

Optimization of the preconcentration system of cadmium with 1(2-thiazolylazo)-*p*-cresol using a knotted reactor and flame atomic absorption spectrometric detection

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Abstract

The present paper proposes an on-line preconcentration procedure for cadmium determination in drinking water samples. It is based on the precipitation of cadmium(II) ions on a knotted reactor (KR) using 1(2-thiazolylazo)-*p*-cresol (TAC) as complexing reagent. The optimization step was performed using a full factorial design involving the variables: pH, eluent concentration (nitric acid) and TAC concentration. The results of this experiment demonstrated that these variables at chosen levels are not statistically significant. Under optimized experimental established conditions, analytical parameters for the preconcentration method were: a detection limit of 40.0 ng/l, precision as relative standard deviation (RSD) of 1.2 and 1.0%, for cadmium concentration of 2.5 and 20.0 µg/l, respectively. The preconcentration factor considering the slopes of the analytical curves with and without preconcentration is 23 for a sample volume of 10 ml. This system shows a sampling frequency of 25 h⁻¹. In order to check the accuracy, the standard reference material, NIST SRM 1643d trace elements in water was analyzed. A comparison, using *t*-test demonstrates that there is not significant difference among the achieved results with proposed method and the certified values. The addition/recovery experiments in the samples analyzed demonstrated the accuracy and applicability of the system developed for cadmium determination in water samples.

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1. Introduction

The determination of heavy metals, especially some toxic metals which play important roles in biological mechanisms, has been receiving much attention. Even very low concentrations of some toxic metals can cause serious biological disorders that can lead to some serious diseases. Cadmium enters the organism primarily via the alimentary and/or respiratory tract [1]. The sources of this metal are food, drinking water and air.

The FAO/WHO Joint Expert Committee on Food Additives, recommended provisional maximum tolerable daily

intake of Cd from all sources (food, air, and water) of 1.0–1.2 µg/kg body mass [2].

National and International regulations on food quality are lowering the maximum permissible levels of toxic metals in human food; thus, the maximum permissible level of Cd in drinking water is 3.0 µg/l [3]. Hence, the analytical control of cadmium in drinking water is becoming very important. Considering the low cadmium concentration levels in drinking water, sensitive analytical techniques are required to obtain adequate detection limits.

The content of cadmium at low concentrations has been determined by several techniques, including flame atomic absorption spectrometry (FAAS) [4,5], electrothermal atomic absorption spectrometry (ETAAS) [6], inductively coupled plasma–mass spectrometry (ICP–MS) [7], inductively coupled plasma optical emission spectrometry

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(ICP–OES) [8,9], and instrumental neutron activation analysis (INAA) [10].

FAAS appears to be one of the most attractive approaches for trace element analysis [11–14]; however, the direct determination of ultratrace amounts of elements by FAAS is usually difficult owing to an insufficient detection power. Consequently, preconcentration procedures, such as ion exchange, adsorption, solvent extraction and coprecipitation, are often needed before the FAAS determination [15].

In the last years, on-line separation and preconcentration, using flow injection techniques have shown to be efficient and effective at enhancing the sensitivity of FAAS [5,14,16,17]. With the on-line operation, the drawbacks of the off-line (batchwise) operation can be overcome to a great extent while the benefits of separation and preconcentration are further enhanced. To date, various kinds of separation techniques have been adapted to FI-on-line separation and preconcentration FAAS systems.

Flow injection-on-line preconcentration based on the sorption of metallic complexes on the inner walls of a PTFE knotted reactor (KR) has been successfully applied [18–23].

Although, the studies on FI-on-line sorption preconcentration started with FAAS detection only a few papers on its application to FAAS determination of trace elements have been published [18]. So far, in most of the work in which KR's have been used, they have been coupled to ETAAS [21–23]. FAAS also constitutes an interesting alternative for its coupling to KR in order to perform preconcentrations and determinations of metal traces. Additionally, KR has the advantage of a low hydrodynamic back-pressure, permitting high load sample rates, and elevated throughput sample.

The most widely used reagents for cadmium preconcentration in KR have so far been diethyldithiocarbamate (DDTC) [24,25], ammonium pyrrolidine dithiocarbamate (APDC) [26,27] and diethyldithiophosphate [28]. The 2-(2-thiazolylazo)-*p*-cresol (TAC) reagent forms insoluble chelates with numerous metal ions. For preconcentration procedures, it was used in liquid liquid extraction for iron determination [29] and for solid phase extraction for cobalt determination [30]. However, it was not used for preconcentration systems, using KR.

