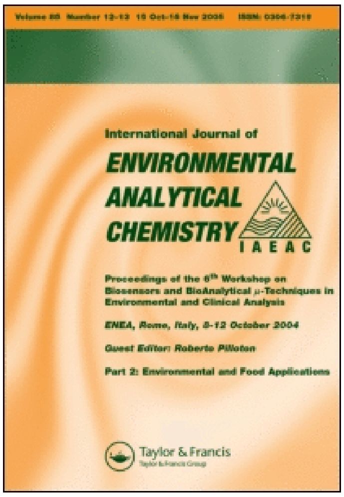

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Selective solid phase extraction of trace cadmium(II) and lead(II) from biological and natural water samples by ofloxacin-modified-silica gel

Yuemei Cui[ab]; Xijun Chang[a]; Xiangbing Zhu[a]; Xiaojun Zou[ac]
[a] Department of Chemistry, Lanzhou University, Lanzhou, P.R. China [b] Jining Bureau of Quality and Technical Supervision, Jining, P.R. China [c] Shandong Lukang Pharmaceutical Company Limited, Jining, P.R. China

To cite this Article Cui, Yuemei , Chang, Xijun , Zhu, Xiangbing and Zou, Xiaojun(2008) 'Selective solid phase extraction of trace cadmium(II) and lead(II) from biological and natural water samples by ofloxacin-modified-silica gel', International Journal of Environmental Analytical Chemistry, 88: 12, 857 — 868

To link to this Article: DOI: 10.1080/03067310802208360

URL: http://dx.doi.org/10.1080/03067310802208360

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 12, 15 October 2008, 857–868

Selective solid phase extraction of trace cadmium(II) and lead(II) from biological and natural water samples by ofloxacin-modified-silica gel

Yuemei Cui[ac], Xijun Chang[a]*, Xiangbing Zhu[a] and Xiaojun Zou[ab]

[a]*Department of Chemistry, Lanzhou University, Lanzhou, P.R. China;* [b]*Shandong Lukang Pharmaceutical Company Limited, Jining, P.R. China;* [c]*Jining Bureau of Quality and Technical Supervision, Jining, P.R. China*

(*Received 15 January 2008; final version received 14 May 2008*)

Ofloxacin was successfully used as a chemical modifier to improve the reactivity of silica gel in terms of selective binding and extraction of heavy metal ions. This new functionalised silica gel (SG-ofloxacin) was as an effective sorbent for the solid-phase extraction (SPE) of Cd(II) and Pb(II) in biological and natural water samples and their determination by inductively coupled plasma optical emission spectrometry (ICP-OES). Experimental conditions for effective adsorption of trace levels of Cd(II) and Pb(II) were optimised with respect to different experimental parameters using the batch and column procedures. The time for 70% sorption for Cd(II) and Pb(II) was less than 2 min. Complete elution of the adsorbed metal ions from the SG-ofloxacin was carried out using 2.0 mL of 0.5 mol L^{-1} of HCl. Common coexisting ions did not interfere with the separation and determination at pH 4.0. The maximum static adsorption capacity of the sorbent at optimum conditions was found to be 39.17 and 48.69 mg g^{-1} for Cd(II) and Pb(II), respectively. The detection limits of the method were found to be 0.29 and 0.13 ng mL^{-1} for Cd(II) and Pb(II), respectively. The relative standard deviation (RSD) of the method under optimum conditions was lower than 3.0% ($n = 5$). The method was applied to the recovery of Cd(II) and Pb(II) from the certified reference material (GBW 08301, river sediment) and to the simultaneous determination of these cations in different water and biological samples with satisfactory results and yielding 100-folds enrichment factor.

Keywords: silica gel; ofloxacin; Cd(II), Pb(II); solid-phase extraction (SPE); ICP-OES

1. Introduction

Heavy metals in water and food have been a major preoccupation for many years because of their toxicity towards aquatic life, human beings and the environment. The International Agency for Research on Cancer classified cadmium as a human carcinogen [1] and lead compounds are known to be highly toxic especially to children whose intestinal absorption of Pb(II) is more efficient than adults [2]. Cadmium and lead enters the organism primarily via the alimentary and respiratory tract. The sources of these metals are food, drinking water and air [3], so extraction and removal of toxic heavy metal ions from various matrices at trace level is of paramount importance [4,5]. Due to the very low concentration of most elements in environmental samples, their separation and

---

*Corresponding author. Email: cuiyuem03@lzu.cn; cuiyuem@163.com

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802208360
http://www.informaworld.com

sensitive determination necessitate the use of a preconcentration or trace enrichment method [6–8].

