On-line Preconcentration and Determination of Cd(II) in Water by Flow Injection-Flame Atomic Absorption Spectrometry (FI-FAAS) Using Salicylic Acid Functionalized Amberlite XAD-2 Resin-Packed Minicolumn

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ABSTRACT

A simple, sensitive, and inexpensive flow injection solid phase extraction (SPE) system was developed for the determination of trace level concentrations of Cd(II). The salicylic acid immobilized on Amberlite XAD-2 (AXAD2-SA) has been synthesized via azo-coupling and was used for on-line preconcentration of Cd(II) with a flow injection-flame atomic absorption spectrometer (FI-FAAS) as the detection method. This novel setup demonstrates the determination of trace Cd(II) in underground water samples.

All main parameters affecting the complex formation, sorption, and elution of Cd(II) were optimized thoroughly. The results demonstrated that the AXAD2-SA resin enriched Cd(II) quantitatively over an optimal pH range

of 5.5-6.0 and elution with $0.1 \text{ mol L}^{-1} \text{ HNO}_3$.

The effects of potentially interfering species occurring in underground water samples were also studied. The calibration graph obtained was linear over the concentration range of $1.4 - 60 \mu\text{g L}^{-1}$. An enrichment factor of 118 was achieved by using the time-based technique with a preconcentration period of 180 seconds and a detection limit (3s) of $0.14 \mu\text{g L}^{-1}$. Good precision (relative standard deviation) of 3.70% at $20 \mu\text{g L}^{-1}$ for Cd(II) was obtained and accuracy was assessed through recovery experiments using a certified Cd(II) nitrate solution. The accuracy of the proposed preconcentration procedure was confirmed by Cd(II) determination in standard reference material SRM-1643e Trace Elements in Water.

the development of reliable methods for the removal and determination of Cd(II) in environmental and biological samples is of particular significance. Flame atomic absorption spectrometry (FAAS) is most commonly employed for this purpose due to its high sensitivity, low operational and instrumental costs, easy operation, and high sample throughput. The two main limitations in FAAS determination of trace heavy metal ions are that the levels of the analyte ions are lower than the detection limits of FAAS, and the contaminant ions cause positive or negative influences on the signal of the analytes. In order to solve these problems, various separation and preconcentration procedures before determination of the metal ions have been used, including solvent extraction (3), cloud point extraction (4), membrane filtration (5), coprecipitation (6), and solid phase extraction (7). Solid phase extraction (SPE) is an approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation. Consequently, SPE has in recent years been successfully used for the separation and sensitive determination of metal ions, mainly in water samples. However, among different methods used, online separation and preconcentration based on SPE, such as flow injection coupled with FAAS, has received considerable attention. The growing interest in the use of flow injection (FI) techniques in

INTRODUCTION

Heavy metal contamination represents a significant threat to the ecosystem with severe toxicological effects of metal ions on living organisms, even at low concentrations. Cd(II) is one of the most toxic and most notorious heavy metals to animals and humans and is transferred through the food chain system. Therefore, human exposure to Cd(II) is essentially unavoidable. Due to its biologically

long half-life, which has been estimated to be 10–30 years in humans, Cd(II) has been demonstrated to cause pathological changes in organs such as the liver, brain, kidneys, and lungs. It also accumulates in various ocular tissues such as the lens, retina, ciliary body, and vitreous humor (1). Contamination of the aqueous environment by Cd(II) is a worldwide environmental problem due to its toxic effects. The U.S. Environmental Protection Agency (USEPA) established the maximum permissible limit for Cd(II) in drinking water as $5 \mu\text{g L}^{-1}$ (2). Consequently,

