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Determination of cadmium in water and environmental samples by inductively coupled plasma atomic emission spectrometry after solid phase extraction using thiosemicarbazide derivative on alumina

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Environmental sample.

Abstract. A simple and selective method for the determination of cadmium ions in environmental samples by ICP-AES after solid-phase extraction was developed. The method is based on the sorption of Cd^{2+} ions on alumina modified by 1-((5-nitrofuran-2-yl)) thiosemicarbazide (NFMTC) at pH of 6. The metal ion retained on solid phase by complexation with ligand was then eluted with 5.0 mL of 1 mol L^{-1} nitric acid. A preconcentration factor of 120 was achieved by passing 600 mL of sample through the solid phase, while the Limit Of Detection (LOD) was found to be 0.025 ng mL^{-1} and relative standard deviation of ±2.2% (for 1.0 μg mL^{-1}), under optimum conditions. The proposed method was successfully applied to the determination of cadmium in water, soil, some food samples, and environmental samples including black tea, rice, wheat, carrot, pistachio and tobacco.

1. Introduction

The presence of heavy metals in the environment is major concern because of their toxicity and threat to human life and environment [1-8]. The accurate and precise determination of heavy metals in the food samples is important to obtain accurate results of them [9-14]. High levels of matrix components are influential in the determination of heavy metal ions. In order to remove matrix components from the traces heavy metals, separation methods like solid phase extraction, cloud point extraction, solvent extraction, etc. have been widely used [15-23]. Another important advantage of usage of separation methods is improvement in the limit of detection of the analytes, due to lower final volumes [24-31].

Solid-Phase Extraction (SPE) is a universal technique in this respect compared to the conventional liquid-liquid extraction [32-34]. Solid-phase extraction is based on the utilization of a major constituent as bonded stationary phase immobilized with different ligand or functional group [35-39]. Some advantages of SPE are higher enrichment factors, absence of emulsion, and safety with respect to hazardous samples, minimal costs due to low consumption of reagents, and flexibility and easier incorporation into automated analytical techniques [40,41]. Various solid phase extraction materials include microcrystalline naphthalene [42,43], Chelest Fiber [44], activated carbon [45], SDS coated alumina [46], polyurethane foam [47],

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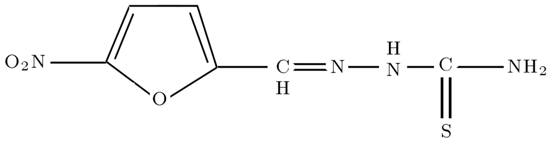

Figure 1. 1-((5-nitrofuran-2-yl)methylene) thiosemicarbazide (NFMTC).

functionalized polyurethane foam [48], modified silica [49,50] biomass loaded TiO_2 nanoparticles [51] and sulfur powder [52].

In the present study, a solid phase extraction scheme has been given for the preconcentration of cadmium ions on alumina modified 1-((5-nitrofuran-2-yl)methylene) thiosemicarbazide [NFMTC] (Figure 1). The developed method was applied to the analysis of environmental samples such as water, food and plant samples.

2. Experimental

2.1. Apparatus and reagents

A Perkin-Elmer model 7000 DV inductively coupled plasma atomic emission spectrometer (Norwalk, CT, USA) was used for determination of cadmium. The instrumental parameters were those recommended by the manufacture. A mechanical shaker Gerhardt Bonn (Deutschland, Germany) having speed control and timer was used for preparation of the sorbent. Funnels-tipped glass tube (5×100 mm) equipped with stopcock was used as column for the preconcentration purposes. A digital pH meter model WTW Inolab (Deutschland, Germany) was employed for pH measurements.

All reagents were of analytical grade. Deionized and distilled water was used in all experiments. The working standard solutions of Cd^{2+} were prepared by appropriate stepwise dilution of a 1000.0 μg mL^{-1} stock standard solution (Titrisol, Merck) to the required microgram per liter. A 0.1% (w/v) solution of the ligand was prepared by dissolving 0.10 g of NFMTC in $\sim$ 5 mL of DMF and diluting to 100.0 mL with ethanol. Buffer solution was prepared from 0.2 M potassium dihydrogen phosphate and 0.2 M dipotassium hydrogen phosphate (Aldrich) for pH of 6. Al_2O_3 (0.063-0.2 mm or 70-230 mesh ASTM) (Merck) was used as sorbent.