The traditional separation and preconcentration methods for metal ions include liquid–liquid extraction, coprecipitation, ion exchange, etc. These methods often require large amount of high-purity organic solvents, some of which are harmful to health and cause environmental problems. Nowadays, the SPE method is one of the most effective multi-elemental preconcentration methods because of its advantages such as ease of use, high preconcentration factor and flexibility to choose the solid phase for optimum results [9]. Hence, SPE has been widely used for the isolation and concentration of target analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry [10].

SPE is mainly based on the utilisation of inorganic and organic solid sorbents such as XAD resins [11–13], ion exchange resins [14], silica gel [15,16], cellulose derivatives [17], polyurethane foam [18], active carbon [19], nanometer SiO_2 [20] and rice husks [21]. Extraction and removal of metal ions by these sorbents is well known and mainly based on the possible surface reactivity and adsorptive characters incorporated into these solid phases [22]. However, the basic disadvantage of these solid sorbents is the lack of metal selectivity, which leads to high interference of other existing species with the target metal ion(s) [23]. To overcome this problem, a chemical or physical modification of the sorbent surface with some organic moieties, is usually used to load the surface with some donor atoms such as oxygen, nitrogen, sulphur and phosphorus [24]. Nowadays, the main applications of these modified silicas have been chromatography and preconcentration of trace metals permitting analysis [25,26], such as aminothioamidoanthraquinone [27], glycerol [28], 1,5-diphenylcarbazide [29], 2,4,6-trimorpholino-1,3,5-triazin [30]. There are several recent reports on the use of functionalised silica gel for metal enrichment. The modified silica gel generally exhibits sorption capacities higher than those of organic polymer-based resins. On silica gel, reactive sites exist in large number and, therefore, the number of organic molecules immobilised is high, which results in good sorption capacity for metal ions.

In this report, the new sorbent of SG-ofloxacin was synthesised by a simple and a fast one-step reaction. The sorbent of SG-ofloxacin has a high sorption capacity for the solid-phase extraction of Cd(II) and Pb(II) which were determined by ICP-OES. Parameters that can affect the adsorption and elution efficiency of the metal ions were studied in batch and column modes. Then, the method was validated by analysing the standard reference material (GBW 08301, river sediment) and applied to the analysis of water and biological samples with satisfactory results.

2. Experimental

2.1 *Apparatus*

An IRIS Advantage ER/S inductively coupled plasma spectrometer (TJA, USA) was used for all metal-determinations. The operation conditions and the wavelengths were summarised in Table 1.

An electrothermal atomic absorption spectrometry (ET-AAS) (WFX-1D, China) was used.

The pH value was 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).

Table 1. Instrumental and operating conditions for ICP-OES measurements.

Parameter		Type or amount
R.F. Power (kw)		1.15
Carrier gas (Ar) flow rate (L $\mathrm{min^{-1}}$)		0.6
Auxiliary gas (Ar) flow rate (L $\mathrm{min^{-1}}$)		1.0
Coolant gas (Ar) flow rate (L $\mathrm{min^{-1}}$)		14
Nebulizer flow (psi)		30
Pump rate (r $\mathrm{min^{-1}}$)		100
Observation height (mm)		15
Integration time (s)	on-axis	20
	off-axis	5
Wavelength (nm)		Cd 226.502 Pb 216.999

A YL-110 peristaltic pump (The General Research Academe of Colored Metal, Beijing, China) was used in the separation/pre-concentration process. A self-made glass microcolumn (10 cm × 4 mm i.d.) was used.

2.2 *Reagents and solutions*

All reagents were of analytical grade and all solutions were prepared with double distilled water. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with double distilled water, according to a published procedure [31].

Metal ions (1 mg $\mathrm{mL^{-1}}$) solutions were prepared by dissolving analytical grade salts in double distilled water with addition of hydrochloric acid and further diluted daily prior to use. Ofloxacin was used in this work (Shandong Lukang Pharmaceutical Company Limited, Jining, China). Silica gel (80–120 mesh, Qingdao Ocean Chemical Company, Qingdao, China) and 3-chloropropyltrimethoxysilane (CPTMS, Qingdao Ocean University Chemical Company, Qingdao, China) were used to prepare the ion-imprinted functionalised sorbent. The reference material (GBW 08301, river sediment) was obtained from the National Research Center for Certified Reference Materials (Beijing, China).

2.3 *Synthesis of the sorbent*

Silica gel was first activated by refluxing with concentrated hydrochloric acid for 4 h, and then it was filtered off and washed repeatedly with double distilled water several times until acid-free and then dried in an oven at 160°C for 8 h. The activated silica gel was further homogenised by milling for 2 h.

The ofloxacin-SG sorbent was prepared by a procedure shown in Figure 1. Activated silica gel was functionalised with 3-chloropropyltrimethoxysilane [32] to produce CPSG.