In the present work, an alternative methodology for preconcentration and determination of cadmium in water samples using KR, is proposed. Cadmium was retained as a Cd-(2-(2-thiazolylazo)-*p*-cresol) complex. The determination was performed, using FAAS associated with a FI-methodology.

2. Experimental

2.1. Reagents

All reagents used were of the highest available purity and at least of analytical grade.

A solution of TAC (Sigma-Aldrich, Saint Louis, USA) 10^{-2} M was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution in 17% (v/v) ethanol–water. Working standard solutions were prepared by stepwise dilution from 1000 mg/l Cd stock standard solution immediately before use. A buffer solution was prepared by diluting a 0.05 M solution of borax adjusted to pH 8.5 with hydrochloric acid solution. Ultrapure water (18 M Ω cm) was obtained from an EASY pure RF (Barnstedt, Iowa, USA).

2.2. Apparatus

The measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a deuterium background corrector and the measurements were based on peak height. Cadmium hollow-cathode lamp (Hamamatsu Photonics K.K., Japan) was employed as radiation source; the Cd wavelength was 228.8 nm. The flow injection system used is shown in Fig. 1. A Minipuls 3 peristaltic pump [Gilson (Villiers-Le-Bell, France)] was used. The sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way rotary valve. For the sorption of the complex, a KR was made from a 2 m length PTFE tubing of 0.5 mm internal diameter by tying interlaced knots of approximately 5 mm diameter loops. Pump tubes-Tygon type (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA), were employed to propel the sample, reagent and eluent.

2.3. Preconcentration step

The aqueous sample solution (0.01 M nitric acid) containing cadmium, at a flow rate of 5.0 ml/min, and TAC 7.5×10^{-5} M (at a flow rate of 2.5 ml/min) buffered to pH 8.5, were mixed on-line to form the metal complex. This mixture was then loaded on the KR during 120 s; valve V in load position (a) (Fig. 1). Finally, the peristaltic pump P₁ was stopped, the injection valve V was switched to the injection position (b) and the retained metal complex was eluted with 15% nitric acid at a flow rate of 3.0 ml/min, directly in the FAAS nebulizer. The operating conditions were established and the determination was carried out.

3. Results and discussion

3.1. Experimental conditions

The optimization step of the proposed procedure was performed using a full factorial design (2^3) with (3) replicates of the central point, involving the variables: pH, TAC concentration (RC) and eluent concentration (EC) and as analytical response the signal (absorbance) (the experimental data were processed by using the Statistic computer program). Minimum and maximum levels of each factor (Table 1) were chosen according to data from previous experiments. Table 2

