

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

Determination of Cadmium in Seawater by Vapor Generation Atomic Fluorescence Spectrometry After Online Preconcentration with a Novel Alkyl Phosphinic Acid Resin

Qiang Fu^a; Limin Yang^a; Qiuquan Wang^{ab}

^a Department of Chemistry & The MOE Key Laboratory of Modern Analytical Sciences, Xiamen University, Xiamen, China ^b State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, China

Online publication date: 24 September 2010

To cite this Article Fu, Qiang , Yang, Limin and Wang, Qiuquan(2007) 'Determination of Cadmium in Seawater by Vapor Generation Atomic Fluorescence Spectrometry After Online Preconcentration with a Novel Alkyl Phosphinic Acid Resin', *Spectroscopy Letters*, 40: 3, 547 — 557

To link to this Article: DOI: 10.1080/00387010701296636

URL: <http://dx.doi.org/10.1080/00387010701296636>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Determination of Cadmium in Seawater by Vapor Generation Atomic Fluorescence Spectrometry After Online Preconcentration with a Novel Alkyl Phosphinic Acid Resin

Qiang Fu and Limin Yang

Department of Chemistry & The MOE Key Laboratory of Modern
Analytical Sciences, Xiamen University, Xiamen, China

Qiuquan Wang

Department of Chemistry & The MOE Key Laboratory of Modern
Analytical Sciences, Xiamen University, Xiamen, China and State Key
Laboratory of Marine Environmental Science, Xiamen University,
Xiamen, China

Abstract: Vapor generation atomic fluorescence spectrometry (VG-AFS) coupled with online preconcentration on a short column (4.6 mm × 50-mm length) packed with a newly synthesized alkyl phosphinic acid resin (APAR) was developed for the determination of trace Cd in seawater. During the online preconcentration process, Cd in seawater was concentrated on the column while the matrix of seawater was separated flowing out of the column. Cd concentrated on the column was then eluted effectively from the column with 0.1 mol L⁻¹ tartaric acid within 40 s. When the sample volume was 200 mL, an enrichment factor 189 was achieved. The detection limit of this proposed method for Cd is 2.67 ng L⁻¹. The recovery of Cd is 96.6% obtained by spiking the correspondence standard, and the precision (RSD) is 4.34%

Received 23 October 2006, Accepted 23 January 2007

The authors were invited to contribute this paper to a special issue of the journal entitled “Undergraduate Research and Education in Spectroscopy.” This special issue was organized by Associate Editor David J. Butcher, Professor of Chemistry at Western Carolina University, Cullowhee, North Carolina, USA.

Address correspondence to Qiuquan Wang, Department of Chemistry, Xiamen University, Xiamen 361005, China. E-mail: qqwang@xmu.edu.cn

($n = 6$). The established APAR/VG-AFS was applied to the determination of soluble Cd in the seawater around Xiamen Island, China.

Keywords: Alkyl phosphinic acid resin, atomic fluorescence spectrometry, cadmium, online preconcentration, seawater

INTRODUCTION

Cd is well-known to be a crucial toxic element in the environment.^[1] Information about Cd concentration in the environment is very important in evaluation of its pollution level. Atomic spectroscopic methods of high sensitivity and high selectivity have been applied extensively to Cd determination. Among them, electrothermal atomic absorption spectrometry (ET-AAS) and inductively coupled plasma mass spectrometry (ICP-MS) are preferable analytical techniques.^[2–5] However, ET-AAS and ICP-MS often suffer serious physicochemical interferences arising from complicated environmental and biological sample matrix.^[6] Vapor generation is an effective sample introduction technique for eliminating matrix effects when trace Cd was determined.^[7–9] Atomic fluorescence spectrometry is compatible with online vapor generation system as a flow-through detector and has been extensively studied and applied to the determination of Cd in environmental and biological samples.^[10–13] However, although VG-AFS features low cost in instrumentation and consumption compared with ICP-MS, the direct determination of Cd in seawater is still restricted owing to its extremely low concentration (usually at nanogram levels)^[14] and possible matrix effects to VG process. Thus, many preconcentration and separation methods have been employed such as coprecipitation,^[15] preconcentration with chelating resin or cation exchange fibers,^[16,17] and reversed phase chromatography.^[18,19]

