Solid phase extraction of cadmium on 2-mercaptobenzothiazole loaded on sulfur powder in the medium of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate and cold vapor generation–atomic absorption spectrometric determination

N. Pourreza*, K. Ghanemi

Department of Chemistry, Faculty of Science, Shahid Chamran University, Ahvaz, Iran

ABSTRACT

A novel solid phase extractor for preconcentration of cadmium at $ng\,L^{-1}$ levels has been developed. Cadmium ions were retained on a column packed with sulfur powder modified with 2-mercaptobenzothiazole (2-MBT) in the medium of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]$^+$PF$_6^-$) ionic liquid. The presence of ionic liquid during modification of sulfur enhanced the retention of cadmium ions on the column. The retained cadmium ions were eluted with $2\,mol\,L^{-1}$ solution of HCl and measured by cold vapor generation–atomic absorption spectrometry (CVG–AAS). By using reaction cell-gas liquid separator (RC-GLS), gaseous cadmium vapors were produced and reached the atomic absorption spectrometer, instantaneously. The influence of different variables on both processes of solid phase extraction and CVG–AAS determination of cadmium ions was investigated. The calibration curve was linear in the range of $10–200\,ng\,L^{-1}$ of cadmium in the initial solution with $r = 0.9992$ ($n = 8$) under optimum conditions. The limit of detection based on three times the standard deviation of the blank ($3S_b$, $n = 10$) was $4.6\,ng\,L^{-1}$. The relative standard deviation (R.S.D.) of 25 and $150\,ng\,L^{-1}$ of cadmium was 4.1 and 2.2% ($n = 8$), respectively. The procedure was validated by the analysis of a certified reference material (DORM-3), water and fish samples.

1. Introduction

Cadmium is a well-known toxic and persistent pollutant that is naturally present at very low levels in common aquatic environments [1]. Cadmium can be accumulated in several organs, producing carcinogenic effect [2]. One of the pathways that cadmium enters human body is through daily intake of food and water, thus the monitoring of cadmium concentrations in food and water samples is of significant importance. Moreover, such data can also provide us with cadmium contamination information of the surrounding environment [3].

Flame atomic absorption spectrometry (FAAS) [4,5], graphite furnace atomic absorption spectrometry [6] and inductively coupled plasma atomic emission spectrometry (ICP-AES) [7] are the frequently used analytical techniques for cadmium monitoring. In recent years, cold vapor generation of cadmium by its reaction with NaBH$_4$ and subsequent determination by atomic spectrometric techniques has attracted more attentions [8]. Generation of the analyte as volatile species has a number of advantages over con-

ventional nebulization. The principle advantage is the potential for quantitative transfer of the analyte into the gas phase as either a molecular species or as atoms in the case of mercury [9,10]. In 1995, Sanz-Medel et al. reported the vapor phase generation of cadmium at room temperature via its reduction by NaBH$_4$ in the presence of didodecyldimethylammonium bromide (DDAB) and subsequent measurement by AAS [11]. Cadmium has also been determined in natural water samples by flow injection cold vapor atomic absorption spectrometry with a detection limit of $0.05\,\mu g\,L^{-1}$ [12]. Most of CVG–AAS cadmium systems have produced good results, with detection limits ranging in the sub-ppb levels and relative standard deviations ranging from 1 to 5% [13–15]. Interferences and matrix effects, however, are often problematic. Besides this the very low concentration of this element in some environmental samples is another problem in cadmium determination [16]. Therefore, an effective separation and preconcentration process is necessary prior to CVG–AAS determination. Solid phase extraction (SPE), using chelating adsorbents obtained by immobilization of a suitable organic agent on a solid support such as silica-gel [4], activated carbon [17], naphthalene [18], functionalized resin [19,20] and TiO$_2$ nanotubes [21] are effective methods for trace preconcentration. The typical adsorbents used for cadmium separation contain organic agents that form stable complexes with cadmium

* Corresponding author. Tel.: +98 611 333 1042; fax: +98 611 333 7009.
E-mail address: npourreza@yahoo.com (N. Pourreza).

such as 8-hydroxyquinoline on activated carbon [17] and 2-MBT immobilized on specially treated natural clay [22]. In recent years, ionic liquids have also been reported as a medium for separation and preconcentration of metal ions [23–25] or organic compounds [26] in the literature. We have recently reported the use of sulfur as a solid phase extractor for preconcentration and determination of lead and cadmium by flame atomic absorption spectrometry [27]. Sulfur is a cheap, odorless and tasteless yellow powder that can adsorb some heavy metals such as lead and cadmium.