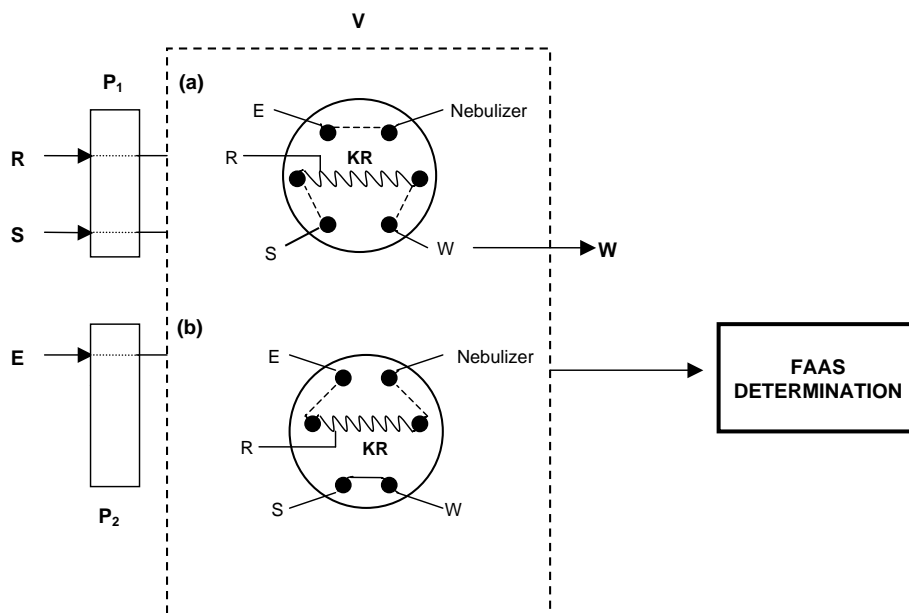


Fig. 1. Schematic diagram of the instrumental setup. R: 7.5×10^{-5} M TAC solution (flow rate: 2.5 ml/min); S: sample (flow rate: 5.0 ml/min); E: eluent (flow rate: 3.0 ml/min); W: waste; P₁, P₂: peristaltic pumps; KR: knotted reactor; V: injection valve. Valve positions: (a) sample loading; (b) injection.

Table 1
Factors and levels used in factorial design

Variable	Low (–)	Central point (0)	High (+)
pH	7.0	8.5	10.0
Reagent concentration (RC) (M)	2.5×10^{-5}	5.0×10^{-5}	1.0×10^{-4}
Eluent concentration (EC) (%)	10	20	30

shows the experimental design matrix and the analytical signal. The results of this study, considering the analysis of variance (ANOVA) as Table 3 and the Pareto Chart (Fig. 2) demonstrate that in the studied levels, all these variables and their interactions are not statistically significant. This way, the pH recommended is 8.5 considering that it is the central point of the pH interval. It guarantees the robustness of the system for this variable. The TAC concentration was studied within the range from 2.5×10^{-5} to 1.0×10^{-4} M.

Table 2
Design matrix and results of the factorial design

	pH	RC	EC	AS
1	+	+	+	0.102
2	+	+	–	0.098
3	+	–	+	0.092
4	+	–	–	0.082
5	–	+	+	0.083
6	–	+	–	0.088
7	–	–	+	0.092
8	–	–	–	0.088
9	0	0	0	0.088
10	0	0	0	0.090
11	0	0	0	0.094

AS: analytical signal.

The chosen concentration was of 7.5×10^{-5} M, in order to assure a small excess of reagent and to guarantee the total complexation of cadmium. The eluent concentration chosen was 15% (v/v) nitric acid.

The sample flow rate through the KR is a very important parameter, since this one of the steps that controls the time of the analysis. We could verify that the optimum sample loading flow-rate was achieved at 5 ml/min. At higher flow rates, the response decreases.

The eluent flow rate was not considered as variable, it was fixed at 3.0 ml/min as aspiration flow rate of the spectrometer.

3.2. Interferences

The effects of representative potential interfering species (at the concentrations levels at which they may occur in the

Table 3
Analysis of data given in Table 2

Factor	SS ^a	DF ^b	MS ^c	F-ratio	P level ^d
pH	0.000066	1	0.000066	7.08482	0.116907
RC	0.000036	1	0.000036	3.87054	0.188018
EC	0.000021	1	0.000021	2.26339	0.271378
pH–RC	0.000153	1	0.000153	16.40625	0.055891
pH–EC	0.000028	1	0.000028	3.01339	0.224714
RC–EC	0.000028	1	0.000028	3.01339	0.224714
Error	0.000019	2	0.000009		
Total	0.000353	10			

^a SS: sum of squares.

^b DF: degrees of freedom.

^c MS: mean of squares.

^d P level: probability level.

