filter paper and TiO_2/cellulose paper

Figure 3 Adsorption capacity of Pb(II) and Cd(II) by TiO_2/cellulose paper

Figure 4 Effect of humic acid on the adsorption of Cd (II) and Pb (II) (C_{metal}=200 μg L^{-1}， pH=8.0； t=3 h； V=1.0 L)

Figure 5 Calibration curves of Cd (II) and Pb (II)

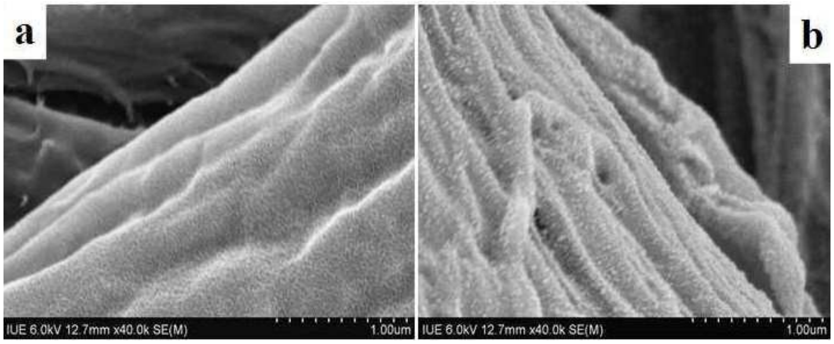

Figure 1 SEM images of cellulose filter paper (a) and TiO_2/cellulose paper (b)

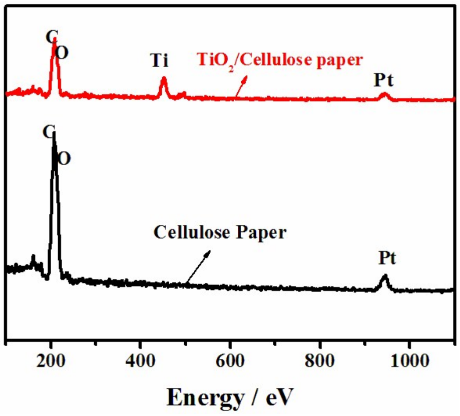

Figure 2 EDX images of cellulose filter paper and TiO_2/cellulose paper

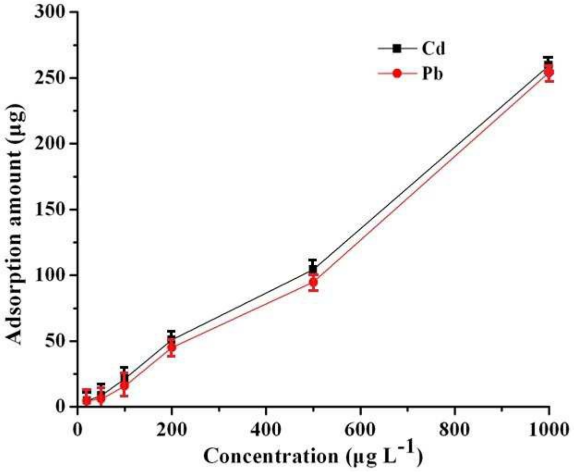

Figure 3 Adsorption capacity of Pb(II) and Cd(II) by TiO_2/cellulose paper

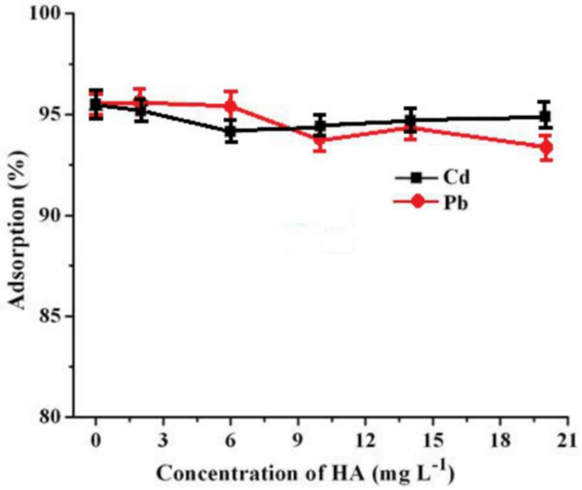

Figure 4 Effect of humic acid on the adsorption of Cd (II) and Pb (II)

(C_{metal}=200 μg L^{-1}， pH=8.0； t=3 h； V=1.0 L)

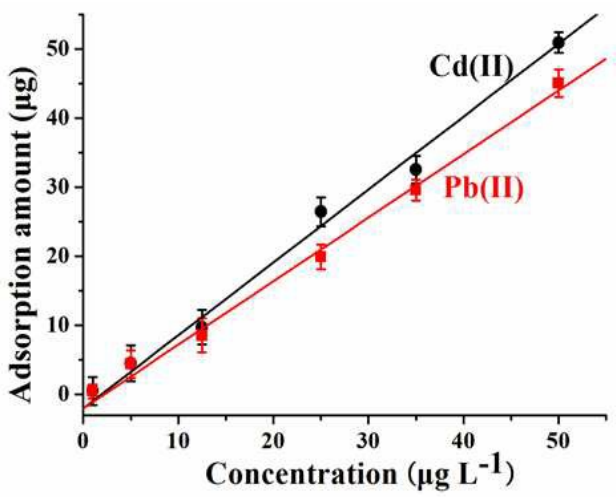

Figure 5 Calibration curves of Cd (II) and Pb (II)