In this work, we used sulfur powder as a support to immobilize 2-MBT in the medium of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Immobilization of 2-MBT in the presence of ionic liquid increased its ability to capture cadmium ions at ultra-trace levels with more selectivity and recovery than the unmodified sulfur. Subsequent generation of gaseous cadmium for AAS determination was carried out by a reaction cell-gas liquid separator (RC-GLS).

2. Experimental

2.1. Instrumentation

Atomic absorption measurements were performed with a Philips (England) Model PU9100X fitted with a cadmium hollow cathode lamp (Unicam, Franklin, MA). A wavelength of 228.8 nm and spectral band pass of 0.5 nm were used throughout. A quartz T-cell tube (120 mm length, 5 mm i.d.) was placed directly on the nitrous oxide/acetylene burner equipped with T-cell tube holder. The nitrous oxide/acetylene flame remained off throughout the process. Cadmium vapor was generated using a homemade reaction cell-gas liquid separator (RC-GLS). The previously described system [28] was slightly modified to incorporate a needle syringe for the injection of NaBH$_4$ solution (Fig. 1).

FT-IR spectra were recorded on a Bomem FT-IR spectrophotometer (Canada).

2.2. Reagents and materials

All reagents were of analytical grade unless otherwise stated and de-ionized double distilled water was used throughout. A stock solution of cadmium (1000 μg mL^{-1}) was prepared by dissolving pure cadmium powder (Merck, Darmastadt, Germany) in 1:1 HNO$_3$ (Merck) and diluting with water. Working standard solutions were obtained daily by successive dilutions of this stock solution. A 3.0% (w/v) sodium tetrahydroborate solution was prepared by dissolv-

ing NaBH$_4$ powder (Merck) in water and adding 0.5% (w/v) NaOH (Merck) to stabilize the solution. A buffer solution was prepared by dissolving appropriate amounts of boric acid (Merck) in water and adjusting its pH to 8.5 by adding NaOH solution. Sulfur powder (mesh 40 μm and purity >99%), 2-mercaptobenzothiazole, 1-methylimidazole and 1-bromobutan were purchased from Merck. Ammonium hexafluorophosphate was obtained from Fluka. The ionic liquid, 1-butyl-3-methylimidazolium bromide ([bmim]$^+$Br$^-$) was synthesized according to standard methods by the reaction of 1-methylimidazole with an excess amount of the haloalkane [29]. The reactants were stirred without any additional solvent for 72 h. The product was then purified by repeated washing with ethyl acetate and then dried overnight at 70 °C under vacuum. 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]$^+$PF$_6^-$) was obtained by anion exchange of 1-butyl-3-methylimidazolium bromide with ammonium hexafluorophosphate. All solutions containing the potential interferent ions were prepared by dissolving appropriate amounts of their nitrate or chloride salts in 0.5 mol L^{-1} of HNO$_3$. All glassware were washed three times with 3 mol L^{-1} hydrochloric acid and nitric acid solutions, respectively and then rinsed several times with water.

2.3. Sample pretreatment

Water samples collected from Karoon River (Ahvaz, Iran) and Persian Gulf (Moosa estuarine, Iran) were stored in 1 L glass bottles and filtered through a filter paper (Whatman No. 40) before use. 50 mL of river water and 10 mL of Persian Gulf water samples were treated under the general procedure.

Fish muscle samples were used and were oven dried at 35–40 °C. For digestion of two types of fish muscle samples and a certified reference material (DORM-3), 500 mg of each dried sample was refluxed with 20 mL of HNO$_3$ (65%) at 200 °C for 2 h [30]. Then 10 mL of K$_2$S$_2$O$_8$ (Merck) (5% w/v) was added and heated for another hour to complete the digestion. It was then cooled, filtered, neutralized with sodium hydroxide and diluted to 500 mL in a volumetric flask. 50 mL of these solutions were treated under the general procedure.