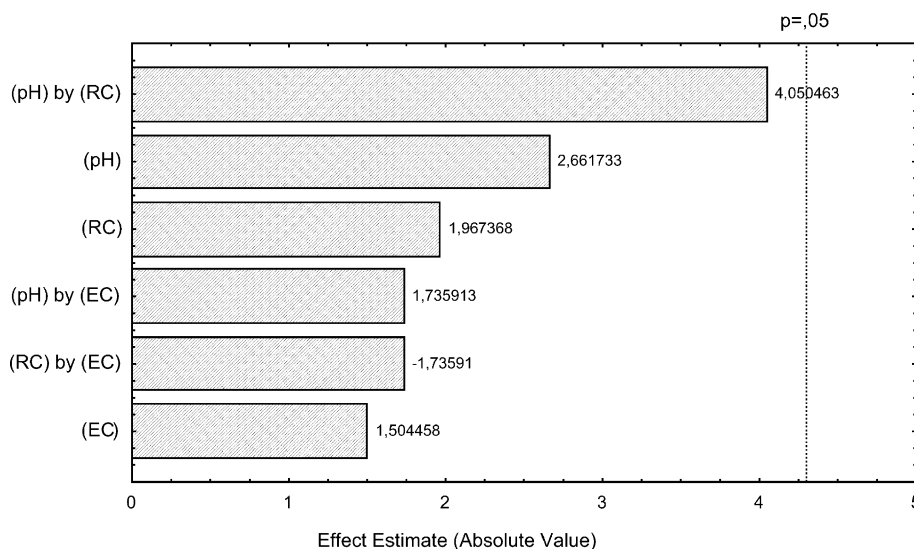


Fig. 2. Pareto chart of standardized effects for variables in the cadmium preconcentration using absorbance as response.

sample under study) were also tested. Thus, Cu^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , and Fe^{3+} , could be tolerated up to at least $2000 \mu\text{g/l}$. Commonly, encountered matrix components, such as alkali and alkaline earth elements do not form stable complexes and are not retained on the KR under the working conditions used for the system.

3.3. Evaluation of the FI-on-line preconcentration system performance

The overall time required for preconcentration of 10 ml of solution (2 min, at a flow rate of 5 ml/min); elution (0.2 min, at a flow rate of 3.0 ml/min) and conditioning (0.2 min, at flow rate of 3.0 ml/min) was about 2.4 min, resulting in a sampling frequency of 25 h^{-1} . A total enrichment factor of approximately 23-fold for a 10 ml sample volume was obtained with the proposed preconcentration system.

The precision values as relative standard deviation (R.S.D.) were of 1.2 and 1.0%, for cadmium concentration of 2.5 and $20.0 \mu\text{g/l}$, respectively. The calibration graph using the preconcentration system for cadmium was linear with a correlation coefficient of 0.9998 at levels near the detection limits up to at least $100 \mu\text{g/l}$. The detection limit (DL) was calculated as the amount of cadmium required to yield a neat peak equal to three-times the standard deviation of the background signal (3σ). The value of DL obtained for the preconcentration of 10 ml of aqueous solution was 40.0 ng/l .

3.4. Recuperation and validation studies

In order to evaluate the cadmium recovery of this method, 100 ml of water sample was collected and divided into 10 portions 10 ml each. The proposed method was applied to six portions and the average quantity of cadmium obtained was

Table 4
Recovery study

Aliquots	Quantity of Cd added ($\mu\text{g/l}$)	Quantity of Cd found ($\mu\text{g/l}$)	Recovery (%)
1	0.0	2.72 ± 0.03	–
2	1.0	3.71	99.0
3	2.0	4.69	98.5
4	4.0	6.72	100.0
5	6.0	8.7	99.7

taken as base value. Then, increasing quantities of cadmium were added to the other aliquots of sample and cadmium was determined by the same method. The results are shown in Table 4

Additionally, the proposed method was applied to a standard reference material, NIST SRM 1643d “Trace Elements in Water”, with a cadmium content of $6.47 \pm 0.37 \mu\text{g/l}$, the density of SRM 1643d at 22°C is 1.016 g/ml . Using the proposed method, the content of cadmium determined in this SRM was $6.32 \pm 0.05 \mu\text{g/l}$. A comparison using *t*-test,

Table 5
Cadmium determination in drinking and mineral water samples

	Cd concentration ($\mu\text{g/l}$)
Drinking water samples	
1	3.15 ± 0.08
2	2.72 ± 0.09
3	2.85 ± 0.08
4	2.50 ± 0.09
Mineral water samples	
1	0.95 ± 0.09
2	1.00 ± 0.09
3	1.00 ± 0.09
4	1.10 ± 0.08

demonstrates that there is not significant difference among the achieved results using the proposed method and the certified values.

The method was applied for cadmium determination in several drinking and mineral water samples from San Luis Province, Argentine. The results are given in Table 5. In the samples analyzed cadmium varied within the range: 0.95–3.20 $\mu\text{g/l}$.

4. Conclusions

The cadmium complexation with TAC and precipitation on KR was efficient to preconcentrate it from water samples.