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atomic absorption spectrometry for the determination of heavy metals has been demonstrated in several reports (8). The preconcentration system combining FI with on-line enrichment requires low consumption of reagents, sample and time, involves less risk of sample contamination and loss, offers increased sampling frequency as well as ease of automation. According to Ruzicka and Hansen (9), FIA is based on three main principles: (a) sample injection, (b) controlled dispersion of the injected sample zone, and (c) reproducible timing of the movement of the injected zone from the injection point to the detector (10). In flow injection online preconcentration of metal ions, the usual stationary phases are chromosorb-102 (11), multi-walled carbon nanotubes (12), alumina/titanium oxide-grafted silica matrix (13), polyurethane foam (PUF) (14), and Amberlite-XAD resins (15-17). They are covalently coupled through an azo (-N=N-) group with many ligands, such as 1-(2-pyridylazo)2-naphthol (18), diethyl-dithiophosphate (19), 1-(2-pyridineazo)-2-naphthol (20), 3,4-dihydroxybenzoic acid (21), o-aminobenzoic acid (22), salicylic acid (23,24), and xylenol orange (25). Amberlite XAD resins show greater adsorption capacity and easier elution than chromosorb-102, polyurethane foam, etc., because these resins have a large surface area and a macroporous structure which is convenient for preconcentration and isolation. The Amberlite XAD porous polymers are suitable supporting materials for any interaction between the reagent and the metal ions. Among the XAD series, Amberlite XAD-2 (25) is the suitable supporting material, which is a crosslinked polystyrene-divinylbenzene copolymer.

In the present work, salicylic acid was loaded onto Amberlite XAD-2 sorbent. A rapid online system for enrichment and determina-

tion of Cd(II) by FAAS was designed, incorporating a minicolumn of functionalized resin. Furthermore, the factors affecting the immobilization of the ligand, deposition, and elution steps were optimized using the multisimplex program. Finally, the procedure was applied to the determination of Cd(II) in water samples.

EXPERIMENTAL

Standard Solutions and Reagents

A 1000 mg L⁻¹ stock solution of Cd(II) was prepared from analytical reagent grade Cd(II) nitrate in doubly distilled water, obtained from a Milli-QTM double distillation unit (Millipore Corporation, USA), and standardized titrimetrically with EDTA before use. The standard solutions were prepared by dilution of the stock solutions with doubly distilled water. The pH adjustments were made with 0.1 mol L⁻¹ HCl, 0.1 mol L⁻¹ NaOH, 0.1 mol L⁻¹ acetic acid-acetate buffer (pH 4 and 5), 0.1 mol L⁻¹ phosphate buffer (pH 6 and 7), and 0.1 mol L⁻¹ ammonia-ammonium chloride buffer (pH 8 and 9). All laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution and washed before use with doubly distilled water. The Amberlite XAD-2 resin (Sigma-Aldrich) has a surface area of approximately 300 m²/g, moisture holding capacity of 54-60%, particle size of 20-60 mesh, pore diameter of 90 Å (mean pore size), and pore volume of 0.65 mL g⁻¹. Salicylic acid used was of analytical reagent grade. All analytical reagents were procured from either E. Merck (Darmstadt, Germany) or Thomas Baker (India). The certified Pb(II) nitrate solution, traceable to National Institute of Standards and Technology, Gaithersburg, MD, USA (NIST), was procured from E. Merck and the standard reference material SRM-1643e Trace Elements in Water was obtained from NIST.

The underground water samples were collected from Noida, U.P., Mayapuri, and Naryana Delhi, India.

Instrumentation

A PerkinElmer® Model AAnalystTM 400 flame atomic absorption spectrometer, coupled with the FIASTM 400 flow injection system, was used for the automatic processing of the method and operated in the preconcentration mode (PerkinElmer, Inc., Shelton, CT, USA). The whole system was controlled by a personal computer and Winlab32TM (Version 6.5.0.0266, PerkinElmer) application software. The flow injection system (FIAS 400) was coupled to the nebulizer system of the spectrometer with a short PTFE capillary of 20.0 cm length and 0.35 mm i.d. to minimize the analyte dispersion. The FIAS 400 preconcentration system comprises two peristaltic pumps, two positional valves, and a preconcentration column (see Figure 1). Peristaltic pump tubing (Tygon®) was adopted to deliver the aqueous solutions. The pH measurements were made with a Model LI614 pH meter (Elico Ltd., India). An IR spectrum was recorded on a PerkinElmer Model Spectrum RX-1. Elemental analysis (CHN) was carried out on a Model Vario EL-III (Elementar, Germany). Thermal analysis was performed with a PerkinElmer Model Diamond DSC. SEM was carried out using the Scanning Electron Microscope Model FEI Quanta 200F (ICON, The Netherlands).

Synthesis of Amberlite XAD-2 Functionalized with Salicylic Acid (AXAD 2-SA) Chelating Resin

The Amberlite XAD-2 (styrene-divinylbenzene copolymer) was modified according to the procedure reported in the literature (24). The synthesis involves nitration of the XAD-2, followed by the reduction to form an aromatic amine.