2.2. Preparation of the ligand NFMTC

A mixture of 5-nitrofuranylcarboxaldehyde (0.01 mol, 2.14 g) (Merck,>99%) and thiosemicarbazide (10.0 mmol, 0.9 g) (Merck, 99.99%) in presence of (0.5 mL) HCl in 20.0 mL ethanol was heated to reflux (temperature $\sim$ 80°C for 2 h). Then, the obtained derivative thiosemicarbazone was separated by filtration and then recrystallized, dried and purified from ethanol.

2.3. Preparation of the alumina coated with NFMTC

4-5 g of the alumina was added to 50.0 mL of the solution containing 0.1% NFMTC and the mixture was shaken at room temperature for 3 h. The reagent coated alumina was filtered, washed with distilled water and dried at room temperature for 24 h.

The modified alumina was confirmed by IR analysis. Comparing the IR spectrum of bare alumina with modified alumina, many new peaks appeared in the spectrum. The infrared spectrum of the ligand showed strong absorption bands at 3463 and 3307 cm^{-1} which were assigned ν(N-H) vibration. The strong band observed at 1601 cm^{-1} in the spectrum was due to the ν(C=N). The bands observed at 1537, 1392, 844 and 566 cm^{-1} were due to the nitro group. The bands observed at 1479, 1257 and 1057 cm^{-1} were assigned to ν(C=C), ν(C=S) and ν(N-N) vibrations, respectively. The alumina adsorbent showed the characteristic peaks at 3481-2800, 1635 and 1000-400 cm^{-1} that are mainly due to the alumina matrix.

However, the IR-spectrum of modified alumina adsorbent with ligand is dominated by the peaks corresponding to the alumina matrix and some of the strong band corresponding to ligand, for example at 3463, 3309, 1601, 1537, 1478, 1257 and 564 cm^{-1} due to ν(N-H), ν(C=N), ν(N=O), ν(C=C) and ν(C=S), respectively. Consequently, the above experimental results suggest that alumina is successfully modified by the ligand NFMTC.

2.4. Pre-treatment of real samples

0.50 g of the different samples (rice, carrot, black tea, wheat, tobacco and soil) was heated in silica crucible for 3 h on a hot plate, separately, and the charred material was transferred to a furnace for 6 h at 550°C. The residue was treated with 10.0 mL of 5% nitric acid and the solutions were cooled, diluted and filtered. The filtered solutions were diluted to 100.0 mL with distilled water in calibration flask. 25.0 mL of each pretreated sample solution was taken individually and cadmium was determined by the proposed procedure.

The proposed preconcentration procedure has been also applied to determine cadmium in water different samples including a tap water from Rafsanjan, wall water from Anar, spring water from Noogh, a mineral water, and distilled water. The water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. 500.0 mL of water samples was transferred to a beaker, and pH was adjusted to 6 by addition of the buffer solution. Then, the proposed procedure was applied to these samples.

In order to evaluate the accuracy of the procedure, recovery experiments were also carried out with spiked samples. The recovery percentages of cadmium ions were evaluated and the results showed that the real samples matrixes did not affect the recovery of this ion.

2.5. Recommended procedure for separation and preconcentration

A small amount of glass wool was placed in the end of the columns to prevent loss of the sorbent during sample loading. Then, the columns were packed with 100.0 mg of the alumina coated with NFMTC and conditioned with a buffer solution at pH=6. An aliquot of the sample solution containing Cd(II) (0.01-15.0 μg) was taken in a 50 mL beaker to which 1.0 mL phosphate buffer solution with pH 6 was added. The total volume of the solution was made up to about 30 mL with distilled water. It was then passed through the column containing 100 mg of the sorbent with flow rate of 1.0 mL min^{-1}. The flow rate of solution was controlled by using a stopcock in end of the column. The retained cadmium ions were eluted from the solid phase with 5.0 mL of 1 mol L^{-1} HNO_3 solution. Finally, the desorbed cadmium was transferred into ICP-AES instrument and determined according to instrumental conditions. Calibration curve for the determination of cadmium was prepared according to the proposed procedure under the optimum conditions.