The sorbent was prepared by adding 5 g of CPSG to 1 g ofloxacin, dissolved in 5 mL dimethylsulfoxide (DMSO) and 70 mL of methanol, and stirring the mixture under reflux for 8 h. In this procedure, ofloxacin was superfluous so the reaction was complete. The product of sorbent thus formed was washed thoroughly with DMSO, methanol and dried at 70°C for 7 h [33].

2.4 *Sample preparation*

Yellow River water was collected from Yellow River, Lanzhou, China. Qinghai Lake water was collected from Qinghai Lake, Qinghai, China. The water sample was 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.

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. A 1.000 g pig liver or balsam pear leaves sample was weighted and transferred into a digestion tube, and then 5 mL of concentrated HNO_3 was added to it. The tube was left at room temperature for one night. Then it was placed in a digester block and heated slowly until the temperature was up to 165°C. This temperature was maintained until the evolution of brown fumes ceased. After the tube was cooled down, 1.3 mL perchloric acid was added to it. The temperature was raised to 210°C until the evolution of white fumes began. The volume was adjusted to 100 mL with double distilled water when the tube was cooled down [20].

2.5 *Procedure*

2.5.1 *Batch method*

The data are given on the simple mean of three replicates, whereas those of the applications were repeated five times from which the statistical evaluation is obtained. A total of 25 mg of SG-ofloxacin sorbent was suspended with constant stirring for 20 min in 10 mL of 1.0 µg mL^{-1} of Cd(II) and Pb(II) at the desired pH value to facilitate

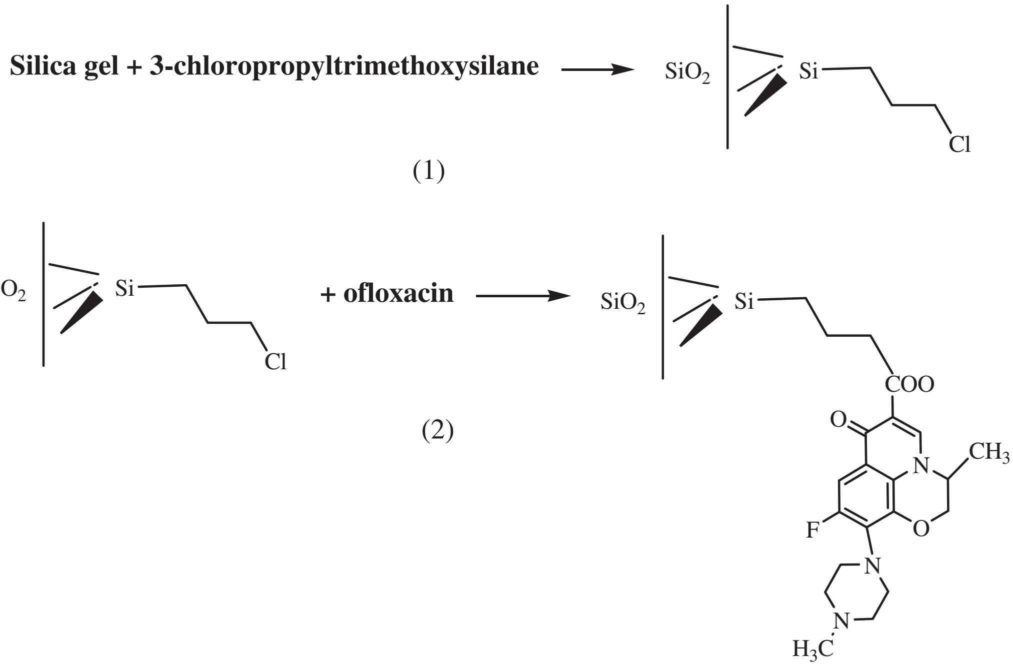

Figure 1. Scheme of ofloxacin-SG sorbent preparation.

adsorption of the metal ions onto the SG-ofloxacin. After extraction, the adsorbent was then eluted with HCl of optimum concentration and the desorbed metal ions were determined by ICP-OES.

2.5.2 *Column method*

About 50 mg of functionalised silica gel adsorbent was packed in a glass column (10 cm × 4 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, the column was treated with 0.5 mol L^{-1} HCl and washed with double distilled water until free from acid. A suitable aliquot of the sample solution containing 1.0 μg mL^{-1} of Cd(II) and Pb(II) in a volume of 50 mL was passed through the column after adjusting its pH to 4.0, at a flow rate of 1.5 mL min^{-1} controlled with a peristaltic pump. The bound metal ions were stripped off from the gel column with 0.5 mol L^{-1} HCl. The concentration of the metal ions in the eluate was determined by ICP-OES.