This amine facilitates the formation of a stable diazonium salt. The diazotized resin was filtered, washed with cold water, and reacted with salicylic acid at 0–3 °C for 24 hours. The resulting brown-colored beads were filtered, washed with water, and finally air-dried. The structure of Amberlite XAD-2-salicylic acid (AXAD 2-SA) is shown in Figure 2.

Minicolumn Preparation

Synthesized AXAD2-SA resin (140 mg) was filled into a home-made glass mini-column (30×3.0 mm i.d.), and plugged with a small portion of glass wool at both ends. Before use, it was treated with 2.0 mol L⁻¹ HNO₃ and washed with doubly distilled water until the resin was free from acid. A suitable aliquot of the solution containing Cd(II) in the concentration range 0–60 µg L⁻¹ was passed through this column after adjusting its pH to an optimum value. The column had a constant performance during all experiments and there was no need for any regeneration or repacking.

Operational Procedure

The preconcentration and determination of Cd(II) was performed using two lines of the FI-manifold and a two-step procedure. Acid-resistant Tygon tubing was used to pump the sample through the mini-column with peristaltic pump P1. A suitable aliquot of the solution containing Cd(II) was passed through this column after adjusting its pH to an optimum value. The enriched Cd(II) - Amberlite XAD2-salicylic acid resin complex was then eluted with HNO₃ at an optimum flow rate of 6.0 mL min⁻¹ by using peristaltic pump P2, and then subjected to on-line FAAS determination. Calibrations were linear in the range of 0–60 µg L⁻¹ of Cd(II). In a similar manner, unknown water sample solutions were also subjected to analysis and the Cd(II) content was determined with reference to the calibration graph. For

Fig. 1. The scheme of the flow injection preconcentration system using FIAS 400.

Fig. 2. Proposed structure of Amberlite XAD-2-salicylic acid resin.

every standard and sample solution, three replicate measurements were made. The FI-FAAS analysis program was controlled by a computer program (26) which includes pre-filling, filling, loading, and elution steps as shown in Table I.

RESULTS AND DISCUSSION

Characterization of Amberlite XAD-2 Functionalized With alicylic Acid (AXAD2-SA) Chelating Resin

The IR spectra, TGA, and CHN (elemental analysis) of Amberlite

XAD-2 loaded with salicylic acid are similar to those reported in the literature (24).

Scanning electron microscopy (SEM) was performed to record pure Amberlite XAD-2 and modified chelating resins and to observe the morphological changes. The micrographs (Figure 3) reveal that the pure resin had a smooth and flat surface, while the modified chelating resin showed roughening of the top layer, which is evidence that the ligand loads onto the support. This implies that the substrate

TABLE I
Online Flow Injection Program For Preconcentration of Pb (II)
(+ = on / - = off)

Step	Time(s)	Pump 1	Pump 2	Loading	Elution	Reading
Pre-fill	1	+	+	+	-	-
1	10	+	-	+	-	-
2	20	-	+	-	+	-
3	50	+	-	+	-	-
4	10	+	+	+	-	-
5	30	-	+	-	+	+

surface was changed after the functionalization with salicylic acid. SEM images of the XAD-2-SA resins show dense microstructures and granular grains. They are agglomerated polymeric materials with irregular shapes and in sizes varying from 50 μm to 200 μm .

Factors Affecting the Preconcentration Procedure

In order to improve the performance of the on-line preconcentration method for Cd(II) determination, all major variables such as sample pH, sample loading flow rate, and the period for sample loading were examined using the FI-FAAS manifold with a standard

solution of 20.0 $\mu\text{g L}^{-1}$ Cd(II). The effect of the sample pH was studied over the range of 2.0 to 10.0 and adjusted using an appropriate buffer. Figure 4 shows that the maximum absorbance readings were in the 5.5 to 6.0 pH range. Low absorbance of Cd(II) at low pH was due to the low complex formation rather than the low retention efficiency of the packing material.

The effect of sample flow rate on the preconcentration of 20.0 $\mu\text{g L}^{-1}$ Cd(II) for a 60-second loading time was studied in the range of 2.0 to 7.0 mL min^{-1} . Figure 5 shows that the absorbance increased almost linearly up to 5.0 mL min^{-1} , whereas for higher loading flow rate values,

the absorbance deviated from linearity because of the lower contact time with the sorbent. Thus, a loading flow rate of 5.0 mL min^{-1} was selected for the preconcentration step. The influence of preconcentration time on the absorbance was examined at 60, 120, and 180 seconds. The absorbance increased almost linearly by increasing the loading time up to 180 seconds. For a longer time, the analytical signal increased at a lower rate, probably due to a partial leaching of the complexes. For higher enrichment factors, a 180-second loading time was chosen as a compromise between sensitivity, sampling frequency, and reasonable sample consumption.