2.4. Preparation of sulfur column

To prepare a modified sulfur adsorbent, 300 mg of 2-MBT and 100 mg of 1-butyl-3-methylimidazolium hexafluorophosphate were added to 30 mL of acetone extra pure (Merck), stirred and heated up to 45 °C for 3 min. Then 10 g of sulfur powder was added gently to the solution and mixed thoroughly. The mixture was left to dry at room temperature for about 30 min. 1.0 g of this adsorbent was placed in a column (7 mm i.d., 70 mm length) for solid phase extraction procedure.

2.5. General procedure

For solid phase extraction and preconcentration of cadmium ions, 200 mL solutions containing cadmium in the range of 10–200 ng L^{-1} and 5 mL of buffer at pH 8.5 were passed through the modified sulfur adsorbent in a column at flow rate of 12 mL min^{-1}. After retention of cadmium ions, 2.5 mL of 2 mol L^{-1} HCl at a flow rate of 8 mL min^{-1} was passed through the column to elute the concentrated cadmium ions from the column. Then, this solution was placed in RC-GLS, and 3 mL of 3.0% (w/v) NaBH$_4$ was injected by a syringe on the top of the glassware. The produced gaseous cadmium was immediately directed to the quarts cell by a stream of N$_2$ at 350 mL min^{-1} for AAS measurements of the amounts of cadmium. The percent recovery of cadmium was calculated from the amounts eluted from the column and the amounts present in the starting standard sample.
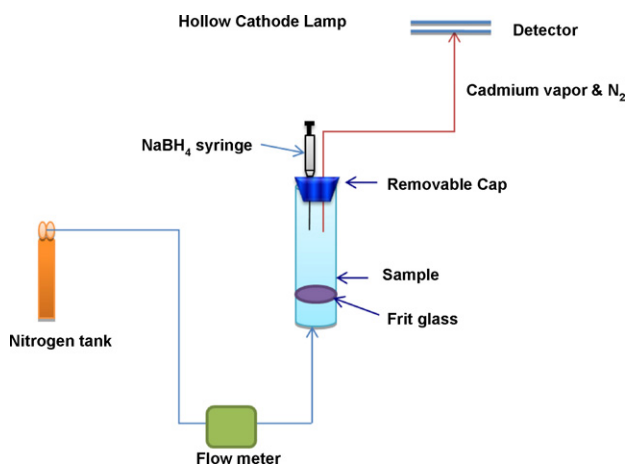

Fig. 1. Schematic diagram of CVG–AAS including reaction cell-gas liquid separator (RC-GLS).

3. Results and discussion

For improvement of the efficiency of the preconcentration, elution and CVG–AAS steps, the effect of various variables was studied and optimized.

3.1. Sulfur column modification

2-MBT was loaded on sulfur powder in the medium of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate and used as a new adsorbent. The FT-IR spectrum of this new adsorbent clearly shows the presence of characteristics bands of both 1-butyl-3-methylimidazolium hexafluorophosphate and 2-MBT such as P—F, S—H, C—N, C=N, C—S together with aromatic and hydrocarbon skeleton bands.

The existence of three sulfur atoms in the structure of 2-MBT was expected to increase the selectivity of its cadmium complex over other transition metal ions. It was also found that the presence of 1-butyl-3-methylimidazolium hexafluorophosphate during modification of sulfur powder with 2-MBT can enhance the recovery of solid phase extraction by a factor of two. This effect may be due to more extraction and retention of cadmium–MBT complex into the ionic liquid phase loaded on the column. The role of 1-butyl-3-methylimidazolium hexafluorophosphate, as a medium, is similar to the extraction mechanism that was mentioned in other papers [23–25]. This ionic liquid is immiscible with water and it was loaded on the surface of sulfur because of its hydrophobic property and it was able to keep the ligand on sulfur surface more firmly. For these reasons the effect of the amount of 1-butyl-3-methylimidazolium hexafluorophosphate was also investigated and it was found that higher amounts than 100 mg have no appreciable effect on the recovery and therefore the value of 100 mg of this ionic liquid was selected as the optimum. For a proper modification of the sulfur adsorbent, the effect of the amount of 2-MBT on the retention of cadmium ions was studied. According to the procedure described in Section 2.4 various amounts (50–600 mg) of 2-MBT were added to a mixture of 10 g of sulfur and 100 mg of 1-butyl-3-methylimidazolium hexafluorophosphate, and 1 g of the dried mixture was used as an adsorbent in a column. As shown in Fig. 2 the sulfur adsorbent modified with 30–50 mg g^{-1} of 2-MBT ligand in the presence of ionic liquid is capable to retain cadmium ions, quantitatively. Each column containing 1 g of the adsorbent can be used three times without any loss in the recovery (>95%). The dried adsorbent is stable and can be stored for at least 2 months after preparation. The recovery values were still quantitative (95%) after 2 months.
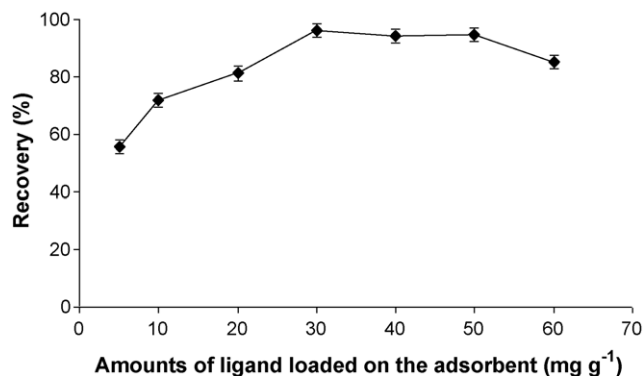