3. Results and discussion

3.1 *FTIR spectra*

The modified silica gel was confirmed by IR analysis. IR absorption spectrum of SG shows bands at 800, 1095, 1631, 2939 and 3437 cm^{-1}, due to ν(Si–O–Si), longitudinal SiO_2 lattice vibration, $\delta(H_2O)$, $\nu(CH_3)$ and ν(Si–OH), respectively [34].

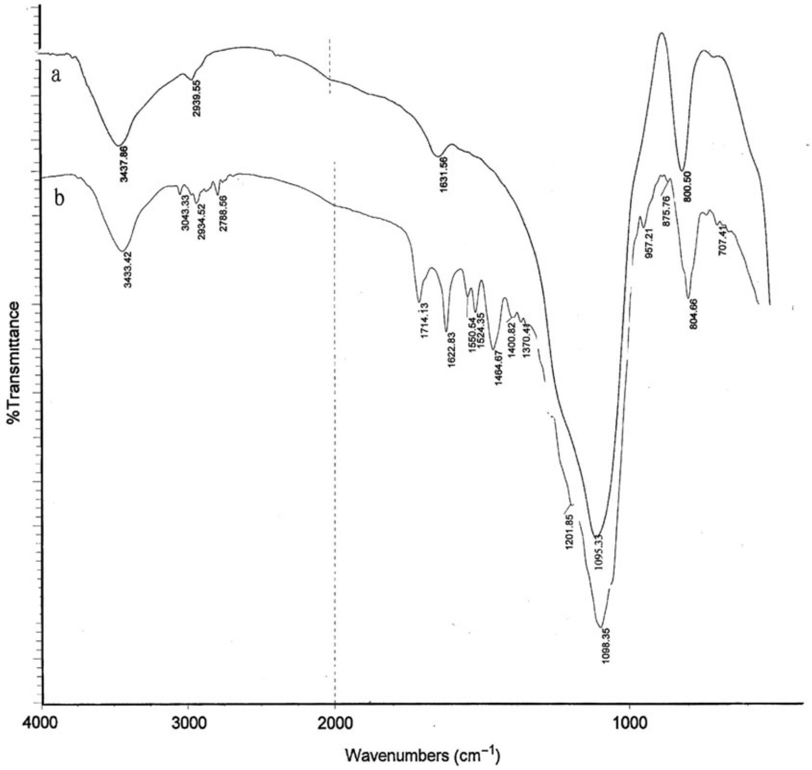

Figure 2. IR spectra of non-modified silica gel (a) and ofloxacin modified silica gel (b).

Comparing the IR spectrum (Figure 2) of the SG-ofloxacin with that of SG, many new bands appeared at 1201, 1400, 1464, 1524, 1550, 1622, 1714, 2788 and 3043 cm^{-1}. The weak band observed at 1201 cm^{-1} can be assigned to the stretching vibration of –C–F and 1400 cm^{-1} due to deformation mode of CH_3– and –CH_2–. The bands around 1464, 1524 and 1550 cm^{-1} are assigned to the benzene ring characteristic vibrations in the ofloxacin. The bands at 1622 and 1714 cm^{-1} are due to ν(C=O) and those at 2788 and 3043 cm^{-1} are caused by CH_3– and –CH_2– stretching vibration in the SG-ofloxacin [35,36].

Consequently, the above analyses of IR spectrum suggest that SG is successfully modified by ofloxacin.

3.2 *Effect of pH*

The acidity of a solution has two effects on metal adsorption. First, protons in acid solution can protonate binding sites of the chelating molecules. Second, hydroxide in basic solution may complex and precipitate many metals. Therefore, the pH of a solution is the first parameter to be optimised.

It was found from Figure 3 that quantitative extraction (>95%) could be obtained from pH 4–7. To avoid hydrolysing at higher pH and determine Cd(II) and Pb(II) simultaneously, pH 4 was chosen for further studies.

3.3 *Effect of shaking time*

The effect of shaking time is another important factor in the evaluation process of the affinity of SG-ofloxacin to Cd(II) and Pb(II). To determine the rate of loading of Cd(II) and Pb(II) on the SG-ofloxacin, the batch procedure was carried out. The contact time was varied from 2 to 40 min. As shown in Figure 4, the adsorption of Cd(II) and Pb(II) was over 95% sorption during the first 15 min. It indicated that the kinetics of adsorption is very fast.

