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Salen impregnated silica gel as a new sorbent for on-line preconcentration of cadmium(II)

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A new sorbent – salen impregnated silica gel – was prepared and characterised for application as a minicolumn packing for flow-injection on-line preconcentration of cadmium(II). The system was coupled with flame atomic absorption spectrometer (FI-FAAS). The optimal pH for Cd(II) sorption was in the range of 7.4–8.8 and nitric acid (1%, v/v) was efficient as eluent. Sorption was most effective within the sample flow rate up to 7 mL min⁻¹. Sorption capacity of the sorbent found in a batch procedure was 26.3 μmol g⁻¹ (2.95 mg g⁻¹). Enrichment factor (EF) and limit of detection (LOD) obtained for 120-second loading time were 113 and 0.26 μg L⁻¹, respectively. The sorbent stability in the working conditions was proved for at least 100 preconcentration cycles. The evaluated method was applied to Cd(II) determination in various water samples.

Keywords: cadmium(II); on-line preconcentration; salen impregnated silica gel; flow-injection flame atomic absorption spectrometry (FI-FAAS)

1. Introduction

Cadmium is a common environmental contaminant and has been long known to be highly toxic for all living organisms [1,2], therefore its determination at trace levels is of great importance and still attracts much attention, especially in the case of spectrometric techniques [3]. However, many popular and widely used analytical techniques, e.g. flame atomic absorption spectrometry (FAAS), suffer from insufficient limit of detection, thus hindering their applicability to trace cadmium(II) determination. The problem may be overcome by introducing a preconcentration step prior to detection. This may be easily realised with flow injection system [4,5]. On-line sorption-based systems for cadmium determination with atomic spectrometry detectors have been recently revised by Pyrzyńska and Kilian [6].

Various sorbents have been proposed for on-line separation and preconcentration of cadmium(II). Many of them are based on modification of already existing both organic and inorganic solid supports, which may be either chemical or physical. In the former case, modification is realised via grafting complexing groups onto a support surface (thus creating a covalent bond between them). Recently, Lemos *et al.* [7] reported application of

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2-aminothiophenol functionalised Amberlite XAD-4 resin to flow-injection preconcentration of cadmium in tobacco samples. Zougagh *et al.* [8] used silica gel functionalised with 1,5-bis(di-2-pyridyl)methylenethiocarbonylhydrazide (DPTH-gel) and silica gel functionalised with methylthiosalicylate (TS-gel) to on-line preconcentration of cadmium(II) coupled with ICP-AES. Chen *et al.* [9] utilised chelating properties of chitosan grafted to mesoporous silica. The new sorbent was applied as a microcolumn packing material for on-line (FI-ICP OES) determination of heavy metals (including cadmium) in environmental water samples. Pacheco *et al.* [10] presented a new sorption material based on L-methionine immobilised on controlled pore glass. The sorbent was applied as a minicolumn filling in FI-ICP OES system. A number of grafted sorbents have also been proposed for off-line preconcentration of cadmium(II). Recently, Burham *et al.* [11] have reported acetylacetone bonded polyurethane foam which was applied to preconcentration of cadmium and lead in tap water and apple leaves. Wongkaew *et al.* [12] functionalised Amberlite XAD-2 with purpurine through an azo linkage and studied its application to extraction of Cd(II), Cr(III) and Pb(II) from leachate of cement-based stabilised waste.

When modification is realised via physical interaction of a modifying agent and a solid support, the process is called impregnation. It is still one of the most popular methods of sorbent modification due to its simplicity in performance. It may be realised via adsorption, inclusion or electrostatic interactions [13]. Gama *et al.* [14] employed polyurethane foam (PUF) impregnated with 2-(6-methyl-2-benzothiazolylazo)chromotropic acid (Me-BTANC) as a minicolumn filling in FI-FAAS system for Cd(II) determination in environmental samples. Ensafi and Ghaderi [15] used activated carbon modified with methyl thymol blue for on-line separation and preconcentration of Cd(II) in water samples. Shabani *et al.* [16] developed on-line solid-phase extraction system based on 1,10-phenantroline immobilised on surfactant coated alumina and utilised it to cadmium determination in tap, river and sea water samples. Also biopolymer-based sorbents have attracted some attention in this field, e.g. chitosan biopolymer modified with 5-sulphonic acid 8-hydroxyquinoline (sulphoxine) via spray drying was employed in on-line preconcentration of cadmium ions in water samples [17].