Fig. 2. Effect of amount of ligand loaded on sulfur for separation of 100 ng L^{-1} of cadmium at pH 8.5 and flow rate 12 mL min^{-1}.
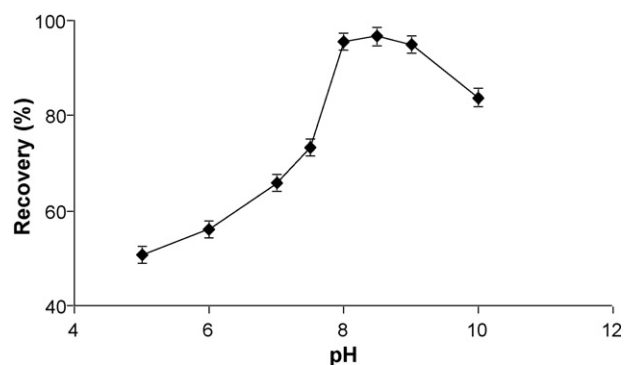

Fig. 3. Effect of pH on sorption of 100 ng L^{-1} of cadmium on the modified sulfur column. Other conditions: flow rate, 12 mL min^{-1}; volume, 200 mL; 2 mol L^{-1} HCl as eluent.

3.2. Effect of pH

The influence of pH on the recovery of 200 mL of 100 ng L^{-1} of cadmium was studied in the range of 5–10. The pH was adjusted using either 0.1 mol L^{-1} nitric acid or sodium hydroxide solutions and the recommended procedure was followed. Fig. 3 shows that percent extraction of cadmium ions increased up to pH 7.5 and remained constant in the pH range of 7.5–9.5. Therefore, the pH 8.5 was selected as the optimum value for sorption of cadmium ions. A boric acid–sodium borate buffer (pH 8.5) was selected as a suitable buffer because it did not change the sorption of cadmium and 5 mL of this buffer solution was adequate to maintain this pH in the solution.

3.3. Effect of flow rate

The effect of flow rate of the sample and the eluent solutions on the retention and elution of cadmium ions from the column was studied. The results showed that the retention of cadmium ions at concentration of 100 ng L^{-1} is not affected by the sample solution flow rate in the range of 5–12 mL min^{-1}. Therefore, to increase the speed of operation, a sample flow rate of 12 mL min^{-1} was selected as the optimum value. On the other hand, the recovery of the retained cadmium ions from the modified sulfur column was quantitative and constant in the range of 2–8 mL min^{-1}. Thus elution flow rate of 8 mL min^{-1} was selected as the optimum value.

3.4. Effect of elution parameters

In order to choose a proper eluent for the retained cadmium ions, after solid phase extraction, the column was eluted with various eluting solutions. As it is observed in Table 1, 2 mol L^{-1} solution of HCl is a proper solvent to elute cadmium ions from the column with 96% recovery. Higher concentrations of HCl cannot be used because of the excessive production of H$_2$ gas leads to an increase in the signal of the blank and annihilates the reproducibility. The effectiveness of HCl as an eluent could be due to its ability to decompose the complex of cadmium and 2-MBT on the column and produce

Table 1
Recovery of 100 ng L^{-1} of cadmium from the modified sulfur column using different elution solutions.