Alkyl phosphinic acid has been proved to be an effective extractant for many metals in our previous studies.^[20–22] In the current work, a newly synthesized alkyl phosphinic acid resin (APAR),—which was prepared by chemically bonding the functioning group of the phosphinic acid onto styrene-divinylbenzene copolymer beads via chloromethylation and phosphorylation reactions,—packed column was used for online preconcentration of Cd. It was then coupled online with VG-AFS for achieving sensitive and accurate determination of trace soluble Cd in the coastal seawater of Xiamen Island, southeastern China.

MATERIALS AND METHODS

Apparatus and Reagents

A BRAIC AF-601A (BRAIC Analytical Instrument Co., Beijing, China) atomic fluorescence spectrometer was used throughout for determination of

Cd. High-intensity Cd hollow cathode lamp (General Research Institute for Non-ferrous Metals, Beijing, China) was used as the radiation source (228.8 nm). The AFS system and data acquisition was done by HWH software version 1.0.^[23] The optimum conditions of AFS are summarized in Table 1. Eluant and ultrapure water (UPW) were delivered by a quaternary gradient pump of the Shimadzu LC-2010 HPLC system (Shimadzu, Kyoto, Japan). The seawater samples were pumped through an APAR column by a YSB-III displacement pump (Shanghai Institute of Atomic Nucleus of CAS, Shanghai, China) for preconcentration. All pH measurements were performed by a Mettler Toledo Delta 320 pH meter (Mettler-Toledo Instruments Co. Ltd., Shanghai, China). An ICP-MS equipped with dynamic reaction cell (DRC ICP-MS) (Perkin-Elmer ELAN DRC II, Sciex, Concord, ON, Canada) was also used in this study.

UPW was prepared by a high-pressure reverse osmosis water purification system (18 M Ω , Pen-Tung Sah Micro-Electro-Mechanical System Research Center of Xiamen University). All reagents used in this work were of the highest purity available and at least of analytical grade. Tartaric acid solution was prepared by dissolving an appropriate amount of the corresponding solid into UPW. Sodium tetrahydroborate solution 4% m/v was prepared daily by dissolving KBH₄ (A. R., Fu-chen Chemicals, Tianjin, China) in 2% m/v sodium hydroxide solution and filtered through a 0.45- μ m membrane before use. Hydrochloric acid solution 6% v/v was prepared by diluting concentrated hydrochloric acid (G. R., Shanghai Chemicals, Ltd., Shanghai, China) in UPW. The 1000 mg L⁻¹ stock solutions of Cd were prepared by dissolving high-purity cadmium granule (G. R., Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) in concentrated nitric acid with gentle heating, then diluting to a certain volume with UPW, and then stepwise diluted to get the desired Cd concentration.

Table 1. Optimum conditions of VG-AFS

Parameter	Value
Resonance wavelength (nm)	228.8
PMT voltage (V)	320
HCL current (mA)	60
Auxiliary current (mA)	40
Atomizer temperature	Ambient temperature
Argon flow rate (mL min ⁻¹)	800
Signal process mode	Peak area
NaBH ₄ concentration (m v ⁻¹)	4%
HCl concentration (v v ⁻¹)	6%
NaBH ₄ flow rate (mL min ⁻¹)	2.0
HCl flow rate (mL min ⁻¹)	2.4

Column Preparation

The APAR was synthesized by sequence reaction of a chloromethylation reaction, a phosphorylation reaction, and an acid-catalyzed hydrolytic reaction on styrene–divinylbenzene copolymer bead (8- μm diameter, cross-linking degree is 10%, H&E, Beijing, China). The unit structure is shown in Fig. 1. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 1162 (P = O) and 937 ν_{s} (P-OH). ^{31}P NMR (400 MHz; CDCl_3 ; Me_4Si): δP 64.12 ppm. APAR 0.5 g was packed into a 4.6 mm i.d. \times 50 mm length IT Modular stainless steel column (Isolation Technologies Inc., Hopedail, MA, USA). The adsorption capacity of APAR for Cd was measured by a conventional batch method.^[22]

Sample Collection and Preparation

Seawater samples were collected around and outside the coast of Xiamen Island (24°25'E, 118°08' N). After sampling, the acidity of the seawater was adjusted to pH 6.0 by adding appropriate amount of 1% nitric acid solution and 0.1 mol L^{-1} sodium acetate solution; and then the sample was filtered with a membrane filter of pore size 0.45 μm to get soluble Cd. The samples were stocked in acid-cleaned polyethylene plastic buckets at 4°C in dark before determination.