3.4 *Effect of the mass of sorbent*

To test the effect of extractant mass on quantitative retention of analytes, different amounts of sorbent (range from 5 to 40 mg) were added into solutions following the

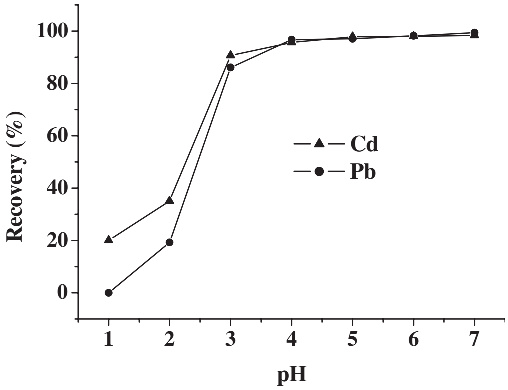

Figure 3. Effect of pH on analytes recovery of 1.0 μg mL^{-1} Cd(II) and Pb(II) after separation on ofloxacin-SG. Other conditions: 25 mg SG-ofloxacin, shaking time 20 min, temperature 25°C.

batch procedure. Quantitative recoveries (>95%) for the examined analytes were obtained in range of 20–40 mg of sorbent. Quantitative retention was not obtained when the mass of extractant was smaller than 20 mg. In order to obtain the quantitative recoveries (>95%) and use little mass of sorbent, 25 mg of sorbent were selected for further studies.

3.5 *Effect of flow rate*

The flow rate of sample solutions containing the Cd(II) and Pb(II) through the packed volume is a very important parameter because the retention of elements on adsorbent depends upon the flow rate of the sample solutions. Its effect was investigated under the optimum conditions (pH, eluent, etc.) by the column method. The flow rates were adjusted in the range of 0.5 to 2.5 mL min^{-1}. As shown in Figure 5, the flow rate had strong influence on the sorption of Cd(II) and Pb(II). The too small flow rates were not employed to avoid the long extraction time. However, at flow rates greater than 1.5 mL min^{-1}, there was a decrease in the percentage of adsorption; probably the metal ions could not

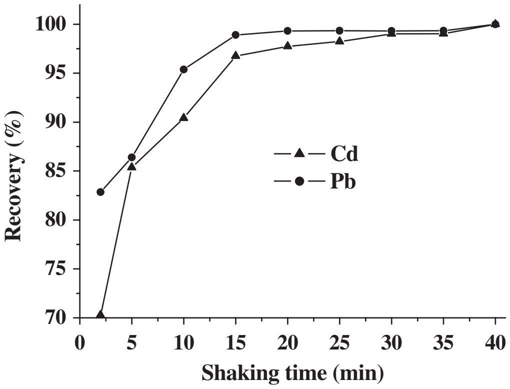

Figure 4. Effect of shaking time on analytes recovery of 1.0 μg mL^{-1} Cd(II) and Pb(II) after separation on SG-ofloxacin at pH 4.0. Other conditions: 25 mg Ofloxacin-SG, temperature 25°C.

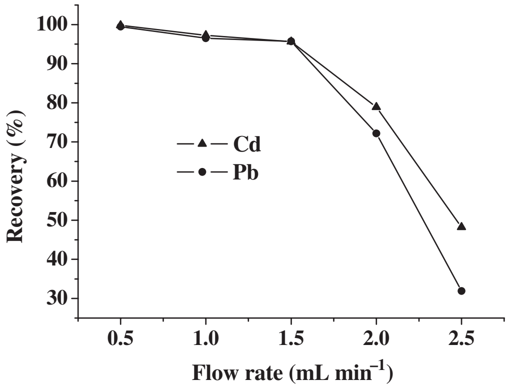

Figure 5. Effect of flow rate on analytes recovery of Cd(II) and Pb(II). Other conditions: sample volume 50 mL, temperature 25°C.

sufficiently equilibrate with the sorbent. Thus, a flow rate of 1.5 mL min^{-1} was selected in this work.

3.6 *Adsorption capacity*

The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from the solutions [37]. The adsorption capacities of various metal ions probably differ due to their size, degree of hydration and the value of their binding constant with the ligand immobilised onto the matrix. The capacity study was adopted from the paper recommended by Maquieira *et al.* [38]. 20 mg of sorbent was equilibrated with a series of various concentrations of Cd(II) and Pb(II) ions solutions and the recommended procedure (batch method) described above was applied. In order to reach 'saturation', the initial metal ions concentrations were increased until the plateau values (adsorption capacity values) were obtained. The maximum of adsorption capacities of the sorbent determined from the saturation condition of the isotherm were 39.17 and 48.69 mg g^{-1} for Cd(II) and Pb(II), respectively.

3.7 *Maximum sample volume, elution condition and enrichment factor*

The enrichment factor was studied by the recommended column procedure using increasing volume of investigated metal ions solution while keeping the total amount of the investigated metal ions loaded constant to 1.0 μg. The maximum sample volume can be up to 200 mL with 95% recovery.