Elution solution	Recovery (%)[a]
H$_2$SO$_4$ (2 mol L^{-1})	89
HNO$_3$ (2 mol L^{-1})	42
HCl (2 mol L^{-1})	96
HCl (2 mol L^{-1}) + EDTA (0.2 mol L^{-1})	24

[a] Recoveries are based on three replications.

stable chloro-cadmium complexes which are not retained on the column. To achieve the highest recovery of cadmium ions from the solution, the effect of volume of the eluent was also studied and 2.5 mL was selected as the optimum value.

3.5. Effect of sample volume

The effect of the sample solution volume on the cadmium sorption was studied by passing 50–500 mL sample solutions each containing 20 ng of cadmium at a flow rate of 12 mL min^{-1}. The results showed that the maximum sample volume of 200 mL can be passed through the column with quantitative recovery. Above 200 mL the percent sorption decreased for the analyte. Thus, a pre-concentration factor of 80 is achieved when 2.5 mL of HCl is used to elute the analyte.

3.6. Study of RC-GLS system variables

Besides optimizing column parameters, the cold vapor generation conditions were also studied and optimized to achieve the best analytical signal.

3.6.1. Effect of reducing agent concentration
The influence of NaBH$_4$ concentration (as the reducing agent) on the cold vapor generation was evaluated within the range of 1–5% (w/v). The results indicated that the efficiency of cadmium cold vapor generation reached a maximum value at 3% (w/v) concentration of NaBH$_4$. Higher concentrations of reducing agent did not promote the signal of the analyte sample with respect to the blank.

3.6.2. Effect of carrier gas flow rate
The flow rate of N$_2$ carrier gas, used to transport the cadmium vapors to the T-cell, was investigated in the range of 100–1000 mL min^{-1}. By monitoring the signal of CVG–AAS, it was found that flow rate of 350 mL min^{-1} is the optimum value.

3.6.3. Effect of connecting tubing length
The length of tubing that connects the RC-GLS to absorption cell is another important parameter that influences the cadmium vapor efficiency. In this system we used a 5 cm connector tubing which was the minimum value that can be used (gas flow rate was 350 mL min^{-1}). This length of tubing was shorter than those mentioned in previous papers [2]. By the presented RC-GLS, gaseous cadmium vapor can be transferred to the atomic absorption spectrometer cell immediately after its production which is critical for unstable vapor atoms.

3.7. Capacity of the adsorbent

In order to determine the maximum amount of cadmium ions retained on the modified sulfur adsorbent, to 1 g of the adsorbent (in a beaker), 100 mL solution of cadmium at concentration of 1.0 μg mL^{-1} was added (batch mode) and stirred for 3 h under optimized conditions. After filtration of the mixture, the cadmium ions were eluted from the adsorbent by 2 mol L^{-1} of HCl. Because of its high concentration, this solution was diluted to 1000 mL, and 200 μL of the diluted solution was analyzed by CVG–AAS. The maximum capacity was found to be 2.0 μg g^{-1} of the adsorbent.

3.8. Analytical performance

The calibration graph was obtained by applying the general procedure for different concentration of cadmium under optimum conditions. A linear calibration graph was obtained in the range of

Table 2
Effect of foreign species in the determination of 100 ng L^{-1} of cadmium.

Species	Tolerance limit (μg L^{-1})
Li$^+$, Na$^+$, K$^+$, NH$_4^+$, NO$_3^-$, ClO$_4^-$	
CH$_3$COO$^-$	50,000
Ca^{2+}, Mg^{2+}, I, Br$^-$, Cl$^-$, CO$_3^{2-}$	
SO$_4^{2-}$, C$_2$O$_4^{2-}$, PO$_4^{3-}$, tartarate	
Ethanol, citrate	2000
Zn^{2+}, Hg	400
Cu^{2+}, Pb^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}	
Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}	200

10–200 ng L^{-1} of cadmium in the initial solution. The linear regression equation was $A = 2 \times 10^{-3}C - 8 \times 10^{-3}$, with $r = 0.9992$ ($n = 8$), where A is the absorbance and C is concentration of cadmium in ng L^{-1}, respectively. The limit of detection (LOD) of the proposed method based on three times of blank standard deviation (3S$_b$) for 10 replicate measurements of blank signal was 4.6 ng L^{-1}. The relative standard deviation (R.S.D.) for the determination of 25 and 150 ng L^{-1} of cadmium was 2.2 and 4.1%, respectively.