In this work application of salen impregnated silica gel to FI-FAAS determination of cadmium(II) in water samples has been presented.

2. Experimental

2.1 Reagents

Salicyl aldehyde pure and ethylenediamine pure for analysis were obtained from Aldrich (Milwaukee, WI, USA). Silica gel was obtained from J.T. Baker (Deventer, Holland).

Standard stock solutions of heavy metal ions were prepared from Titrisol[®] standards (Merck, Darmstadt, Germany). Nitric acid, hydrochloric acid and chloroform were purchased from Merck. Deionised water after reversed osmosis was used throughout the work. Britton-Robinson buffers comprised a mixture of 0.04 mol L⁻¹ acetic acid, 0.04 mol L⁻¹ phosphoric acid, 0.04 mol L⁻¹ boric acid and 0.2 mol L⁻¹ sodium hydroxide in appropriate ratios; ammonia/ammonium chloride buffer was composed of 0.2 mol L⁻¹ NH₃ and 0.2 mol L⁻¹ NH₄Cl. Sodium hydroxide, acetic acid and boric acid were obtained from POCh (Gliwice, Poland). Ammonia (25%) and ammonium chloride were supplied by Lach-Ner (Neratovice, Czech Republic) and Merck, respectively. All reagents were of analytical grade.

Certified reference materials: EnviroMAT Ground Water, High (ES-H-2 CRM) and EnviroMAT Waste Water, High (EU-H-3 CRM) were purchased from SCP Science, Canada.

2.2 Instrumentation

FIAS 400 flow system coupled with PE 3100 flame atomic absorption spectrometer (both Perkin Elmer, Waltham, MA, USA) were used for metal ions preconcentration and determination. Cadmium(II) was determined at 228.8 nm and air-acetylene flame was used with the gases flow rates as recommended by the manufacturer. Deuterium background correction was used for all measurements. Inductively Coupled Plasma Mass Spectrometer (ICP-MS), ELAN DRC-e (Perkin Elmer) was applied to cadmium determinations at trace level and as a reference technique for accuracy evaluation. A home-made minicolumn (5 mm × 3 mm i.d.) and Tygon (Saint-Gobain Performance Plastics, Charny, France) red-tubings (1.14 mm i.d.) were used in the study. Elmetron CPI-551 pH-meter (Zabrze, Poland) was used for pH measurements.

2.3 Salen preparation

Salen (2,2'-(ethane-1,2-diylbis[nitrilo(*E*)methylidene]}diphenol) was prepared as follows: salicyl aldehyde (2.44 g, 0.02 mol) was dissolved in ethanol (20 mL) and the solution was heated to boil. To the boiling solution ethylenediamine (0.6 g, 0.67 mL, 0.01 mol) was added dropwise. Thus obtained suspension of salen was refluxed for 30 min, cooled to 0°C and the product was separated under reduced pressure.

2.4 Preparation of salen impregnated silica gel

To prepare the sorbent, 42 mg of salen was dissolved in 5.4 mL of chloroform, then 1 g of silica gel was added to the solution and mixed thoroughly. The solvent was subsequently evaporated in room temperature. Thus, obtained sorbent was ready to use.

2.5 Sample preparation

Five sorts of water samples, both natural and fortified, were employed in the sorbent applicability test. Spring water and tap water were used without any additional preparation. Stream and river water samples were filtered through cellulose acetate membrane filter (0.45 μm, Sartorius, Goettingen, Germany) and kept refrigerated until used. Fortified water was prepared by spiking deionised water to obtain elements concentrations close to those in surface water (SPS-SW Reference Material for Measurement of Elements in Surface Waters, Spectrapure Standards AS, Oslo, Norway). Certified reference materials were diluted before analysis in a degree corresponding to the working concentration level of the proposed method. Both reference materials and real samples were adjusted to appropriate pH with Britton-Robinson buffer.

2.6 Preconcentration procedure

Extraction was conducted in on-line mode with the use of a flow injection set. The system consisted of a minicolumn, a two positional valve, two peristaltic pumps and flame atomic absorption spectrometer. A typical extraction procedure was as follow. A sample was loaded onto a minicolumn with the use of pump 1. Ten seconds before the elution step was introduced, pump 2 was activated and acid solution (eluent) was directed to the flame so that the conditions were stabilised and the signal was set zero. Then the valve position was changed and cadmium ions retained on the sorbent were eluted with acid solution provided with the use of pump 2. The eluate was transferred through a capillary directly to the nebuliser. The detailed programme is described elsewhere [18]. In preliminary studies, both sorption and elution time (the latter one including 10 s reading time) were set at 30 s. Sorption time was increased up to 120 s for real samples analyses. Signal was recorded as peak height with 1 s read delay.

