Determination of Cadmium in River Water Samples by Flame AAS after On-line Preconcentration in Mini-Column Packed with 2-Aminothiazole-modified Silica Gel

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A rapid and sensitive method was developed to determine trace levels of Cd²⁺ ions in an aqueous medium by flame atomic absorption spectrometry, using on-line preconcentration in a mini-column packed with 100 mg of 2-aminothiazole modified silica gel (SiAT). The Cd²⁺ ions were sorbed at pH 5.0. The preconcentrated Cd²⁺ ions were directly eluted from the column to the spectrometer's nebulizer-burner system using 100 µL of 2 mol L⁻¹ hydrochloric acid. A retention efficiency of over 95% was achieved. The enrichment factor (calculated as the ratio of slopes of the calibration graphs) obtained with preconcentrations in a mini-column packed with SiAT ($A = -1.3 \times 10^{-3} + 1.8 \times 10^{-3}[\text{Cd}^{2+}]$) and without preconcentrations ($A = 4 \times 10^{-5} + 3.5 \times 10^{-5}[\text{Cd}^{2+}]$), was 51 and the detection limit calculated was 0.38 µg L⁻¹. The preconcentration procedure was applied to determine trace levels of Cd in river water samples. The optimum preconcentration conditions are discussed herein.

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Heavy metals (*e.g.*, Cd, Cu, Hg, Pb) at trace levels are proven toxic elements and can be the cause of human health disorders.^{1,2} Because the main sources of these metals for humans are water and food, monitoring the heavy metal content in natural waters is of paramount importance.

The cadmium contamination in environmental samples is generally lower than 5 ng mL⁻¹, so very sensitive techniques are required for determinations. Several analytical techniques exist for determining trace levels of cadmium.^{3,4} Flow injection preconcentration techniques are useful for application in determining heavy metal ions by flame absorption atomic spectrometry (FAAS), providing a superior performance because they allow for the enhancement of sensitivity, separation of the analyte from the matrix and reduction of the risk of contamination.⁵⁻⁸ The Cd²⁺ preconcentration with solid phase extraction (SPE) technique using highly selective sorbent-packed columns has been described elsewhere.⁹⁻¹¹ Compatible detection limits were obtained by the SPE technique.

In recent years, the use of chemically modified silica gel matrixes with attached groups having a selective affinity for metal ions has been described.¹²⁻¹⁵ A manual procedure with this sorbent-packed column has been proposed for Cd preconcentration.^{12,15} However, the routine application of this procedure is limited by the time necessary for each analysis (100 min for each determination).

This work describes the analytical performance of a flow

injection system with online preconcentration on a sorbent mini-column packed with 2-aminothiazole-modified silica gel (SiAT) for determining Cd in a series of river water samples. The material was initially tested with a synthetic aqueous solution containing Cd²⁺; after that it was used in real samples.

Experimental

Reagents, analytical solutions and samples

All the solutions were prepared with high purity chemicals and distilled-deionized water (Milli-Q system, Millipore). The hydrochloric and nitric acids used were of the brand Suprapur quality (Merck).

Cadmium standard solutions (5 – 50 µg L⁻¹) were prepared by stepwise dilution from a 1000 mg L⁻¹ stock solution (Merck Titrisol) with Milli-Q treated water, acidified with nitric acid to pH 2.

The mini-column (a 5 cm long, 3 mm i.d. glass tube) was dry-packed with 100 mg of SiAT.

Samples of river water (Tietê, Parapanema and Parana rivers, SP, Brazil) were collected and immediately filtered through a 0.45 µm membrane. After acidification (pH < 2.0) with 6.0 mol L⁻¹ HNO₃ solution, the samples were stored in highly purified PE containers. Aliquots of 100 mL of the water samples were digested by oxidation with UV-photolysis in the presence of 0.01% of H₂O₂, using a low-pressure Hg-lamp integrated to a closed quartz vessel.¹⁷ The aqueous extract resulting was poured into a 100 mL volumetric flask and this solution was diluted to the final volume with deionized water.