The elution condition was also studied by the batch and column procedures, testing various concentrations $(0.001, 0.01, 0.05, 0.1, 0.25, 0.5, 1.0\,\mathrm{mol\,L^{-1}})$ and HCl volumes $(1, 2, 3, 4, 5, 6, 7\,\mathrm{mL})$ for the desorption of the retained Cd(II) and Pb(II). The results showed that 2.0 mL of 0.5 mol L^{-1} HCl was sufficient for obtaining 95% recovery for Cd(II) and Pb(II) from the sorbent at the same time. So, 2.0 mL of 0.5 mol L^{-1} HCl were used as eluent in further experiments. Because the maximum sample volume is 200 mL, the high enrichment factor was calculated as 100.

3.8 *Effect of coexisting ions*

The effect of different cations and anions on the adsorption of Cd(II) and Pb(II) on the sorbent was studied using the batch procedure. As shown in Table 2, an excess of 4000-fold Cl^-, NO_3^-, NH_4^+; 2000-fold K^+, Na^+, Ca^{2+}, Mg^{2+}; 1000-fold SO_4^{2-}; 500-fold Co^{2+}, Mn^{2+}; 100-fold Cu^{2+}, Zn^{2+}, Cr^{3+} and 50-fold PO_4^{3-}, Ni^{2+}, Fe^{3+} ions do not affect the separation process. High concentrations of Fe^{3+} showed strong competition with the investigated metal ions and can be overcome by adding NH_4F as masking agent. The results showed that high concentrations of the ions tested did not interfere with separation and determination of the analytes. This was due to the low adsorbing capacity or rates for interfering ions.

3.9 *Analytical accuracy, precision and detection limit*

The proposed procedure (column method) was applied to the analysis of Cd(II) and Pb(II) in the certified reference material that was river sediment (GBW 08301, China).

The results shown in Table 3 were compared with the certified values using a *t*-test at 95% confidence limits [39]. Good agreement was obtained between the estimated content by the proposed method and the certified values. The results also indicated that the developed pre-concentration method for Cd(II) and Pb(II) was not affected by potential interferences from the major matrix elements of the analysed standard materials.

Under the selected conditions, 11 portions of standard solutions (10 mL) were enriched and analysed simultaneously following the column procedure. The detection limits (blank + 3σ) of the method defined by IUPAC was found to be 0.29 and $0.13\,\mathrm{ng\,mL^{-1}}$ for Cd(II) and Pb(II), respectively. The quantification limit (blank + 10σ) of the method was found to be 0.65 and $0.30\,\mathrm{ng\,mL^{-1}}$ for Cd(II) and Pb(II), respectively. The relative standard deviation (RSD) of the 11 replicate determinations was lower than 3.0% for $1.0\,\mu\mathrm{g\,mL^{-1}}$ Cd(II) and Pb(II), which indicated that the method had good precision for the analysis of trace Cd(II) and Pb(II) in solution samples.

Table 2. Effect of foreign ions on percent recovery of $1.0\,\mu\mathrm{g\,mL^{-1}}$ Cd(II) and Pb(II) on the sorbent followed by elution with 2.0 mL $0.5\,\mathrm{mol\,L^{-1}}$ HCl.

		Recovery of analytes (%)	
Coexisting ions	Concentration (μg mL^{-1})	Cd^{2+}	Pb^{2+}
Cl^-	4000	97.01	98.49
NO_3^-	4000	96.92	99.01
SO_4^{2-}	1000	95.94	96.52
PO_4^{3-}	50	94.35	95.67
NH_4^+	4000	97.11	99.07
Na^+	2000	95.02	98.12
K^+	2000	95.33	97.73
Mg^{2+}	2000	95.37	97.06
Ca^{2+}	2000	95.71	95.41
Co^{2+}	500	96.70	94.96
Mn^{2+}	500	95.02	96.78
Cr^{3+}	100	95.50	95.38
Cu^{2+}	100	94.25	96.17
Zn^{2+}	100	95.41	95.22
Ni^{2+}	50	92.83	93.45
Fe^{3+}	50	95.27	96.03

Table 3. Analysis of standard reference material (GBW08301).

Analyte	Found by present method (μg g^{-1})[a]	Certified value (μg g^{-1})[b]	Relative error (%)
Cd(II)	2.41 ± 0.16	2.45 ± 0.3	−1.63
Pb(II)	77 ± 6.0	79 ± 12.0	−2.53

Notes: [a]$\bar{x} \pm s(n = 5)$. $\bar{x}$ average value for five determinations ± standard deviation; [b]reference value.

Table 4. Analytical results for the determination of Cd(II) and Pb(II) in water samples ($n = 5$).