3. Results and discussion

3.1 Effect of elution conditions

Nitric acid and hydrochloric acid solutions ($0.01\text{--}0.3\text{ mol L}^{-1}$) were prepared and used as eluents. The results indicated nitric acid to be a slightly more effective eluent than hydrochloric acid. Elution effectiveness for nitric acid was found constant starting from 0.1 mol L^{-1} . To ensure adequate acidity 0.15 mol L^{-1} (1%, v/v) nitric acid was chosen as eluent for further studies. As nebulisation uptake should be close to eluent flow rate to maintain the good sensitivity and stability of FAAS analysis the latter was set at $7.6\text{--}7.8\text{ mL min}^{-1}$ for all measurements.

3.2 Effect of sample flow rate

Loading conditions were optimised in terms of sample flow rate as sorption efficiency is strongly dependent on sorption kinetics. Measurements were carried for Cd(II) standard solution (0.1 mg L^{-1} , pH 8) with sample flow rate within the range of $4\text{--}10\text{ mL min}^{-1}$. Sorption time was changed consecutively in order to keep the sample volume constant for all measurements. The obtained results indicate only slight influence of sample flow rate on cadmium sorption effectiveness in the tested range – it was constant in the case of lower flow rates ($3.8\text{--}7.2\text{ mL min}^{-1}$) and only a slight decrease was observed when introducing flow rates above 8.0 mL min^{-1} . Finally, the flow rate of 8 mL min^{-1} was chosen for further studies as the signal decrease was negligible (only 4%), whereas higher sample loading rate allowed increase in sensitivity.

3.3 Effect of the loading solution pH on Cd(II) sorption

Metal ions complexation reaction is usually influenced by the medium pH, hence cadmium(II) sorption was examined in a pH range of 3–10 (Figure 1). As the plateau region is within pH range of 7.4–8.8, working solutions pH was adjusted to 7.7–8.2 in further studies.

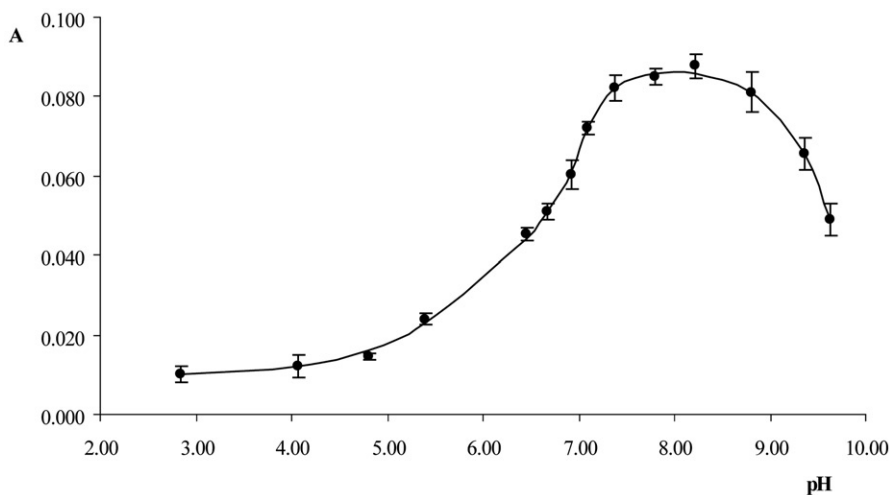


Figure 1. Effect of sample pH on cadmium(II) sorption.

3.4 Evaluation of sorption efficiency in flow mode

Sorption efficiency was evaluated for 30-second loading time, standard flow rate of 8.0 mL min^{-1} and pH 8. The study was conducted at two cadmium(II) concentration levels (0.025 and 0.050 mg L^{-1}). Each standard solution was passed through the minicolumn and the filtrate was collected. Initial and final cadmium concentration was found with the use of ICP-MS. The final result was calculated as an average of four replications. The evaluated sorption efficiency was comparable at both levels and amounted to 90.2%.