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Synthesis of SiAT

Silica gel (Merck) with a specific surface area of $500 \text{ m}^2 \text{ g}^{-1}$ and an average pore diameter of 0.6 nm was activated at 420 K under vacuum (10^{-3} torr). About 50 g of this silica was immersed in 200 mL of purified dimethylformamide (Merck), to which 12 mL of phosphorus oxychloride (Merck) was added. The mixture was refluxed in a nitrogen atmosphere for 36 h , filtered, washed with dimethylformamide and ethanol and heated under a vacuum to eliminate any remaining solvent. The resulting solid was immersed in 135 mL of purified dimethylformamide and 18 g of 2-aminothiazole (Aldrich) was added. The mixture was stirred for 26 h at 380 K in a nitrogen atmosphere. The resulting modified silica (SiAT) was filtered off, washed with dimethylformamide and ethanol and then heated for 8 h at 348 K under a vacuum (10^{-3} torr).

Preparation of the SiAT collector can be expressed by Reactions (1) and (2):

Reaction (1)

Reaction (2)

The number of 2-aminothiazole groups attached to the silica gel was determined by nitrogen analysis using the Kjeldhal method. The specific surface area was determined by the BET¹⁸ method using a automated Micromeritics ASAP 2010 device (Micromeritics Instrument Corporation, USA).

Infrared spectra

Diffuse reflectance infrared Fourier Transform (DRIFT) spectra were obtained in Kubelka-Munk units, using a Nicolet Model Nexus 670 spectrometer equipped with a Smart Collector. One milligram of material was mixed with 500 mg of KBr.¹⁹

Apparatus

A SHIMADZU Model AA-6800 atomic absorption spectrometer equipped with a hollow cadmium cathode lamp and a deuterium lamp for background correction was used. The spectrometer's monochromator was adjusted to 228.8 nm (the resonance line corresponding to a highly cadmium-sensitive wavelength). Several selections were made to adjust the spectrometer, including: slit width, 0.5 nm ; burner height, 8 mm ; sample uptake rate, 1 mL min^{-1} ; air flow rate, 2.2 L min^{-1} ; and acetylene flow rate, 0.9 L min^{-1} . The atomic signal was measured in peak height mode.

The on-line preconcentration system was equipped with an Ismatec Model IPC-8 peristaltic pump furnished with Tygon pumping tubes (i.d. 0.5 mm) and a homemade Perspex injector-commutator.

On-line preconcentration system

Figure 1 shows the flow diagram of the system, which consists of a peristaltic pump, an injection valve (homemade injector-commutator) and a mini-column packed with SiAT.

Fig. 1 Flow system for cadmium preconcentration by FAAS: (1) peristaltic pump; (2) injection valve; (3) aqueous waste; (4) mini-column; (5) FAAS; (6) aqueous waste.

Fig. 2 Infrared spectra of pure silica gel (PSG) and silica gel modified with 2-aminothiazole (SiAT).

Standard solutions (or water samples) in a concentration range of $5 - 50 \mu\text{g L}^{-1} \text{ Cd}^{2+}$, after being adjusted at convenient pH with acetate buffer solution, were percolated through a mini-column that adsorbed the Cd^{2+} ions. The remaining solution was discharged (3-aqueous waste). If one slides the injection valve bar, a stream of water (CR) carries $100 \mu\text{L}$ of a $2.0 \text{ mol L}^{-1} \text{ HCl}$ solution that desorbs the Cd^{2+} ions. This eluate was taken directed to the nebulizer-burner system of the spectrometer and the signals were measured as peak heights by using instrument software. The Cd^{2+} concentrations were read from the analytical curves.

Results and Discussion

Characteristics of the material

The infrared SiAT spectra shown in Fig. 2 confirm the presence of 2-aminothiazole groups bound to the silica surface. The small absorption band visible at 2784 cm^{-1} was due to the C-H stretching of aromatic olefins. Two other bands of interest, which are visible at 1471 and 1395 cm^{-1} , were attributed to $\delta\text{C=N}$ and $\delta\text{N-H}$, both dislocated from low frequencies due to the remaining $\delta\text{Si-O}$ in the silica gel, which shows a strong absorption at 1630 cm^{-1} .