3. Results and discussion

The preliminary experiments showed that the bare alumina can adsorb a lot of metal ions, but, adsorption was not selective and the recoveries were incomplete. By immobilization of the ligand NFMTC on the alumina, only Cd can be adsorbed in the specified pH. On the other hand, the coating of alumina with the ligand increases the adsorption capacity for Cd.

In order to achieve the best performance, the separation/preconcentration procedure was optimized for various analytical parameters, such as pH of the sample, the flow rate of eluent and sample solution, amount of the adsorbent, volume and type of the eluent solution, volume of the buffer and volume of the sample solution. Various ions interference effects were also investigated.

3.1. Effect of the sample pH

Since the pH of the aqueous solutions is an important analytical factor in solid phase extraction studies of metal ions [53], the influence of pH on the recovery of cadmium was examined in the pH range of 2-10 by using the diluted solution HNO_3 and NaOH or the proper buffers. As can be seen from Figure 2, Cd (II) ions were quantitatively recovered at pH range of 5.5-6.5. Therefore, pH 6 was selected for further study and kept using KH_2PO_4 buffer solution.

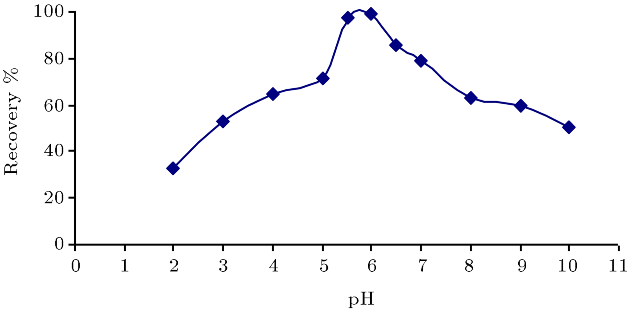

Figure 2. Effect of pH on the recovery of Cd after preconcentration with the proposed method. Conditions: Cd, 5.0 μg; flow rate, 1 mL min^{-1}; sorbent, 100.0 mg; elution solution, 5.0 mL of 1.0 mol L^{-1} HNO_3.

3.2. Effect of type and concentration of eluent

There are many different methods for desorption of analyte on solid phase. One of them is simply to wash the modified adsorbent with a small amount of an organic solvent, such as acetone, acetonitrile, or methanol. This will usually dissolve the metal complexes and cause them to elute quickly and completely. Another possibility is to wash the column with an aqueous solution that is sufficiently acidic to break up the metal organic complex. A combination of these two, as the third desorption approach, is possible; a solution of strong mineral acid in an organic solvent will simultaneously break up the complex and eluent analyte. In order to choose the most effective eluent for desorbing of the retained Cd (II) from the column, a series of selected eluent solutions such as different acids were tested. The results showed that the recovery is best when nitric acid was used. 5.0 mL of 1.0 mol L^{-1} HNO_3 solution was applied as the eluent for further works.

3.3. Effect of flow rate of sample and eluent solution

The retention of an element on a sorbent also depends on the flow rate of the sample solution. Thus, the effect of flow rate of the sample and elution solution on the retention and recovery of cadmium ions was investigated under optimum conditions. The solution containing Cd (II) was passed through the column with the flow rates adjusted in a range of 0.15-3.0 mL min^{-1}. It was observed that, at flow rates greater than 1.0 mL min^{-1}, there was a decrease in the recovery Cd. The reason for this decrease is probably insufficient contact of the metal ions and the sorbent to reach equilibrium. Therefore, a flow rate of 1.0 mL min^{-1} was selected for subsequent experiments.

For desorption of cadmium ions, flow rate was varied between 0.5-3.0 mL min^{-1}. The flow rate of 2.0 mL min^{-1} was adequate for desorption of the analyte. Therefore, a flow rate of 1.0 mL min^{-1} was used in the sorption step and flow rate of 2.0 mL min^{-1}

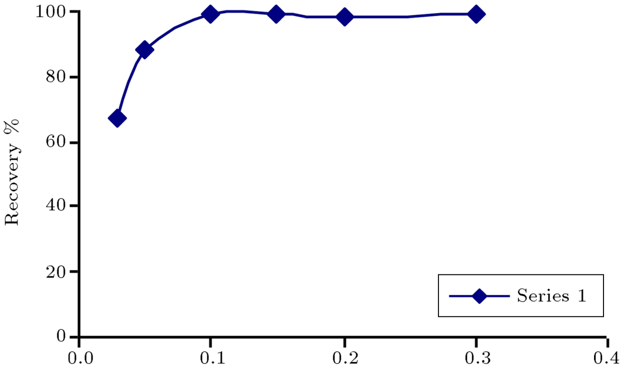

Figure 3. Effect of amount of the sorbent.

for desorption, and adjusted with a stopcock in end of the column.