Online Preconcentration Procedures

The online preconcentration system is shown schematically in Fig. 1. A six-way valve was used for flow path switching. Before sample loading, the column was preconditioned with UPW at flow rate of 1 mL min^{-1} for 3 min; and then the six-way valve was switched to position 1 letting the sample pass through the column for preconcentration and the matrix separation. In the elution step, the six-way valve was switched to position 2, Cd

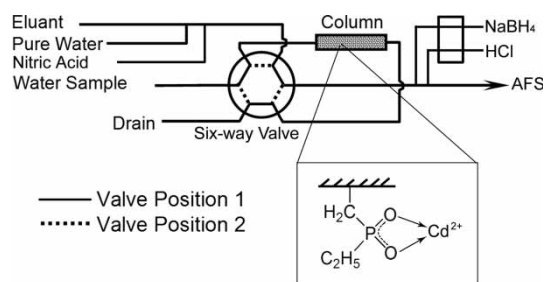


Figure 1. Schematic diagram of the online preconcentration system and the unit structure of APAR.

retained on the column was eluted with tartaric acid after washing with 1 mL of UPW and then mixed with HCl and NaBH₄/NaOH for vapor generation; finally, Cd vapor was swept by argon into AFS through a gas–liquid separator for determination. Once the elution process completed, 3 mL of 0.1 mol L⁻¹ nitric acid was pumped through the column for stripping the metal ions that have greater capacity factors on the column, for example, rare earth elements.

RESULTS AND DISCUSSION

Preconcentration and Elution conditions

The functional group of APAR is similar to some alkyl phosphinic acid extractants such as bis(2-ethylhexyl)phosphinic acid^[24] and bis(1,1,3,3-tetramethylbutyl)phosphinic acid.^[22] The biggest difference between them is that the alkyl phosphinic acid extractant may form dimer in nonpolar solvent while the phosphinic groups are fixed on the polymer structure through chemical bond. Its pK_a should be between 4.96 of bis(2-ethylhexyl)phosphinic acid and 4.10 of 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester due to the inductive effect of ethyl and aryl-methylene between 2-ethylhexyl and alkoxy of the extractants.^[24] The adsorption mechanism of Cd on APAR should follow the cation exchange mechanism similar to that of the extractant.

The effect of sample acidity on the recovery of Cd by APAR was studied by adjusting the pH values of the samples in a range of 1 to 9 prior to online preconcentration. The adsorption and desorption behavior of Cd on the resin obviously depends on pH. Results indicated that the recovery of Cd increases along with the increase in pH, reaching a plateau (>99%) from pH 6 to 8, and then gradually decreases to 95% at pH 9. The result implies that seawater sample (normally pH > 7) can directly pass the column for preconcentration just after simple filtration in field operation.

Hydroxycarboxylic acids such as citric acid, tartaric acid, and α -hydroxyisobutyric acid are typical complexing ligands for eluting metal ions from ion-exchanger.^[22,25] In this study, tartaric acid was chosen to elute Cd from the APAR column. The elution profile of Cd is shown in Fig. 2. Cd can be eluted entirely from the column by 0.1 mol L⁻¹ tartaric acid within 40 s at a flow rate of 1 mL min⁻¹. Such a small elution volume (about 0.67 mL) makes it possible to use relatively smaller sample volume to achieve high enrichment factor. Increasing the concentration of tartaric acid to 0.2 mol L⁻¹ did not benefit the elution efficiency but led to an obvious decrease of signal due to the stable complex formed by Cd and high-concentration tartaric acid reducing vapor generation efficiency, and the interaction between KBH₄ and tartaric acid^[26] resulting in a decrease of free KBH₄ concentration, which in turn decrease the vapor generation efficiency.