The chemical analysis of nitrogen in SiAT revealed that $1.24 \pm 0.07 \text{ mmol g}^{-1}$ of the functional groups were attached to the silica surface, and that the specific surface area of the SiAT was $354 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$. The attached 2-aminothiazole groups displayed high stability under the various adsorption-elution cycles of metal ions by the adsorbent in the column.

Effect of physical and chemical parameters

To adjust the physical and chemical variables for Cd^{2+} ion preconcentration and elution, we tested the following

Fig. 3 Effect of flow rate on peak absorbance: a, preconcentration flow rate; b, elution flow rate.

parameters were tested.

The preconcentration and elution flow rates were varied from 0.3 to 3 mL min⁻¹, while the amount of injected Cd²⁺ ions was kept at 20 µg L⁻¹. As shown in Fig. 3 (graph a), the optimum peak absorbance was obtained at a preconcentration flow rate of about 1 mL min⁻¹. The sensitivity increased with increasing elution flow rate (Fig. 3, graph b), reaching the maximum value from 1.5 mL min⁻¹ on. Considering the best values of absorbance, the preconcentration and elution flow rates we selected were 1.0 and 2.0 mL min⁻¹, respectively. As a compromise between loading capacities and eluent volumes, different column lengths and inner diameters were tested; the dimensions we selected were 5.5 cm and 3 mm, respectively.

The effect of pH on the sorption of Cd²⁺ in the column's reactive phase was evaluated by varying the pH in the 1 – 5 range with a constant 20 µg L⁻¹ injection of Cd²⁺ solution and a 3 min sampling time (using a flow rate of 1 mL min⁻¹). These experiments showed that the sorption of Cd²⁺ ion decreases with the acidity of the solution and that the pH value 5.0 was optimal for the sorption of Cd²⁺, results in accordance with these in previous papers.^{15,16} Experiments at pH values higher than 5 were not carried out because of the possibility of hydrolytic processes and the formation of complexes of type [Cd(OH)]⁺, that could decrease the transfer of Cd²⁺ ions from the solution to the SiAT surface.¹⁵ Thus, the pH value 5.0 was chosen for further experiments, using 5 × 10⁻³ mol L⁻¹ acetate buffer.

The efficiency of Cd²⁺ ion elution was investigated using HNO₃ and HCl in varying concentrations. Figure 4 illustrates the influence of eluent concentrations, revealing that the HCl solutions were more favorable for eluting metal ions. However, elution efficiency increased with increasing HCl concentrations, remaining constant at about 2.0 mol L⁻¹. Therefore, the 2 mol L⁻¹ HCl solution was chosen as the eluent.

Analytical performance

Linear analytical curves were obtained for the 5 – 50 µg L⁻¹ range of Cd²⁺ preconcentrated using sampling times of 3, 4, and 5 min (volumes injected in triplicate at a flow rate of 1 mL min⁻¹). Accordingly, the calibration slopes increased, but not proportionally with the increase of sampling time, which means that the retention efficiency is not constant.

The enrichment factors, calculated as the ratios of slopes of the calibration graphs obtained with preconcentration in a mini-column packed with SiAT ($A = -1.3 \times 10^{-3} + 1.8 \times 10^{-3}[\text{Cd}^{2+}]$) and without preconcentration ($A = 4 \times 10^{-5} + 3.5 \times 10^{-5}[\text{Cd}^{2+}]$), were evaluated under the same conditions as described before. Figure 5 shows the calibration graphs obtained for the 5 – 50 µg

Fig. 4 Influence of eluent concentration on peak absorbance: eluent 1, HCl; eluent 2, HNO₃.

Fig. 5 Calibration graphs: a, with preconcentration in SiAT mini-column; b, without preconcentration. Experimental conditions: pH, 5.0, 2 mol L⁻¹ HCl as eluent; flow rate of eluent, 1.5 mL min⁻¹; sampling time, 5 min at a flow rate of 1.0 mL min⁻¹.

L⁻¹ range of Cd²⁺ preconcentrated for 5 min. The preconcentration factor, which was calculated by comparing it with the calibration graphs without preconcentration (Fig. 5, graph b) and with preconcentration in the SiAT mini-column (Fig. 5, graph a), was 51.