3.9. Interferences studies

In order to examine the effect of different ions and organic substances on solid phase extraction and determination of cadmium, constant concentration of Cd (100 ng L^{-1}) was taken with different concentration of ions and organic substances and general procedure was followed. Individual components were deemed not to cause interference if the variation in the analytical signal was within ±5% of that for cadmium in aqueous solution. On this basis the tolerance limits in μg L^{-1} of interfering species were determined. The results in Table 2, indicate that the proposed method is relatively selective for the determination of cadmium.

4. Application

4.1. Analysis of certified reference material

In order to evaluate the accuracy of the developed method, cadmium was determined in a certified material (DORM-3). The results listed in Table 3 reveal that this method has good accuracy.

4.2. Analysis of water samples

The proposed methodology was successfully tested by determination of cadmium in Karoon River and Persian Gulf water samples. In order to validate the proposed method, recovery experiments were also carried out for these water samples by spiking water samples with two standard solutions of cadmium before applying SPE procedure. The results shown in Table 4 confirm that despite the presence of diverse ions and species with different concentrations, cadmium ions can be separated and determined with good recoveries in the range of 95.5–100.5%.

4.3. Analysis of fish samples

The proposed method was also applied to the determination of cadmium ions in Persian Gulf fish samples, Shoorideh (*Otolithes*

Table 3
Determination of cadmium in a certified reference material.

Certified reference material	Certified[a] (μg g^{-1})	Found[a] (μg g^{-1})	Relative error (%)
DORM-3	0.290 (±0.020)	0.301 (±0.076)	3.8

[a] Values in parentheses are SD based on five replications.

Table 4
Determination of cadmium in water samples.

Sample[a]	Added (ng L^{-1})	Found[b] (ng L^{-1})	Recovery (%)	Initial concentration (ng L^{-1})
Karoon River	–	117.5 ($\pm$1.4)		470.0 ($\pm$4.0)
	20	136.8 ($\pm$2.6)	96.5	
	60	174.8 ($\pm$ 5.4)	95.5	
Persian Gulf	–	134.5 ($\pm$3.2)	–	2700 ($\pm$4.0)
	20	154.6 ($\pm$3.6)	100.5	
	60	192.3 ($\pm$4.0)	96.3	

[a] Taken from a polluted area.
[b] The values in parentheses are the 95% confidence intervals based on five replications.

Table 5
Determination of cadmium in fish samples.

Sample	Added (ng L^{-1})	Found[a] (ng L^{-1})	Recovery (%)	Amounts of cadmium (ng g^{-1})
Otolithes ruber	–	42.9 ($\pm$2.5)	–	171.6
	20	61.7 ($\pm$3.7)	94.0	
	60	101.5 ($\pm$4.9)	97.7	
Scomberomorus commerson	–	54.5 ($\pm$3.6)	–	218.0
	20	73.6 ($\pm$2.4)	95.5	
	60	112.0 ($\pm$4.8)	95.8	

[a] The values in parentheses are the 95% confidence intervals based on five replications.

ruber) and Shirmahi (*Scomberomorus commerson*) which were purchased from Abadan local fish market. These types of fishes are of most demanding and consuming fishes in this region (Abadan). 500 mg of each dried sample was initially digested as described in Section 2.3 and then subjected to the proposed method (under optimum condition). The recovery of the spiked standard solutions to the fish samples before applying SPE procedure are shown in Table 5. The recoveries were in the range of 94.0–97.7% which demonstrates that this method is well operative for solid phase extraction of cadmium ions in these matrices.