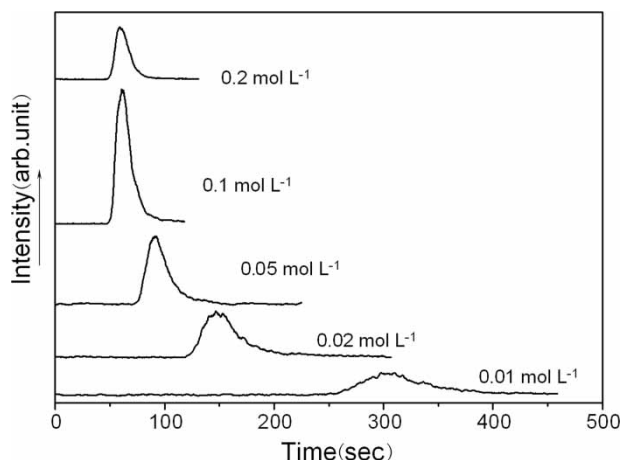


Figure 2. The elution profile of Cd by various concentrations of tartaric acid: Cd concentration, $1 \mu\text{g L}^{-1}$; sample volume, 10 mL; sample flow rate, 3 mL min^{-1} ; eluant flow rate, 1 mL min^{-1} .

Investigation of the effect of elution flow rate indicated that there is no obvious effect on the recoveries of Cd in the range from 0.5 to 2.0 mL min^{-1} . Consequently, 1.0 mL min^{-1} was adopted to suit the sampling rate for AFS determination.

Faster uptake flow rate and smaller volume of the sample will shorten analysis time. The effect of the sample flow rate on the preconcentration efficiency of Cd was tested in the range $1.0\text{--}3.5 \text{ mL min}^{-1}$. The results shown in Fig. 3 indicated that Cd was quantitatively recovered ($>97\%$) at a flow rate ranging from 1.0 to 3.0 mL min^{-1} . Considering that the concentration of Cd in seawater is very low, a large sample volume was usually needed. It was desirable to pump the sample as fast as possible to shorten the analysis time. Thus, a flow rate of 3.0 mL min^{-1} was used as the optimum flow rate.

In order to investigate the effect of sample volumes on the recovery of Cd, 10, 20, 50, 100, 200 mL of sample solutions containing $1 \mu\text{g L}^{-1}$ of Cd were pumped through the column. The results shown in Fig. 3 also suggested that the sample volume should be larger than 50 mL for obtaining satisfactory recovery and precision. When the sample volume was less than 50 mL, low concentration of Cd in the eluent that approaches the detection limit of VG-AFS for Cd, the low peak height made it difficult to integrate the peak area accurately, leading to relatively large experimental error. When the sample volume was larger than 50 mL, Cd was quantitatively recovered ($>98\%$). As mentioned above, the Cd adsorbed on column can be quantitatively eluted by less than 1 mL 0.1 mol L^{-1} tartaric acid, and an enrichment factor of 189 was achievable when the sample volume was 200 mL. In

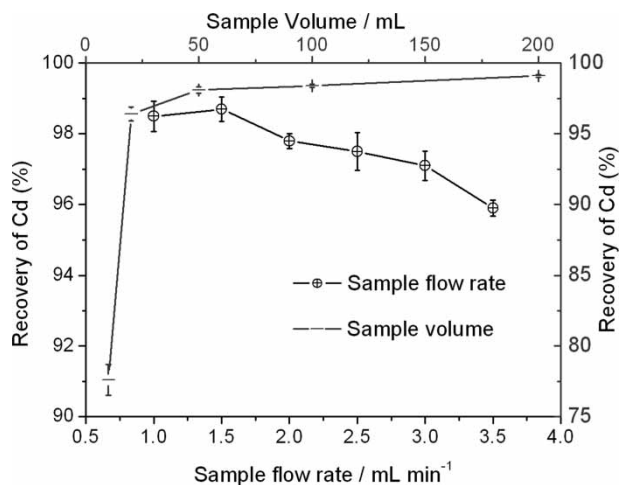


Figure 3. Effect of sample flow rate and sample volume on recoveries of Cd: concentration of Cd, $1 \mu\text{g L}^{-1}$; sample pH, 6.0; eluant, 0.1 mol L^{-1} tartaric acid; elution time, 1 min; error bar, standard deviation ($n = 4$).

order to shorten the analysis time, a sample volume of 100 mL at 3.0 mL min^{-1} was adopted for the preconcentration of Cd in seawater.