Differences between the preconcentration factor and the added and eluted volumes may have occurred due to loss of efficiency as the sample volumes were increased. As Table 1 indicates, the preconcentration efficiency declined from 99% to 93% when sample volumes, gradually increased from 3 to 5 mL, were run through the column. The preconcentration factor under these conditions increased from 29 to 46. The precision, expressed as RSD for twelve independent determinations, was 3% for 20 µg L⁻¹ of Cd²⁺ ions. The detection limit, defined as the Cd²⁺ concentration that gives a response equivalent to three times the standard deviation (SD) of the blank ($n = 12$),²⁰ was found to be 0.38 µg L⁻¹ for 5 min of sampling time. The sampling frequency was fifteen samples per hour.

The reproducibility of column preconcentration, expressed as SD and tested by sampling a 20 µg L⁻¹ Cd²⁺ solution for 5 min in 12 separately prepared mini-columns, was about 99 ± 3% (19.80 ± 0.60 µg L⁻¹).

The influence of dissolved salts on the preconcentration of Cd²⁺ was evaluated by adding 500 µg L⁻¹ of Cu²⁺, Ni²⁺, Fe³⁺/Fe²⁺, Pb²⁺, Zn²⁺, Mn²⁺, Cl⁻, NO₃⁻ or SO₄²⁻. The interference study (Table 2) showed that the method proposed is fairly selective for Cd²⁺. The Cd²⁺ ions are adsorbed selectively in

Table 1 Enrichment factors and efficiency of Cd²⁺ preconcentration mini-column

Sampling time/ min	Experimental preconcentration factor	Theoretical preconcentration factor ^a	Efficiency, %
3	29.7	30	99
4	38.8	40	97
5	46.5	50	93

Cadmium concentration, 20 µg L⁻¹; eluent, 100 µL of 2 mol L⁻¹ HCl solution; flow rate, 1.0 mL min⁻¹.

a. Volume added/volume eluted.

Table 2 Effect of foreign ions

Ion 500 µg L ⁻¹	Cd recovery, %	Ion 500 µg L ⁻¹	Cd recovery, %
Cu(II)	98 ± 3	Cr(III)	97 ± 5
Ni(II)	96 ± 4	Cl ⁻	98 ± 6
Fe(III)/Fe(II)	94 ± 4	NO ₃ ⁻	97 ± 4
Pb(II)	98 ± 3	SO ₄ ²⁻	96 ± 5
Zn(II)	97 ± 5	PO ₄ ³⁻	92 ± 5
Mn(II)	99 ± 4		

20 µg L⁻¹ of Cd(II), 5 min sampling time.

SiAT-packed columns because of the strong affinity of Cd²⁺ ions for the thiazole groups of SiAT. This behavior is congruent with Pearson's classification of hard and soft acids and bases,²¹ according to which soft acids (Cd²⁺) bind preferentially to soft bases (thiazole groups, in this case).

Determination of cadmium in river water samples

The method proposed here was successfully applied to determine cadmium in samples of river water from various sources (Tietê, Parapanema and Parana rivers, SP, Brazil, which are contaminated by heavy metals). Table 3 lists the results obtained through the proposed method. As Table 3 indicates, the SiAT-FAAS determinations revealed cadmium concentrations 16 – 25% lower in undigested river water samples than in the photolyzed samples. This difference in results has been attributed to the formation of inert complexes of Cd with aquatic humic substances (HS), which are less accessible for the functional groups of the collector.²² After digestion (by oxidizing UV-photolysis in the presence of 0.01% H₂O₂), the Cd²⁺ ions bound to HS in the form of inert complexes can react quantitatively with functional SiAT groups. These findings are congruous with results obtained by direct determination through GFAAS (graphite furnace absorption atomic spectrometry), also listed in Table 3.

Conclusions

The method proposed represents a good alternative for determining cadmium at ultra low trace levels in an aqueous medium. The high stability of the SiAT-packed mini-column is evidenced by life times of at least one year if unused and at least one month if used 5 h per day. The proposed method allows for online cadmium determination in natural water samples by FAAS, although it requires predigestion of samples, e.g., by a sample oxidizing UV photolysis, which is necessary to eliminate the interference of aquatic organic matter, particularly aquatic humic substances that can form inert complexes with Cd²⁺ ions.