3.4. Effect of amount of the sorbent

The amount of sorbent is another important parameter that affects the recovery. A quantitative retention is not obtained when the amount of sorbent is less. On the other hand, an excess amount of resin prevents the elution of the retained chelates by a small amount of eluent quantitatively [54]. For this purpose, different amounts of the sorbent (30.0-300.0 mg) were examined. The results showed that quantitative recovery (>95%) of the cadmium was obtained when the sorbent quantity was greater than 100.0 mg (Figure 3). Therefore, 100.0 mg of the sorbent was selected for further experiments.

The column filled 100.0 mg adsorbent can be regenerated with good precision and high recovery (>95%), over 100 cycles of adsorption-desorption without any significant change in the retention of Cd. It can regenerate with about 10 mL of distilled water.

3.5. Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample [53]. The volume of the first aqueous phase, containing a fixed amount of the analyte (5.0 μg Cd), was varied in the range of 200.0-700.0 mL under the optimum conditions, keeping other variables constant, and passed through column for preconcentration. It was found that recovery was quantitative to 600.0 mL (Figure 4). At sample volumes more than 600.0 mL, the recoveries decreased gradually with increasing volume of sample solution. Since the elution solution volume was 5.0 mL, preconcentration factor was obtained 120.

3.6. Sorption capacity of the sorbent

To determine the amount of analyte retained on the column, for a specific mass of sorbent, several solutions differing in concentrations were made and introduced into the column. Ten milliliters of the solutions containing Cd at concentrations in the range of 50.0-200.0 mg L^{-1} were passed through the column containing exactly 100.0 mg of the sorbent under optimum conditions. The eluting solutions were collected and the presence of the analyte in each tested by ICP-AES. When Cd was detected in the eluate, the test stopped and the sorption capacity calculated. The sorption capacity was found to be 15.0 mg Cd^{2+} for 1.0 g sorbent.

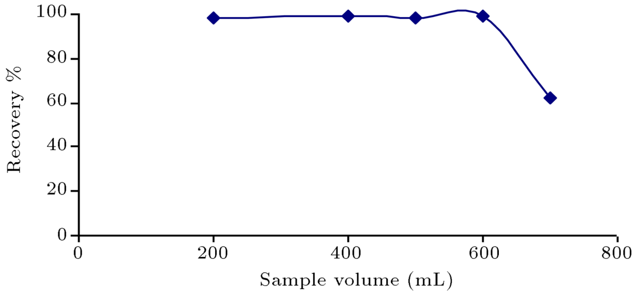

Figure 4. Effect of sample volume on recoveries.

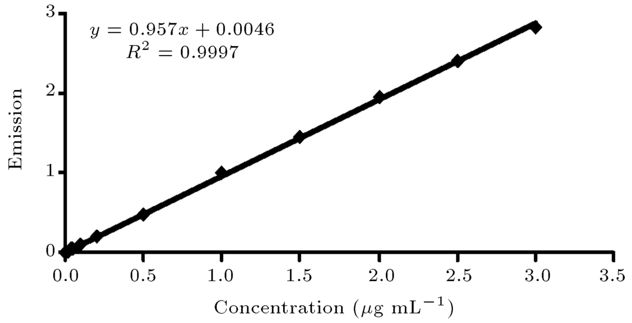

Figure 5. Calibration curve for cadmium. Conditions setting were the same as Figure 2.

3.7. Matrix effects

Various salts and metal ions were added to a solution 1.0 μg mL^{-1} Cd (II) and the general procedure was applied. The tolerance limit was set as the concentration of the ion required to cause ±3% error [55]. The results obtained are given in Table 1. Among the metal ions and salts studied, most did not interfere. Thus, this method is selective and can be used for the determination of Cd in the various samples.