Water samples	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)
Yellow River water			
Cd(II)	0	0.53 ± 0.02	–
	5	5.29 ± 0.01	95.2
	10	10.38 ± 0.05	98.5
Pb(II)	0	3.08 ± 0.10	–
	5	7.97 ± 0.09	97.8
	10	12.97 ± 0.20	98.9
Qinghai Lake water			
Cd(II)	0	–	–
	5	4.89 ± 0.02	97.8
	10	9.83 ± 0.04	98.3
Pb(II)	0	6.57 ± 0.20	–
	5	11.49 ± 0.30	98.4
	10	16.33 ± 0.50	97.6

Note: The value following "±" is the standard deviation.

Table 5. Analytical results of biological sample ($n = 5$).

Ion	Found by the proposed method ($\mu g\,g^{-1}$)	Found by ET-AAS method ($\mu g\,g^{-1}$)
Pig liver		
Cd	–	–
Pb	11.06 ± 0.07	11.29 ± 0.10
Balsam pear leaves		
Cd	0.04 ± 0.01	0.04 ± 0.02
Pb	20.87 ± 0.20	21.09 ± 0.14

3.10 *Application of the method*

The proposed method was then applied for the determination of Cd(II) and Pb(II) in biological and natural water samples by ICP-OES. Meanwhile, for the analysis of natural water samples, the standard addition method was used (Table 4). The analytical results for biological samples were in agreement with the ET-AAS method (Table 5). The results show that the proposed method is suitable for the pre-concentration of Cd(II) and Pb(II) in biological and natural water samples.

3.11 *Comparison with other sorbents*

The sorption capacities of SG-ofloxacin of Pb(II) and Cd(II) were compared with those of other important matrices used for the separation and preconcentration of these metals (Table 6). SG-ofloxacin exhibits comparable or better capacity values than a large number of the metal–matrix combination. Only, ethyleneimine showed evident higher adsorption capacity.

Table 6. Comparison of sorption capacity of some sorbents used for the separation and preconcentration of Cd(II) and Pb(II).

		Sorption capacity (mg g^{-1})		
Support	Ligand	Pb(II)	Cd(II)	References
Silica gel	1,8-Dihydroxyanthraquinone	15.73	7.86	[40]
	N-[3-(trimethoxysilyl)propyl]-ethylenediamine	38.08	–	[41]
	Poly(ethyleneimine)	35.19	–	[42]
	8-Hydroxyquinoline	25.25	8.25	[43]
	5-Benzylidene-2-thiobarbituric acid	12.42	12.32	[44]
	Gallic acid	12.63	6.09	[45]
	Zirconium(IV) Phosphate	2.07	0.56	[46]
	Ethyleneimine	262.89	114.24	[47]
	Ofloxacin	48.69	39.17	This work

4. Conclusions

A selective and sensitive method was established for the determination of trace levels of Cd(II) and Pb(II) in biological as well as natural water samples based on silica gel modified with ofloxacin as a solid phase extractant. Quantitative enrichment of the analytes from very dilute aqueous matrices was achieved with this method. The most important characteristic of the silica gel-ofloxacin is its excellent selectivity towards Cd(II) and Pb(II) over other ions. In addition, the preparation of SG-ofloxacin is relatively simple and rapid. The data in this paper revealed that the proposed method is simple, sensitive and reliable.

References

[1] International Agency for Research on Cancer (IARC), Scand. J. Work. Environ. Health **19**, 360 (1993).

[2] Department of Environment and Conservation Incorporating Environment Protection Authority, *How Lead Gets into People*, August 2003, <http://www.epa.nsw.gov.au/leadsafe/leadinf3.htm>.

[3] H.G. Seiler, A. Sigel, and H. Sigel, *Handbook on Toxicity of Inorganic Compounds* (Marcel Dekker, New York, 1998).

[4] C. Kantipuly, S. Katragadda, A. Chow, and H.D. Gesser, Talanta **37**, 491 (1990).

[5] P.E. Warwick, I.W. Croudace, and A.G. Howard, Anal. Chem. **72**, 3960 (2000).

[6] A. Mitsuike, *Methods for Preconcentration of Trace Elements* (Khimiya, Moscow, 1986).

[7] C.C. Huang and M.H. Yang, Anal. Chem. **69**, 3930 (1997).

[8] C.H. Lee, J.S. Kin, M.Y. Suh, and W. Lee, Anal. Chim. Acta **339**, 303 (1997).

[9] K. Pyrzynska and M. Trojanowicz, Crit. Rev. Anal. Chem. **29**, 313 (1999).

[10] J. Haginaka, Trends Anal. Chem. **24**, 407 (2005).

[11] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, and J. Liu, Talanta **62**, 207 (2004).

[12] Y.S. Kim, G. In, C.W. Han, and J.M. Choi, Microchem. J. **80**, 151 (2005).