Table 3 Determination of Cd in different water samples by FAAS with on-line preconcentration in a SiAT-packed mini-column with and without digestion by UV-photolysis (µg L⁻¹)

Sample	GFAAS		SiAT-FAAS	
1	14 ± 3 ^a	10 ± 2	12 ± 3 ^a	9 ± 0.27
2	9 ± 0.3 ^a	7 ± 0.2	10 ± 2 ^a	8 ± 0.24
3	5 ± 0.15 ^a	4 ± 0.12	6 ± 0.18 ^a	5 ± 0.15

1, Tiete river; 2, Parapanema river; 3, Parana river.

a. Photolyzed water samples.

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References

1. A. Taylor, *Clin. Endocrinol Metabolism*, **1985**, *14*, 662.
2. R. D. Wilken, *Fresenius J. Anal. Chem.*, **1992**, *342*, 795.
3. C. J. Rademeyer, B. Radziuk, N. Romanova, N. P. Skaugset, A. Skogstad, and Y. J. Thomassen, *Anal. At. Spectrom.*, **1995**, *10*, 739.
4. E. C. Lima, F. J. Krug, and K. W. Jackson, *Spectrochim. Acta, Part B*, **1998**, *53*, 1791.
5. Z. Fang, "Flow Injection Separation and Preconcentration", **1993**, John Wiley and Sons, New York, 146.
6. R. A. Nickson, S. J. Hill, and P. J. Worsfold, *Anal. Proc. Incl. Anal. Comp.*, **1995**, *32*, 387.
7. P. C. Ruder, A. G. Torres, J. M. C. Pavón, and F. S. Rojas, *Talanta*, **1998**, *46*, 1095.
8. J. C. Rocha, J. J. Sene, P. Burba, and D. Klockow, *J. Braz. Chem. Soc.*, **1998**, *9*, 79.
9. M. Sperling, X. Yin, and B. Welz, *J. Anal. At. Spectrom.*, **1990**, *5*, 639.
10. P. M. Padilha, J. C. Rocha, J. T. S. Campos, J. C. Moreira, and C. C. Federici, *J. Braz. Chem. Soc.*, **1997**, *8*, 333.
11. P. M. Padilha, J. C. Rocha, J. T. S. Campos, J. C. Moreira, and C. C. Federici, *Talanta*, **1997**, *45*, 317.
12. N. L. D. Filho, Y. Gushikem, W. L. Polito, J. C. Moreira, and E. O. Ehrim, *Talanta*, **1995**, *42*, 1625.
13. P. Lessi, N. L. D. Filho, J. C. Moreira, and J. T. S. Campos, *Anal. Chim. Acta*, **1996**, *306*, 175.
14. L. A. M. Gomes, P. M. Padilha, J. C. Moreira, N. L. D. Filho, and Y. Gushikem, *J. Bras. Chem. Soc.*, **1998**, *9*, 494.
15. P. M. Padilha, L. A. M. Gomes, C. C. F. Padilha, J. C. Moreira, and N. L. D. Filho, *Anal. Lett.*, **1999**, *32*, 1807.
16. F. V. Moraes, G. R. Castro, I. L. Alcântara, P. S. Roldan, M. A. L. Margionte, and P. M. Padilha, *Ecl. Quím.*, **2003**, *28(1)*, 9.
17. P. Burba and R. E. Wilmer, *Fresenius J. Anal. Chem.*, **1992**, *324*, 167.
18. S. Brunaur, P. Emmet, and E. Teller, *J. Am. Chem. Soc.*, **1938**, *60*, 309.
19. Y. Gushikem and J. C. Moreira, *J. Colloid Interface Sci.*, **1985**, *13*, 70.
20. K. Zih-Perényi, A. Lásztity, Zs. Horváth, and A. Lévai, *Talanta*, **1998**, *47*, 673.
21. R. G. Pearson, *J. Am. Chem. Soc.*, **1963**, *85(22)*, 3533.
22. J. C. Rocha, I. A. S. Toscano, and P. Burba, *Talanta*, **1997**, *44*, 69.