3.8. Analytical performance

The analytical performance of the proposed procedure can be shown for the results of ICP-AES measurements. The linearity was maintained in the concentration range of 0.002-3.0 μg mL^{-1} in the final solution or $1.6 \times 10^{-2} - 3.0 \times 10^{3}$ ng mL^{-1} in the original solution. The equation of the line is $A = 0.957C + 0.0046$ with regression coefficient 0.9997 (Figure 5) in the final solution, where A is the absorbance and C is concentration of the Cd (μg mL^{-1}).

Table 1. Effect of diverse salts and metal ions on the extraction and preconcentration of Cd(II).

Salt or ion	**Tolerance limit (mg)**
Na^+, Ca^{2+}, Mg^{2+}	500
CH_3COONa, NaF	450
$NaNO_3$	600
Na_2SO_4, Na_2CO_3	450
$Na_2C_2O_4$, MgS_2O_3, $NaHCO_3$	500
EDTA	350
Citrate	400
Co^{2+}, Fe^{2+}	5
Fe^{3+}, Ag^+, Hg^+	4.7
Cu^{2+}	4
Pb^{2+},Cr^{6+}	4.5
Cr^{3+}	4.8
Ni^{2+}	4.3
Mn^{2+}	4.6
Mo(IV)	4
Ba^{2+}	4

Tolerance limit is defined as concentration of the ion required to cause ±3% error.

Conditions: Cd, 5.0 μg; pH $\sim$ 6; flow rate, 1 mL min^{-1}; sorbent, 100.0 mg; elution solution, 5.0 mL of 1.0 mol L^{-1} HNO_3.

Eight replicate determinations of 5.0 μg cadmium in the 5.0 mL final solution gave a relative standard deviation of ±2.2%. The Limit Of Detection (LOD) based on $3\sigma_{\mathrm{bl}}/m$ ($n = 8$) and LOQ based on $10\sigma_{\mathrm{bl}}/m$ were 0.025 and 0.182 ng mL^{-1}, respectively, in the original solution.

3.9. Application to real samples

To assess the capability of the method for real samples with different matrices containing varying amounts of diverse ions, the method was applied to determine cadmium in different water samples. The results are given in Table 2. According to the results, the concentration of cadmium in analyzed water samples was below the LOD of the method. The suitability of the proposed method for the analysis of natural water samples was checked by spiking the samples with 5.0 and 10.0 mL of 2.0 μg mL^{-1} of the analyte ions. Good recoveries were obtained for all analyzed samples (Table 2).

The procedure was also applied to plant and soil samples that have a more complex matrix than water. The correctness of the results was tested by analysis of the spiked samples. The recovery percentage of cadmium ions was evaluated and the results showed that the real samples matrixes did not affect the recovery of cadmium. The results are given in Table 3.

Table 2. Determination of cadmium in the water samples after preconcentration with the proposed method.

Sample	**Cadmium (ng mL^{-1})**		**Recovery**
	Spiked	**Found**[a]	**(%)**
Distilled water	0.00	ND	–
	5.00	5.01 ± 0.11	100.2
	10.00	10.35 ± 0.19	103.5
Spring water (Noogh)	0.00	ND	–
	5.00	5.00 ± 0.06	100.0
	10.00	10.03 ± 0.18	100.3
Wall water (Anar)	0.00	ND	–
	5.00	5.02 ± 0.04	101.4
	10.00	10.05 ± 0.14	100.5
Tap water[b]	0.00	ND	–
	5.00	5.00 ± 0.11	100.0
	10.00	10.20 ± 0.21	102.0
Mineral water	0.00	ND	–
	5.00	5.00 ± 0.07	100.0
	10.00	10.08 ± 0.14	100.8

ND: Not Detected;
Sample volume: 500.0 mL;
Conditions: Cd, 5.0 μg; pH $\sim$ 6; flow rate, 1 mL min^{-1}; sorbent, 100.0 mg; elution solution, 5.0 mL of 1.0 mol L^{-1} HNO_3.

[a]: Average of three determinations, ± S.D;

[b]: Rafsanjan, Iran.

Table 3. Determination of cadmium in environmental samples after preconcentration with the proposed method.