Fig. 3. SEM images (a) Amberlite XAD-2 (b) Amberlite XAD 2-Salicylic acid resin.

Fig. 4. Effect of pH on the absorbance. Conditions: preconcentration of 20.0 $\mu\text{g L}^{-1}$ Cd (II) with flow rate of 5 mL min^{-1} and elution with 0.1 mol L^{-1} HNO_3 with flow rate of 6 mL min^{-1} .

Fig. 5. Effect of sample flow rate. Conditions: preconcentration of 20.0 $\mu\text{g L}^{-1}$ Cd (II) buffered at pH 5.5 and elution with 0.1 mol L^{-1} HNO_3 at flow rate of 6 mL min^{-1} .

Factors Affecting the Elution Procedure

The choice of a suitable eluent is an important task for the performance of FI on-line SPE preconcentration systems. Hydrochloric, sulphuric, and nitric acid in concentrations ranging from 0.01 to 2.0 mol L⁻¹ were examined as potential eluents for the proposed system. Nitric acid is considered to be more suitable for FAAS assays because of improved and sharper signals as a result of the synergistic effect on flame atomization. Hence, HNO₃ was selected as the eluent for the elution of the adsorbed analyte. The effect of eluent flow rate was studied in the range of 2.0 to 7.0 mL min⁻¹. The absorbance increased with an increase in the nitric acid concentration up to 0.1 mol L⁻¹, then decreased slightly at higher concentrations (see Figure 6). Therefore, 0.1 mol L⁻¹ nitric acid was chosen as the eluent, and best absorbance was obtained using a 6.0 mL min⁻¹ eluent flow rate (see Figure 7), which was adopted for the elution procedure. Moreover, high flow rates increase the back pressure which could cause leakage, while the elution time was fixed at 30 seconds in order to

ensure the complete elution of adsorbed Cd(II) ions even at high concentrations.

Analytical Figures of Merit

The analytical performance data of the proposed method for the preconcentration of Cd(II) ion under the optimum experimental conditions and analytical characteristics of the optimized method, including the regression equation before and after the preconcentration method, are summarized in Table II. The preconcentration factor was calculated as the ratio of the calibration curve slopes obtained when applying the preconcentration step (FI-FAAS) and the slope obtained without FAAS. With the pH of 5.5 and using the 60, 120, and 180 second preconcentration times and a sample flow rate of 5.0 mL min⁻¹, the enhancement factors were 36, 75, and 118. The detection limits, corresponding to three times the standard deviation for five determinations of the blank, were found to be 0.43, 0.23, 0.14 µg L⁻¹, respectively. A precision (RSD) of 3.70% was obtained at the 20 µg L⁻¹ Cd(II) concentration level for seven replicate measurements. Higher sensitivities can be

obtained by modifying the method, i.e., using a longer preconcentration time of 180 seconds at the expense of lower sample throughput of 15 h⁻¹.

Interference Studies

Using the optimized on-line FI-SPE-FAAS system, the effect of potential interferents encountered in environmental water samples on the determination of 20 µg L⁻¹ Cd(II) was examined. A variation on the recovery greater than ±5% was considered as interference. The chloride, nitrate, sulfate, and phosphate ions commonly found in natural water samples have the capability to complex with many metal ions. Therefore, in their presence, the efficiency of the chelating resins to bind metal ions may be hampered resulting in the reduction of overall enrichment. Thus, the effects of NaCl, NaNO₃, Na₂SO₄, Na₃PO₄, NaBr, MgCl₂, citric acid, tartaric acid, and ascorbic acid on the sorption efficiency of Amberlite XAD-2-SA resin for 20 µg L⁻¹ Cd(II) were studied using the recommended optimum conditions given in Table II. The tolerance limits for the electrolytes are listed in Table III.

Fig. 6. Effect of eluent concentration on the absorbance. Conditions: preconcentration of 20.0 µg L⁻¹ Cd(II) buffered at pH 5.5 with flow rate of 5 mL min⁻¹ and elution HNO₃ at flow rate of 6 mL min⁻¹.