5. Conclusion

Sulfur powder modified with 2-mercaptobenzothiazole (2-MBT) in the presence of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid has been introduced as a novel adsorbent for preconcentration of cadmium. The presence of ionic liquid improved the extraction efficiency of the adsorbent for cadmium by a factor of two. In comparison with solid phases that have been used for preconcentration, the sulfur used for the preparation of the adsorbent is an inexpensive and neutral material that has no detrimental effects on human health and environment. The enrichment factor of this method is 80. Owing to high selectivity of the modified sulfur column, the proposed method can be applied for sorption of cadmium ions in complex and saline matrices such as river water, sea water and fish samples. The proposed RC-GLS used for cold vapor generation of cadmium, offers efficient sample-reductant mixing and immediate transfer of cadmium vapors to the atom cell for atomic absorption spectrometry measurement. The detection limit of 4.6 ng L^{-1} was obtained which is better than some of the previously reported values using cold vapor atomic absorption spectrometry [2,11–15]. The method was validated by the analysis of a certified reference material (DORM-3).

References

[1] P.J. Wangersky, Marine Chemistry, Springer-Verlag, Berlin, Heidelberg, 2001, p. 86.
[2] M.L. Garrido, R.M. Olivas, C. Camara, Determination of cadmium in aqueous media by flow injection cold vapor atomic absorption spectrometry. Application to natural water samples, J. Anal. At. Spectrom. 13 (1998) 295–300.
[3] X. Wen, P. Wu, L. Chen, X. Hou, Determination of cadmium in rice and water by tungsten coil electrothermal vaporization–atomic fluorescence spectrometry and tungsten coil electrothermal atomic absorption spectrometry after cloud point extraction, Anal. Chim. Acta 650 (2009) 33–38.
[4] F. Xie, X. Lin, X. Wu, Z. Xie, Solid phase extraction of lead (II), copper (II), cadmium (II) and nickel (II) using gallic acid-modified silica gel prior to determination by flame atomic absorption spectrometry, Talanta 74 (2008) 836–843.
[5] O.M. Kalfa, O. Yalcınkaya, A.R. Turker, Synthesis of nano B$_2$O$_3$/TiO$_2$ composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium, J. Hazard. Mater. 166 (2009) 455–461.
[6] G. Yanga, W. Fena, C. Lei, W. Xiaoa, H. Suna, Study on solid phase extraction and graphite furnace atomic absorption spectrometry for the determination of nickel, silver, cobalt, copper, cadmium and lead with MCI GEL CHP 20Y as sorbent, J. Hazard. Mater. 162 (2009) 44–49.
[7] F. Cubadda, A. Raggi, Determination of cadmium, lead, iron, nickel and chromium in selected food matrices by plasma spectrometric techniques, Microchem. J. 79 (2005) 91–96.
[8] L. Lampugnani, C. Salvetti, D. Tsalve, Hydride generation atomic absorption spectrometry with different flow systems and in-atomizer trapping for determination of cadmium in water and urine—overview of existing data on cadmium vapor generation and evaluation of critical parameters, Talanta 61 (2003) 683–698.
[9] Y.L. Feng, J.W. Lam, R.E. Sturgeon, A novel approach to the estimation of aqueous of some noble metal vapor species generated by reaction with tetrahydroborate (III), Spectrochim. Acta: Part B 59 (2004) 667–675.
[10] X. Duan, R.L. McLaughlin, I.D. Brindle, A. Conn, Investigations into the generation of Ag, Au, Cd, Co, Cu, Ni, Sn and Zn by vapor generation and their determination by inductively coupled plasma atomic emission spectrometry, together with a mass spectrometric study of volatile species. Determination of Ag, Au, Co, Cu, Ni and Zn in iron, J. Anal. At. Spectrom. 17 (2002) 227–231.
[11] A. Sanz-Medel, M.C. Temproano, N.B. Garcia, M.R.F. de la Campa, The use of surfactants to obtain cadmium atoms at room temperature and its application for the cold vapor AAS determination of the metal, Anal. Proc. 32 (1995) 49–52.
[12] W. Chuachuad, J.F. Tyson, Determination of cadmium by flow injection atomic absorption spectrometry with cold vapor generation by a tetrahydroborate-form anion-exchanger, J. Anal. At. Spectrom. 20 (2005) 273–281.
[13] T. Duan, X. Song, D. Jin, H. Li, J. Xu, H. Chen, Preliminary results on the determination of ultratrace amounts of cadmium in tea samples using a flow injection on-line solid phase extraction separation and preconcentration technique to couple with a sequential injection hydride generation atomic fluorescence spectrometry, Talanta 67 (2005) 968–974.
[14] J. Ha, H.W. Sun, W.J. Kang, S.X. Liang, Continuous flow chemical vapor generation for the determination of cadmium in foodstuffs by atomic absorption spectrometry using derivative signal processing, Microchim. Acta 150 (2005) 277–282.