Column Capacity and Matrix Separation

The adsorption capacity of the APAR for Cd was measured by conventional batch method. APAR, 100 mg, was equilibrated by shaking for 2 hr in the solution containing excess Cd^{2+} (100 mg L^{-1} , 10 mL) at pH 6.0. Then the solid phase was filtered out and the concentration of Cd^{2+} in the aqueous phase was determined by VG-AFS. The static adsorption capacity of the APAR for Cd was founded to be $9.87 \mu\text{mol g}^{-1}$. This result indicated that the adsorption capacity of the column (about $4.94 \mu\text{mol}$) is sufficient for the preconcentration of trace Cd in seawater. Synthetic seawater sample containing $1 \mu\text{g L}^{-1}$ Cd^{2+} and Na^+ , Mg^{2+} , K^+ , and Ca^{2+} respectively of 10,000, 2000, 500, and 500 mg L^{-1} ^[14] was employed to test the efficiency of matrix separation. ICP-MS was used to determine the matrix ions in the eluate containing Cd. Results indicated that almost no matrix ions were detected significantly in the eluate, suggesting that they flowed out of the column when Cd was adsorbed on the column, while the recovery of Cd was more than 98%. It should be noted that some soluble trace metal ions such as REEs(III), Cu(II), Pb(II), Bi(III), In(III), Hg(II), U(VI), and Th(IV) could also adsorb on the column. The adsorption of these onto the column would occupy some active sites of the resin.

However, they could be eluted effectively out of the column by suitable concentration of HNO₃, mercaptoethanol, or l-cysteine and EDTA–Na₂, respectively.

Method Evaluation and Analytical Application

The proposed method was applied to determine the soluble Cd in Xiamen coastal seawater, and the same sample was also determined by ICP-MS for method validation. The data obtained by the current method and by ICP-MS are given in Table 2, showing that soluble Cd concentration in the seawater obtained by VG-AFS with online APAR preconcentration was well in agreement with that by ICP-MS.

The detection limit (DL) of VG-AFS and method detection limit (MDL) with online APAR preconcentration were calculated based on three times higher of signal-to-noise ratio of the blank solution. The DL of VG-AFS for Cd and the MDL of the APAR online preconcentration VG-AFS with 200 mL sample volume were found to be 345 and 2.67 ng L⁻¹, respectively. The MDL of Cd is much improved and low enough for accurate determination of trace Cd in seawater and is comparable with that of ICP-MS; the relative standard deviation was 4.34% for 1 μg L⁻¹ Cd of six replicate runs. Because there was no available certified reference material on hand, trace amount of Cd was spiked into the seawater sample before preconcentration. The comparison of spike recoveries of different methods is also given in Table 2. The poor spike recovery of Cd by direct VG-AFS determination might be caused by the nonlinearity of the AFS signal owing to the high background noise when seawater sample was directly introduced into AFS.

The established integrated method was applied to determine soluble Cd in the seawater samples. Three of the four samples collected were sampled near

Table 2. Comparison of the performance of different methods^a

Method	VG-AFS without preconcentration	VG-AFS with preconcentration	ICP-MS
Detection limit (ng L ⁻¹)	345	2.67	0.979
Found in seawater (ng L ⁻¹) ^c	ND ^d	77 ± 0.1	74.2 ± 0.1
Spike added (ng L ⁻¹)	100	100	100
Total found (ng L ⁻¹)	97 ± 0.1	171 ± 0.1	174.2 ± 0.4
Recovery of spike (%)	54.8	96.6	99.9

^an = 4.
^bSample volume: 200 mL. Sample flow rate: 3.0 mL min⁻¹. Concentration of tartaric acid: 0.1 mol L⁻¹. Elution flow rate: 1 mL min⁻¹.
^cseawater no. 1.
^dNot detected.

the coast of Xiamen island (nos. 1–3), and another one was sampled in the sea far from the Island (no. 4). The Cd concentrations determined were 77 ± 0.1 (no. 1), 76 ± 0.1 (no. 2), 73 ± 0.1 (no. 3), and 61 ± 0.1 (no. 4) ng L^{-1} , respectively, indicating slight Cd pollution near the coast of the island compared with that in the sea.