Sample	**Cadmium (μg g^{-1})**		**Recovery**
	Spiked	**Found**[a]	**(%)**
Soil	0.00	2.51 ± 0.03	–
	5.00	7.54 ± 0.14	100.6
	10.00	12.35 ± 0.21	100.2
Pistachio[b]	0.00	1.12 ± 0.03	–
	5.00	6.10 ± 0.11	99.6
	10.00	11.09 ± 0.30	99.7
Carrot	0.00	0.31 ± 0.01	–
	5.00	5.24 ± 0.11	98.6
	10.00	10.33 ± 0.18	100.2
Black tea	0.00	0.65 ± 0.01	–
	5.00	5.61 ± 0.14	99.2
	10.00	10.63 ± 0.21	99.8
Wheat	0.00	0.21 ± 0.01	–
	5.00	5.19 ± 0.11	99.6
	10.00	10.23 ± 0.21	100.2
Tobacco	0.00	1.71 ± 0.04	–
	5.00	6.74 ± 0.14	100.6
	10.00	11.69 ± 0.22	99.8
Rice	0.00	Not detected	–
	5.00	4.99 ± 0.07	99.8
	10.00	10.08 ± 0.18	101.8

Sample volume: 25.0 mL;
Conditions: pH $\sim$ 6; flow rate, 1 mL min^{-1}; sorbent, 100.0 mg; elution solution, 5.0 mL of 1.0 mol L^{-1} HNO_3.

[a]: Average of three determinations, ± S.D;

[b]: Digestion with microwave.

Table 4. Analysis of cadmium in standard sample.

Sample	Composition	Found[a]	Recovery (%)
NIES, No. 3 Chlorella	K: 1.24 ± 0.06, Mg: 0.33 ± 0.02, Ca: 0.46 ± 0.03, Fe: 0.185 ± 0.010 P: (1.7)%, Cu: 3.5 ± 0.3, Zn: 20.5 ± 1.0 Sr: 40 ± 3, Co: 0.87 ± 0.05 Cd: (0.026), Mn: 69 ± 5 (μg g^{-1})	Cd: 0.0252 ± 0.0005	96.9

NIES: National Institute of Environmental Studies;

[a]: Average of three determinations, ± S.D;

Conditions: pH ~ 6; flow rate, 1 mL min^{-1};

sorbent, 100.0 mg; elution solution, 5.0 mL of 1.0 mol L^{-1} HNO_3.

Table 5. Comparative data from some extraction methods on preconcentration of cadmium.

Method	Determination technique	PF[a]	LOD (μg L^{-1})	RSD%	Sorption capacity (mg g^{-1})	Ref.
SPE	FAAS	40	0.6	3.9	—	[42]
SPE	FAAS	74	0.14	2.2	3.7[b]	[56]
SPE	FAAS	80	0.24	1.4	3.5	[57]
SPE	FAAS	31	0.37	2.5	8.9	[58]
SPE	FAAS	100	1.19	1.4	4.4	[59]
SPE	ICP-AES	50	0.048	3.5	2.9	[60]
SPE	FAAS	100	0.20	—	4.4	[61]
SPE	ICP-AES	120	0.026	2.2	15.0	This work

[a]PF: Preconcentration Factor;

[b]mmol g^{-1}.

3.10. Analysis of cadmium in standard samples

The accuracy of the proposed method was tested by using a standard samples: National Institute for Environment Studies (NIES) No. 3 Chlorella. A 0.1000 g standard sample was taken in a beaker and dissolved in concentrated nitric acid with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100.0 mL with distilled water in a calibration flask. A suitable aliquot of the pre-treated sample solution was taken and analyzed by the proposed procedure. The results are given in Table 4, which are in good agreement with the certified values.

3.11. Comparison with other methods

Comparative data from some papers on solid phase extraction of trace Cd summarized in methods are described in the literatures (Table 5). The detection limit is superior to those of other preconcentration/separation methods. The sorption capacity and preconcentration factor is also better or comparable with the other methods. The matrix effects with the proposed method were reasonably tolerable. Good recoveries were obtained for the environmental samples, demonstrating that the method can be successfully applied to these samples.

4. Conclusions

A new solid phase extraction technique was developed based on the preconcentration of cadmium in environmental samples on alumina coated with thiosemicarbazide prior to determination by FAAS. Preparation of the sorbent is simple, rapid and low cost. The modified alumina can be regenerated over 100 cycles of adsorption-desorption without any significant change in the retention of Cd. The accuracy of the results was verified by analyzing the spike samples. The good precision and high tolerance to interferences from matrix ions are other advantages. Thus, it may be concluded that the method is an effective approach in separation and preconcentration of cadmium in environmental samples.

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