The connection of an on-line preconcentration system using a KR with a FI-FAAS allowed reducing sample consumption and contamination risks, compared with a batch preconcentration procedure. The preconcentration system permitted cadmium determination in drinking and mineral water samples in which the concentration was on the order of the $\mu\text{g/l}$. A 23-fold enrichment factor was obtained. The methodology showed excellent reproducibility and accuracy. We think that the preconcentration method proposed coupled to FAAS can be consider an alternative methodology for Cd determination in water samples.

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References

- [1] H.G. Seiler, A. Sigel, H. Sigel, Handbook on Toxicity of Inorganic Compounds, Marcel Dekker, New York, 1998.
- [2] FAO/WHO Joint Expert Committee on Food Additives, WHO Tech. Rep. Senal No. 505, 32, 1972.
- [3] Guidelines for Drinking-Water Quality, Health Criteria and Other Supporting Information, second ed., World Health Organization, Geneva, 2 (1998) 281.
- [4] R. Fernandez Orsi, R. Wuilloud, J. Wuilloud, R. Olsina, L. Martinez, J. AOAC Int. 85 (2002) 1410.
- [5] M.H. Melo, S.L.C. Ferreira, R.E. Santelli, Microchem. J. 65 (2000) 59.
- [6] H. Sato, J. Ueda, Anal. Sci. 16 (2000) 299.
- [7] D. Pozebon, V. Dressler, A.J. Curtius, J. Anal. At. Spectrom. 13 (1998) 363.
- [8] S. Cerutti, M. Silva, J. Gásquez, R. Olsina, L. Martinez, Spectrochim. Acta B 58 (2003) 43.
- [9] G. de la Rosa, J.R. Peralta-Videa, J.L. Gardea-Torresdey, J. Hazard. Mater. 97 (2003) 207.
- [10] N. Lavi, Z.B. Alfassi, Analyst 115 (1990) 817.
- [11] H. Chen, S. Xu, Z. Fang, Anal. Chim. Acta 298 (1994) 167.
- [12] S. Saracoglu, L. Elci, Anal. Chim. Acta 452 (2002) 77.
- [13] Y. Ye, A. Ali, X. Yin, Talanta 57 (2002) 945.
- [14] R.W.W. Min, E. Hansen, Chem. Anal. 40 (1995) 361. Warsaw.
- [15] M. De Godoi Pereira, M.A. Zezzi Arruda, Microchim. Acta 141 (2003) 115.
- [16] C. Dittfurth, E. Ballesteros, M. Gallego, M. Valcárcel, Spectrochim. Acta B 51 (1996) 1935.
- [17] G.M. Wuilloud, R.G. Wuilloud, J.C.A. Wuilloud, R.A. Olsina, L.D. Martinez, J. Pharm. Biomed. Anal. 31 (2003) 117.
- [18] X-P. Yang, Y. Jiang, Trends Anal. Chem. 20 (2001) 552.
- [19] R.G. Wuilloud, J.A. Salonia, R.A. Olsina, L.D. Martinez, Spectrochim. Acta B 55 (2000) 671.
- [20] R.F. Lara, R.G. Wuilloud, J.A. Salonia, R.A. Olsina, L.D. Martinez, Fresenius J. Anal. Chem. 371 (2001) 989.
- [21] X-P. Yang, F. Adams, J. Anal. At. Spectrom. 12 (1997) 459.
- [22] S. Nielsen, E.H. Hansen, Anal. Chim. Acta 366 (1998) 163.
- [23] E. Ivanova, F. Adams, Fresenius J. Anal. Chem. 361 (1998) 445.
- [24] J. Liu, H. Chen, X. Mao, X. Jin, I. J. Environ. Anal. Chem. 76 (2000) 267.
- [25] H. Chen, J. Jin, and Y. Wang, Anal. Chim. Acta 353 (1997) 181.
- [26] K. Benkhedda, H. Goenaga Infante, E. Ivanova, F. Adams, J. Anal. At. Spectrom. 15 (2000) 1349.
- [27] S. Liawruangrath, W. Som-Aum, A. Townshend, Talanta 58 (2002) 1177.
- [28] E. Ivanova, W. Van Mol, F. Adams, Spectrochim. Acta B 53 (1998) 1041.
- [29] S.L.C. Ferreira, A.S. Queiroz, J.C.R. Assis, M.G. Korn, A.C. Spinola Costa, J. Braz. Chem. Soc. 8 (1997) 621.
- [30] S.L.C. Ferreira, C.F. de Brito, Anal. Sci. 15 (1999) 189.