CONCLUSIONS

VG-AFS coupled with online APAR preconcentration provides an alternative for trace Cd determination in seawater compared with ICP-MS. The novel APAR preconcentration, which can be used for online preconcentration of target metal ions and simultaneous separation of the matrix of seawater, greatly improved the detection power of VG-AFS. It is expected to be useful not only for Cd determination but also for other trace vapor-generable elements in seawater after suitable modifications in the future.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (20475046, 20535020) and the National Basic Research Program of China (2003CD415001, 2003CCA00500). We thank Prof. Benli Huang for continual encouragement and Mr. Dong Yan for assistance with ICP-MS determination. The loan of the Shimadzu HPLC 2010 and the BRAIC AF-601A is gratefully acknowledged.

REFERENCES

1. William, G. S.; David, W. E.; Roger, M. T. Effect of chemical speciation on toxicity of cadmium to grass shrimp, *Palaemonetes pugio*: importance of free cadmium ion. *Environ. Sci. Technol.* **1978**, *12*, 409.
2. Acar, O. Molybdenum, Mo–Ir and Mo–Ru coatings as permanent chemical modifiers for the determination of cadmium and lead in sediments and soil samples by electrothermal atomic absorption spectrometry. *Anal. Chim. Acta* **2005**, *542*, 280–286.
3. Vassileva, E.; Quetel, C. R. Certification measurement of the cadmium, copper and lead contents in rice using isotope dilution inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **2004**, *519*, 79–86.
4. Taylor, A.; Branch, S.; Halls, D.; Patriarca, M.; White, M. Atomic spectrometry update. Clinical and biological materials, foods and beverages. *J. Anal. At. Spectrom.* **2005**, *20*, 323–369.
5. Fisher, A.; Goodall, P.; Hinds, M. W.; Nelms, S. N.; Penny, D. M. Atomic spectrometry update. Industrial analysis: metals, chemicals and advanced materials. *J. Anal. At. Spectrom.* **2005**, *20*, 1398–1424.