Fig. 7. Effect of eluent flow rate on the absorbance. Conditions: preconcentration of 20.0 µg L⁻¹ Cd(II) buffered at pH 5.5 with flow rate of 5 mL min⁻¹ and elution with 0.1 mol L⁻¹ HNO₃.

In general, the tolerance limits suggest that common ions and organic acids (such as citric acid, tartaric acid, and ascorbic acid ions) do not adversely affect sorption on the proposed resin when present in moderate amounts. The results obtained demonstrate that the proposed method is very tolerant to high concentrations of foreign ions and helpful for the Cd(II) determination in water samples.

Resin Stability and Reusability

The chelating resin is quite stable and was studied in 1.0 to 5.0 mol L⁻¹ HNO₃ acid. The resin was kept in acid for 24 hours and then filtered. The solid was washed with doubly distilled water until free from acid, then air-dried, and its total sorption capacity determined (25). The sorption capacity was found to vary < 3.0% than that of untreated resin. Thus, the present resin can withstand acid concentrations up to 5.0 mol L⁻¹. The reproducibility of the recovery data of Cd(II) was good even after ~100 cycles of sorption-desorption without any significant change in sorption capacity.

Accuracy of the Method

To evaluate the accuracy of the developed FI on-line microcolumn preconcentration method for the determination of Cd(II), standard reference material NIST SRM 1643e Trace Elements in Water was used. The certified values and the analytical results are listed in Table IV. It was found that there is no significant difference between the achieved results by the proposed method and the certified results.

TABLE II
Analytical Performance of Flow Injection On-Line Method for Cd(II) Determination

Parameters	Optimum Conditions		
pH Range	5.5–6.0		
Sample flow rate (mL min ⁻¹)	5.0		
Eluent flow rate (mL min ⁻¹)	6.0		
Acid conc. for desorption	0.1 mol L ⁻¹ HNO ₃		
Preconcentration time (PT, s)	60	120	180
Linear range (µg L ⁻¹)	1.4–60	0.77–30	0.47–25
Limit of detection (µg L ⁻¹)	0.43	0.23	0.14
Sample throughput (h ⁻¹)	30	20	15
Enhancement factor	36	75	118
Regression equation [(6 standards, n=3; Cd(II)/µg L ⁻¹ , with preconc.]	A ₆₀ = -0.01874+0.01396 [Cd(II)] A ₁₂₀ = -0.04365+0.02942 [Cd(II)] A ₁₈₀ = 0.02183+0.04609 [Cd(II)]		
Regression equation [6 standards, n=3; Cd(II)/µg L ⁻¹ , without preconcentration]	A = -0.00066+0.000392 [Cd(II)]		
Correlation coefficient (r)	0.997037	0.991208	0.995572
Precision (RSD%)	3.70, [Cd(II)] = 20 µg L ⁻¹		

TABLE III
Effect of Neutral Electrolytes and Ions on the FI On-line Preconcentration of Cd(II)

Foreign Species	Tolerance Limit	Foreign Species	Tolerance Limit
NaCl	0.3 mol L ⁻¹	K(I)	20 mg L ⁻¹
Na ₂ SO ₄	0.04 mol L ⁻¹	Ca(II)	13 mg L ⁻¹
NaBr	0.02 mol L ⁻¹	Cu(II)	5 mg L ⁻¹
NaNO ₃	0.05 mol L ⁻¹	Al(III), Pb(II)	8 mg L ⁻¹
Na ₃ PO ₄	0.07 mol L ⁻¹	EDTA	0.1 mmol L ⁻¹
MgCl ₂	0.02 mol L ⁻¹	Citric acid	0.7 mol L ⁻¹
NaI	0.15 mol L ⁻¹	Tartaric acid	0.4 mol L ⁻¹
Fe(III), Zn(II)	18 mg L ⁻¹	Ascorbic acid	0.2 mol L ⁻¹

TABLE IV
Cd(II) Determination in SRM 1643e Trace Elements in Water

Sample	Cd(II) amount (µg L ⁻¹)		Recovery (%)
	Certified Value	Proposed Method	
SRM1643e Trace Elements in Water	6.568±0.073	6.267±0.416	95.4

Application to Cd(II) Determination in Ground Water Samples

Water samples, collected from Noida, U.P, Naraina, and Mayapuri, Delhi, India, were filtered through a 0.45 μm pore size filter to remove any suspended particulate matter prior to its preconcentration. After the samples were filtered, the filtrate was adjusted to pH 5.5 to 6.0 by addition of a buffer solution and subjected to on-line FI-FAAS determination using Amberlite XAD2-salicylic acid resin as column material by following the procedure described below.