[15] E.T. Ritschdorff, N. Fitzgerald, R.L. Mclaughlin, I.D. Brindle, The use of a modified multimode sample introduction system for the simple and rapid determination of cadmium by chemical vapor generation atomic absorption spectrometry, Spectrochim. Acta: Part B 60 (2005) 139–143.

[16] M.L. Garrido, R. Munoz-Olivas, C. Camara, Interference removal for cadmium determination in waste water and sewage sludge by flow injection cold vapor generation atomic absorption spectrometry, J. Anal. At. Spectrom. 13 (1998) 1145–1449.

[17] S. Cerutti, M.F. Silva, J.A. Gásquez, R.A. Olsina, L.D. Martinez, On-line preconcentration/determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer, Spectrochim. Acta: Part B 58 (2003) 43–50.

[18] N. Pourreza, H. Zavvar Mousavi, Determination of cadmium by flame atomic absorption spectrometry after preconcentration on naphthalene–methyltrioctylammonium chloride adsorbent as tetraiodocadmate (II) ions, Anal. Chim. Acta 503 (2004) 279–282.

[19] V.A. Lemos, C.G. Novaes, A.S. Lima, D.R. Vieira, Flow injection preconcentration system using a new functionalized resin for determination of cadmium and nickel in tobacco samples, J. Hazard. Mater. 155 (2008) 128–134.

[20] E. Melek, M. Tuzen, M. Soylak, Flame atomic absorption spectrometric determination of cadmium(II) and lead(II) after their solid phase extraction as dibenzyldithiocarbamate chelates on Dowex Optipore V-493, Anal. Chim. Acta 578 (2006) 213–219.

[21] Q.X. Zhoua, X. Zhao, J. Xiao, Preconcentration of nickel and cadmium by TiO_2 nanotubes as solid-phase extraction adsorbents coupled with flame atomic absorption spectrometry, Talanta 77 (2009) 1774–1777.

[22] N.L. Filho, Y. Gushikem, W.L. Polito, 2-Mercaptobenzothiazole clay as matrix for sorption and preconcentration of some heavy metals from aqueous solution, Anal. Chim. Acta 306 (1995) 167–172.

[23] Z. Li, Q. Wei, R. Yuan, X. Zhou, H. Liu, H. Shan, Q. Song, A new room temperature ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate as a solvent for extraction and preconcentration of mercury with determination by cold vapor atomic absorption spectrometry, Talanta 71 (2007) 68–72.

[24] L. Zaijun, N. Lu, X. Zhou, Q. Song, Extraction spectrophotometric determination of aluminum in dialysis concentrates with 3,5-ditertbutylsalicylfluorone and ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate, J. Pharmaceut. Biomed. Anal. 43 (2007) 1609–1614.

[25] L. Zaijun, P. Qiping, S. Haixia, Use of a novel medium, the ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate, for liquid–liquid extraction of lead in water and its determination by graphite furnace atomic absorption spectrometry, J. AOAC 90 (2007) 1191–1196.

[26] N. Fontanalsa, S. Ronkab, F. Borrulla, A.W. Trochimczukb, R.M. Marcéa, Supported imidazolium ionic liquid phases: a new material for solid-phase extraction, Talanta 80 (2009) 250–256.

[27] H. Parham, N. Pourreza, N. Rahbar, Solid phase extraction of lead and cadmium using solid sulfur as a new metal extractor prior to determination by flame atomic absorption spectrometry, J. Hazard. Mater. 163 (2009) 588–592.

[28] N. Pourreza, K. Ghanemi, Determination of mercury in water and fish samples by cold vapor atomic absorption spectrometry after solid phase extraction on agar modified with 2-mercaptobenzimidazole, J. Hazard. Mater. 161 (2009) 982–987.

[29] J. Bowers, P. Butts, J. Martin, C. Vergara-Gutierrez, K. Heenan, Aggregation behavior of aqueous solutions of ionic liquids, Langmuir 20 (2004) 2191–2198.

[30] K. Helrich, Official Methods of Analysis, vol. 1, 15th ed., AOAC Int., 1990, p. 247.