6. Long, X. B.; Chomchoei, R.; Gala, P.; Hansen, E. H. Evaluation of a novel PTFE material for use as a means for separation and preconcentration of trace levels of metal ions in sequential injection (SI) and sequential injection lab-on-valve (SI-LOV) systems: determination of cadmium(II) with detection by electrothermal atomic absorption spectrometry (ETAAS). *Anal. Chim. Acta* **2004**, *523*, 279–286.
7. Valdes-Hevia, T. M. C.; Campa, M. R. F de la; Sanz-Medel, A. Generation of volatile cadmium species with sodium tetrahydroborate from organized media: application to cadmium determination by inductively coupled plasma atomic emission spectrometry. *J. Anal. At. Spectrom.* **1993**, *8*, 847–852.
8. Guo, X. W.; Guo, X. M. Studies on the reaction between cadmium and potassium tetrahydroborate in aqueous solution and its application in atomic fluorescence spectrometry. *Anal. Chim. Acta* **1995**, *310*, 377–385.
9. Sanz-Medel, A.; Valdes-Hevia, T. M. C.; Garcia, N. B.; Campa, M. R. F de la.; Generation of cadmium atoms at room temperature using vesicles and its application to cadmium determination by cold vapor atomic spectrometry. *Anal. Chem.* **1995**, *67*, 2216–2223.
10. Huan, Y. F.; Wan, Y.; Zhang, H. Q.; Jin, Q. H.; Li, X. X. Applications of vapour generation atomic spectrometry for the determination of cadmium. *Chinese Analytical Instrumentation* **2002**, *1*, 40–42.
11. Li, G.; Wu, L.; Xin, J. J.; Hou, X. D. Chemical vapor generation by reaction of cadmium with potassium tetrahydroborate and sodium iodate in acidic aqueous solution for atomic fluorescence spectrometric application. *J. Anal. At. Spectrom.* **2004**, *19*, 1010–1013.
12. Wang, Y.; Chen, M. L.; Wang, J. H. Sequential/bead injection lab-on-valve incorporating a renewable microcolumn for co-precipitate preconcentration of cadmium coupled to hydride generation atomic fluorescence spectrometry. *J. Anal. At. Spectrom.* **2006**, *21*, 535–538.
13. Matusiewicz, H.; Kopras, M.; Sturgeon, R. E. Determination of cadmium in environmental samples by hydride generation with in situ concentration and atomic absorption detection. *Analyst* **1997**, 122331.
14. Bruland, K. W. Trace elements in seawater. In *Chemical Oceanography*; Riley, J. P., Chester, R., (Eds.); Academic Press: London, **1983**, p. 398.
15. Vircavs, M.; Rone, V.; Pelne, A. Coprecipitation behaviour of 5,8-polyquinolyl polydisulphide for trace element preconcentration from aqueous solution. *Anal. Chim. Acta* **1994**, *299*, 291–298.
16. Santos, E. J.; Herrmann, A. B.; Ribeiro, A. S.; Curtius, A. J. Determination of Cd in biological samples by flame AAS following online preconcentration by complexation with O,O-diethyldithiophosphate and solid phase extraction with Amberlite XAD-4. *Talanta* **2005**, *65*, 593–597.
17. Willie, S. N.; Sturgeon, R. E. Determination of cadmium in environmental samples by hydride generation with in situ concentration and atomic absorption detection. *Spectrochim. Acta B* **2001**, *56*, 1707–1716.
18. Robards, K.; Starr, P.; Patsalides, E. Metal determination and metal speciation by liquid chromatograph. *Analyst* **1991**, *116*, 1247–1273.
19. Li, B.; Wang, Q. Q.; Yan, H.; Yang, L. M.; Huang, B. L. Chromatographic behavior of cadmium in an ion-pair reversed-phase micro HPLC system and its application to the determination of bio-available cadmium in soil samples. *Anal. Bioanal. Chem.* **2003**, *376*, 923–927.
20. Wang, Q. Q.; Tsnoda, K.; Akaiwa, H. Extraction separation of aluminium(III), gallium(III), and indium(III) using bis(1,1,3,3-tetramethylbutyl)phosphonic acid and its sulfur analogues. *Anal. Sci.* **1996**, *12*, 231–236.

21. Wang, Q. Q.; Tsnoda, K.; Akaiwa, H. Separation of Zr(IV) and hafnium(IV) by extraction chromatography using di(1-methyl) methylphosphonate as a stationary phase. *Anal. Sci.* **1997**, *13*, 27–31.
22. Wang, Q. Q.; Huang, B. L.; Tsnoda, K.; Akaiwa, H. Extracted species of rare earth elements using bis(1,1,3,3-tetramethylbutyl) phosphinic acid as an extratant and their effective mutual separation by high-performance extraction chromatography. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2693–2697.
23. Hong, Y. C.; Wang, Q. Q.; Yan, H.; Yang, L. M.; Huang, B. L. Digital signal acquisition and processing software for atomic fluorescence spectrometry and its application to elemental speciation. *Spectrosc. Spect. Anal.* **2003**, *23*, 354–357.
24. Wang, Z. H.; Meng, S. L.; Song, W. Z.; Guo, C. Z.; Qi, J. R.; Li, D. Q. Extraction separation of rare earth elements (III) with bis(2,4,4-trimethylpentyl)phosphinic acid. *Chin. J. Anal. Chem.* **1995**, *23*, 391–394.
25. Chuachud, W.; Tyson, J. F. Determination of cadmium by flow injection atomic absorption spectrometry with cold vapor generation by a tetrahydroborate-form anion-exchanger. *J. Anal. Atom. Spectrom.* **2005**, *20*, 273–281.
26. Nesterov, V. V.; Kolodyazhnyi, O. I. Enantioselective reduction of ketophosphonates using chiral acid adducts with sodium borohydride. *Russ. J. Gen. Chem.* **2006**, *76*, 1022.