For these samples, the only pre-treatment was acidification to pH 2.0 with nitric acid, which was performed immediately after collection in order to prevent adsorption of the Cd(II) ions on the flask walls. All water samples were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter and stored at 4 °C. The standard addition method was used in all instances and the results were obtained by extrapolation. The recovery was estimated by adding a known volume of standard solution of the analytes in the examined samples. The recovery was calculated from the added and found concentrations and ranged from 96 to 98%. The analytical results along with the recovery are summarized in Table V.

For comparative purposes, the performance characteristics of the proposed method and other selected on-line SPE preconcentration FAAS methods reported in the literature are listed in Table VI. The proposed method shows good sensitivity (detection limit), better precision (%RSD), and high sample throughput with a very high enhancement factor over other on-line preconcentration methods.

TABLE V
Results of Determination of Cd(II) in Underground Water Samples

Sample	Conc. Determined ^a ($\mu\text{g L}^{-1}$)	Conc. Determined ^a of 20 $\mu\text{g L}^{-1}$ Spiked Cd(II) ($\mu\text{g L}^{-1}$)	Recovery (%)
Noida, U.P, India	5.10 $\pm$ 0.12	24.51 $\pm$ 0.30	97.6
Mayapuri, Delhi, India	6.15 $\pm$ 0.32	25.70 $\pm$ 0.41	98.2
Naraina, Delhi, India	5.62 $\pm$ 0.56	24.74 $\pm$ 0.48	96.5

^a Confidence interval: 95%.

CONCLUSION

The use of Amberlite XAD-2-SA in the form of beads as column packing material for FI-FAAS preconcentration and determination of trace Cd(II) was successfully performed. The chemical inertness, excellent swelling, shrinking resistance, hydrophilic nature, and fast kinetics of the proposed sorbent material make it very attractive for on-line column preconcentration systems. The chelate functionalized Amberlite XAD-16-SA beads can be used for several hundreds of preconcentration and elution cycles as there is no bleeding of the chelate. A high sample loading flow rate in conjunction with longer preconcentration times resulted in a more pronounced improvement in retention efficiency. The proposed method proved to be simple, rapid, and accurate for Cd(II) determination in water samples.

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TABLE VI
Comparison of Performance Characteristics Among Selected On-line SPE
and the Developed Methods for Cd(II) Determination With FAAS

Support	Chelating Agent	PT(s)	Eluent	EF	DL ($\mu\text{g L}^{-1}$)	RSD (%)	Ref.
Amberlite XAD-2	Pyrocatechol	180	HCl	44	0.27	6.1	27
Amberlite XAD-2	2-aminothiophenol	180	HNO ₃	74	0.14	5.8	28
Amberlite XAD-2	2-(2-thiazolylazo)-5-dimethyl-aminophenol (TAM)	60	HCl	108	1.2	9	29
Amberlite XAD-2	Xylenol Orange	120	HNO ₃	32	1.038	1.68	30
Amberlite XAD-4	Diethylditiophosphate	300	HNO ₃	20	1.0	3	31
Amberlite XAD-4	2-aminothiophenol	180	HCl	99	0.3	3.1	32
Amberlite XAD-4	2,6-dihydroxyphenyl-diazoaminoazobenzene	60	HCl	42	0.1	2.4	33
Polyurethane Foam	2-(6'-methyl-2'-benzothiazolylazo) chromotropic acid	180	–	37	0.80	3.1	34
Polyurethane Foam	2-(2-benzothiazolylazo)-2-p-cresol (BTAC)	60	HCl	41	0.27	1–5	35
Knotted Reactor	Dithione	60	Isobutyl-methyl-ketone	23.4	1.88	2.63	36
Chloromethylated Polystyrene	N,N-bis(naphthylidene-imino)diethylene-triamine	120	-	50	0.25	5.1	37
Bamboo Charcoal	-	80	HCl	63	0.36	3.2	38
Amberlite XAD-2	Salicylic acid	180	HNO ₃	118	0.14	3.70	This work

PT: preconcentration time; EF: enhancement factor; DL: detection limit; RSD: precision (relative standard deviation).

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