3.5 Sorption capacity test

Sorption capacity was examined in a batch procedure. Sorbent portions of 50 mg were transferred to plastic vials and soaked with 10 mL of cadmium standard solution within the concentration range of $1\text{--}250 \text{ mg L}^{-1}$. The vials were subsequently placed in a sonic bath and sonicated for 60 min. Afterwards Cd concentration in both standard solutions and filtrates was determined by FAAS. Sorption capacity was calculated according to Equation (1):

$$Q = (C_0 - C_f) * V/m \quad (1)$$

where Q represents sorption capacity (mg g^{-1}), C_0 and C_f are the initial and final Cd(II) concentration (mg L^{-1}), V and m represent volume of Cd(II) solution (L) and sorbent mass (g), respectively.

Sorption capacity of salen impregnated silica gel found in a batch test was 2.95 mg g^{-1} ($26.3 \text{ } \mu\text{mol g}^{-1}$).

3.6 Sorbent stability test

For sorbent stability evaluation, a portion (22 mg) of salen modified silica gel was packed in a minicolumn and subjected to a number of repetitive preconcentration cycles in the

Table 1. Selectivity evaluation of salen impregnated silica gel.

Interferent	Concentration (mg L ⁻¹)	Cd(II) recovery (%)		Interferent	Concentration (mg L ⁻¹)	Cd(II) recovery (%)	
		Sorbent mass				Sorbent mass	
		21 (mg)	87 (mg)			21 (mg)	87 (mg)
Cu(II)	0.1	92.4	98.3	Mn(II)	2.0	103.3	
	0.2	85.6	85.1		5.0	104.3	
	0.5	66.3	72.8				
Zn(II)	0.1	101.9		Mg(II)	2.0	106.1	
	0.2	101.3			5.0	84.9	103.0
	0.5	69.2					
	1.0		100.4				
	2.0		97.9				
	5.0		84.0				
Fe(III)	0.1	89.6		Ca(II)	10.0	101.5	
	0.2	62.8	86.9		15.0	102.0	
			75.7		20.0	103.1	
Pb(II)	0.1	90.1	91.2	K(I)	2.0	100.7	
	0.2	91.4	85.6		5.0	104.1	
	0.5	58.0	72.2				
Ni(II)	2.0	102.2					
	5.0	94.3	101.6				

optimal conditions. The test was performed for Cd(II) concentration of 0.05 mg L⁻¹ (30 s loading time) and proved the sorbent stability in the working conditions for at least 100 preconcentration cycles. The obtained results did not exhibit any descending trend of the sorbent activity and the readings precision (RSD) was 4%.

3.7 Selectivity test

Selectivity studies were performed towards the following ions: Cu(II), Zn(II), Fe(III), Pb(II), Ni(II), Mn(II), Mg(II), Ca(II) and K(I). The effect of the above-mentioned ions on Cd(II) sorption (0.05 mg L⁻¹) was evaluated for interferent concentration up to 5 mg L⁻¹ for heavy metals, Mg(II) and K(I) and up to 20 mg L⁻¹ for Ca(II) (Table 1).

Cadmium(II) preconcentration with the use of the proposed sorbent was free from interferences from Ni(II), Mn(II) and light metal ions in the whole studied concentration range, whereas the strongest influence was observed for Cu(II), Pb(II), Fe(III) and Zn(II). The interference effect from Zn(II) was eliminated via sorbent mass increase, whereas for the rest of the interferents the effect was thus reduced.

3.8 Analytical figures of merit

Enrichment factor (EF) was calculated as a ratio of the calibration slope found when applying on-line preconcentration (FI-FAAS) and the one found without it (FAAS).

Table 2. Analytical characteristics of the proposed method.

Parameter	
Loading time (s)	120
Enrichment factor (EF)	113
Calibration range ($\mu\text{g L}^{-1}$)	1.0–10.0
Correlation coefficient (R^2)	0.9985
Precision (RSD, $n = 5$) (%)	3.3 ($2.0 \mu\text{g L}^{-1}$)
Limit of detection (LOD) (3σ) ($\mu\text{g L}^{-1}$)	0.26
Limit of quantification (LOQ) (10σ) ($\mu\text{g L}^{-1}$)	0.87
Concentration efficiency (CE) (min^{-1})	38.0
Sample consumption (mL)	16
Eluent consumption (mL)	3

Note: $\text{CE} = \text{EF} \times \text{samples per minute}$.

Table 3. Applicability of the sorbent to preconcentration of cadmium(II) in real water matrices.