[13] V.A. Lemos, D.G. da Silva, A.L. de Carvalho, D.D. Santana, G.D. Novaes, and A.S. dos Passos, Microchem. J. **84**, 14 (2006).

[14] O. Abollino, M. Aceto, C. Sarzanini, and E. Mentasti, Anal. Chim. Acta **411**, 223 (2000).

[15] P.K. Jal, S. Patel, and B.K. Mishra, Talanta **62**, 1005 (2004).

[16] A.R. Khorrami, T. Hashempur, A. Mahmoudi, and A.R. Karimi, Microchem. J. **84**, 75 (2006).

[17] V. Gurnani, A.K. Singh, and B. Venkataramani, Talanta **61**, 889 (2003).
[18] P. Pohl and B. Prusisz, Anal. Chim. Acta **508**, 83 (2004).
[19] I. Narin, M. Soylak, L. Elci, and M. Dogan, Talanta **52**, 1041 (2000).
[20] Y. Cui, X. Chang, Y. Zhai, X. Zhu, H. Zheng, and N. Lian, Microchem. J. **83**, 35 (2006).
[21] C.R.T. Tarley, S.L.C. Ferreira, and M.A.Z. Arruda, Microchem. J. **77**, 163 (2004).
[22] P. Liu, Q. Pu, Z. Hu, and Z. Su, Analyst **125**, 1205 (2000).
[23] H.A. Mottola and J.R. Steimetz, *Chemically Modified Surfaces* (Elsevier, Amsterdam, 1992).
[24] M.E. Mahmoud, M.M. Osman, and M.A. Amer, Anal. Chim. Acta **413**, 33 (2000).
[25] C. Ekinci and U. Köklu, Spectrochim. Acta Part B **55**, 1491 (2000).
[26] L.N.H. Arakaki, L.M. Nunes, J.A. Simoni, and C. Airoldi, J. Colloid Interface Sci. **228**, 46 (2000).
[27] W. Ngeontae, W. Aeungmaitrepirom, and T. Tuntulani, Talanta **71**, 1075 (2007).
[28] A. Safavi, N. Iranpoor, N. Saghir, and S. Momeni, Anal. Chim. Acta **569**, 139 (2006).
[29] A. Khan, F. Mahmood, M.Y. Khokhar, and S. Ahmed, React. Funct. Polym. **66**, 1014 (2006).
[30] T. Madrakian, A. Afkhami, M.A. Zolfigol, and M. Solgi, J. Hazard. Mater. **128**, 67 (2006).
[31] D.P.H. Laxen and R.M. Harrison, Anal. Chem. **53**, 345 (1981).
[32] R.D. Badley, W.T. Ford, F.J. McEnroe, and R.A. Assinks, Langmuir **6**, 792 (1990).
[33] M.M. Hamed and Kh. Abou-El-Sherbini, Talanta **68**, 1550 (2006).
[34] Kh. Abou-El-Sherbini, I. Kenawy, M. Hamed, R. Issa, and R. Elmorsi, Talanta **58**, 289 (2002).
[35] D. Lin-Vien, N.B. Colthup, W.G. Fateley, and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules* (Academic Press, London, 1991).
[36] R.W. Mitchell, J.C. Burr Jr, and J.A. Merritt, Spectrochim. Acta **195**, 23A (1967).
[37] K. Dev and G.N. Rao, Talanta **42**, 591 (1995).
[38] A. Maquieira, H. Elmahadi, and R. Puchades, Anal. Chem. **66**, 3632 (1994).
[39] J.C. Miller and J.N. Miller, *Statistics for Analytical Chemistry* (Ellis Horwood, New York, 1988).
[40] Anupama Goswami and Ajai K. Singh, Talanta **58**, 669 (2002).
[41] N. Chiron, R. Guilet, and E. Deydier, Wat. Res. **37**, 3079 (2003).
[42] M. Ghoul, M. Bacquet, and M. Morcellet, Wat. Res. **37**, 729 (2003).
[43] A. Goswami, A.K. Singh, and B. Venkataramani, Talanta **60**, 1141 (2003).
[44] M.E. Mahmoud, S.S. Haggag, and A.H. Hegazi, J. Colloid Interface Sci. **300**, 94 (2006).
[45] F. Xie, X. Lin, X. Wu, and Z. Xie, Talanta **74**, 836 (2008).
[46] N. Nagata, L.T. Kubota, M.I.M.S. Bueno, and P.G. Peralta-Zamora, J. Colloid Interface Sci. **200**, 121 (1998).
[47] L.N.H. Arakaki, V.L.S. Augusto Filha, K.S. de Sousa, F.P. Aguiar, M.G. da Fonseca, and J.G.P. Espínola, Thermochimica Acta **440**, 176 (2006).