Sample	FI-FAAS ($\mu\text{g L}^{-1}$)	ICP-MS ($\mu\text{g L}^{-1}$)	RE (%)
Tap water	2.17 ± 0.34	2.163 ± 0.048	0.3
Vistula river water	2.34 ± 0.22	2.272 ± 0.035	3.1
Spring water	2.02 ± 0.15	1.937 ± 0.028	4.4
Stream water	1.91 ± 0.23	2.051 ± 0.039	-6.7
Fortified water	2.93 ± 0.10	2.979 ± 0.040	-1.5
CRM	FI-FAAS (mg L^{-1})	CRM certified value (mg L^{-1})	CRM confidence interval
ES-H-2	0.204 ± 0.025	0.200	0.194–0.205
EU-H-3	0.226 ± 0.015	0.228	0.225–0.230

EF value obtained for the proposed sorbent for 120-second sorption time was 113, while the limit of detection (LOD, 3σ) and limit of quantification (LOQ, 10σ) values were 0.26 and $0.87 \mu\text{g L}^{-1}$, respectively. The obtained analytical figures of merit for cadmium(II) preconcentration with the use of the proposed salen impregnated silica gel coupled with FAAS determination found for 120 s preconcentration time have been summarised in Table 2.

3.9 Applicability of the proposed method

The proposed method was applied to cadmium(II) determination in tap, stream, river (Vistula River) and spring water spiked with $2 \mu\text{g Cd L}^{-1}$. Additionally, fortified water was prepared and subjected to FI-FAAS determination of cadmium(II). In all cases, the standard addition method (SAM) was used for calibration purposes. The FI-FAAS results were compared with those obtained with the use of ICP-MS as a reference method and relative error (RE) was calculated. For accuracy evaluation of the proposed method, certified reference materials (ES-H-2 CRM and EU-H-2 CRM) were examined (Table 3).

Table 4. Comparison of the obtained preconcentration parameters with the ones found for other reported sorbents.

Sorbent	LOQ (10σ) ($\mu\text{g L}^{-1}$)	CE (min^{-1})	EF	Preconcentration time (s); sample volume (mL)	Ref.
2-aminothiophenol functionalised Amberlite XAD-4 resin	3.6	26.4	33	60; 7.0	[7]
	0.9	29.7	99	180; 21.0	
(1) Silica gel functionalised with 1,5- bis(di-2-pyridyl)methylenethio- carbohydrazide (DPTH-gel)	3.3	57.3	86	60; 6.0	[8]
(2) Silica gel functionalised with methylthiosalicylate (TS-gel)	18.5	24.8	62	120; 11.8	
Polyurethane foam impregnated with 2-(6-methyl-2-ben- zothiazolylazo)chromotropic acid (Me-BTANC)	6.1	19	22	60; 7.0	[14]
	2.4	12	37	180; 21.1	
Chitosan biopolymer modified with 5-sulphonic acid 8-hydroxy-quinoline (sulphoxine)	0.6	9.3	14	90; 10.8	[17]
Salen impregnated silica gel	0.87	38.0	113	120; 16.0	This work

The presented results prove that the proposed salen impregnated silica gel may find practical application in Cd(II) determination in water samples at trace level. The method accuracy was confirmed by analysis of two certified reference materials and in both cases cadmium content found for the proposed method was in good agreement with the certified values.

4. Conclusions

In the presented work, the application of salen impregnated silica gel as a minicolumn filling in FI-FAAS determination of cadmium(II) in water samples has been elaborated. Good stability of the sorbent in the working conditions together with its fairly fast kinetics makes it a suitable material for cadmium(II) sorption in on-line systems. Competence between cadmium(II) and some foreign ions, revealed in the selectivity study, was reduced via increasing the number of active sites (the sorbent mass) which enabled to apply the sorbent to preconcentration of Cd(II) from water samples of different matrices. The proposed method was utilised in Cd(II) determination in several water samples and two certified reference materials with good results. Natural cadmium content in environmental samples is at ppb level – hence an employed preconcentration method requires applying loading time sufficient to obtain the demanded preconcentration level. For salen impregnated silica gel, applying 120 s preconcentration time resulted in achieving LOD of $0.26 \mu\text{g L}^{-1}$ and enrichment factor of 113.

When compared to recently reported sorbents applied to on-line preconcentration and FAAS determination of cadmium(II), salen impregnated silica gel offers comparable or even better preconcentration parameters, especially when EF is taken into consideration. An appropriate comparison has been presented in Table 4.

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