PRECONCENTRATION AND DETERMINATION OF CADMIUM AND LEAD BY ION-PAIR SOLID PHASE EXTRACTION ON SILICA GEL FOLLOWED BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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The ion-pair formation between the metal complex with 4-(4′-nitrophenylazo)-1-naphthol and cetyltrimethylammonium bromide and its sorption on silica gel form the basis for preconcentration of cadmium and lead, which are subsequently determined on-line by flame AAS. The method was applied to the quantitation of cadmium and lead in potable and surface waters, with limits of determination (10*s*) of 0.5 and 2 μg l^{-1}, respectively.

Cadmium and lead in waters are mostly determined by AAS. The flame technique is sufficiently rapid, simple and free from the majority of interferences encountered in trace analyses of metals and thus is very popular in practice. However, the limits of detection are relatively high, because of a poor efficiency of the nebulizer, dilution of the aerosol by the fuel gas combustion products and short life-times of free atoms in the optical path.

The problem of a poor sensitivity for some elements can be alleviated by using a suitable preconcentration technique[1–3], thus decreasing the limit of detection down to values typical for graphite furnace AAS.

Liquid–liquid extraction is among the oldest preconcentration techniques[4,5]. Coprecipitation of traces of metals by adsorption on a suitable precipitate is also possible[6–9]. Very important are modified ion exchangers with bound chelating agents[10–13]. Preconcentration techniques that combine the advantages of liquid–liquid extraction and ion exchange have gained in popularity recently; they can be referred to as preconcentration techniques on modified sorbents or techniques of solid phase extraction[14]. Some authors have used for solid phase extraction ion-pairing between water-soluble complexes of metals with anionic dyes and long-chain quaternary ammonium salts; the ion pairs are then sorbed on a support[15–17]. Many divalent metal cations have so been extracted, using several anionic dyes and silica gel as the sorbent[18–21].

This paper deals with the preconcentration of cadmium and lead through ion pairing of the metal complex with 4-(4′-nitrophenylazo)-1-naphthol (NPAN) and cetyltri-

methylammonium bromide (CTAB) and sorption of the ion pair on silica gel, followed by on-line determination by flame AAS (FAAS).

One of the principal advantages of the on-line technique is the fact that the preconcentration occurs in a closed system and thus the sample is protected from atmospheric influences; it only comes in contact with a small area of Tygon tubing and the silica gel column walls. All these surfaces are continuously washed with the carrier liquid and thus the hazard of sample contamination is considerably reduced and the blank values are low and reproducible. The blank value can further be decreased by including a column for on-line purification of the reagents[22]. The whole procedure, involving sample aspiration, column washing, elution and sample transport to the AAS nebulizer, can be readily automated, thus improving the accuracy and precision of the determination.

EXPERIMENTAL

Apparatus

A Varian SpectrAA-300 instrument (Varian Techtron, Mulgrave, Australia) was used in the flame mode. The measurements were performed on analytical lines at 288.8 and 217.0 nm for cadmium and lead, respectively, with deuterium background correction. Peak areas were evaluated and blank values were obtained for each sample.

Computer-controlled eight-channel Cole–Parmer model 7550-62 peristaltic pumps with Ismatec 7623-10 heads were used for the preconcentration, with Tygon and silicone rubber tubings and Cole–Parmer PTFE solenoid valves. All the connecting Tygon tubings (1.02 mm i.d.) and polyethylene connecting pieces (model 6365-90) were obtained from Cole–Parmer.

Reagents

A stock solution of NPAN (m.w. 293.28; Lachema, Brno, The Czech Republic) was prepared in a concentration of $5.0 \cdot 10^{-4}$ mol l^{-1} by dissolving 0.0147 g of the substance in a 2 mol l^{-1} solution of sodium hydroxide and making up to 100 ml with the NaOH solution. A stock solutions of NPAN ($2.0 \cdot 10^{-4}$ mol l^{-1}) for on-line preconcentration was prepared in 0.2 mol l^{-1} NaOH. The NPAN substance was purified prior to use by repeated precipitation from 1 mol l^{-1} HCl and double recrystallization from methanol; the purity was checked by thin-layer chromatography using two different mobile phases[1].

A $5.0 \cdot 10^{-3}$ mol l^{-1} stock solution of CTAB (m.w. 364.46; Lachema, Brno, The Czech Republic) was prepared by dissolving 0.1822 g of the purified substance in redistilled water and diluting with water to 100 ml. The substance was purified by double crystallization from methanol.

The NPAN and CTAB substances were analyzed for cadmium and lead by graphite furnace AAS; the values obtained were at the detection level.

A standard TRIS–HCl buffer solution (pH 10.5) was used in the on-line preconcentration system.

Stock solutions (100 μg ml^{-1}) of cadmium and lead salts were obtained by diluting commercial standard solutions (Analytika Ltd., Prague, The Czech Republic; 1 000 μg ml^{-1}) with deionized water.

Nitric and hydrochloric acids were of semiconductor grade purity and the other chemicals were of analytical grade. All the glassware, silicone rubber, Tygon and polyethylene utensils were washed with 5 mol l^{-1} HNO_3 and redistilled water.

The polyethylene columns were prepared from classical single-use hypodermic syringes 40 mm long, 10 mm i.d. The columns were packed with unmodified Separon L 250 μm silica gel (Tessek, Prague, The Czech Republic) (0.2 g), which was purified by repeated washing with concentrated HCl and redistilled water, dried at 110 °C and stored in a dessicator. The columns were packed with new sorbent for measurement of all characteristics of the preconcentration system.

Procedure

The optimal conditions for the preconcentration system (the effect of pH, break-through curve, sorption rate, kind of eluent and elution rate) were studied in an off-line column arrangement and the solution flow was controlled by using the peristaltic pump. All the measurements were evaluated with respect to the recovery of the preconcentrated metal as the value characterizing the preconcentration process from the beginning to the end. Most experiments, except for the pH effect, were carried out for cadmium only, and the optimized procedure was then also applied to lead.

The procedure was as follows: A volume of 100 ml of a solution containing 10 μg l^{-1} Cd or 100 μg l^{-1} Pb and appropriate concentrations of the tenside, complexing agent and buffer was pumped through the column at a rate of 20 ml min^{-1}; the column was then washed with a small amount of redistilled water (ca 5 ml), and the metal was eluted at a rate of 5 ml min^{-1} into a 10 ml volumetric flask (preconcentration factor 10). The metal was then determined by AAS.

The interferences, calibration, reproducibility, detection limit and limit of quantitation (3*s* and 10*s*, respectively) and practical analyses were carried out in the on-line system; the layout of the apparatus is shown in Fig. 1.

The sample passes through the first channel at a rate of 10 ml min^{-1}. The second channel feeds a buffer of pH 10.5 at a rate of 5 ml min^{-1}, the third channel feeds a $2 . 10^{-4}$ mol l^{-1} solution of NPAN and the fourth channel a $1 . 10^{-3}$ mol l^{-1} solution of CTAB, both at a rate of 5 ml min^{-1}. The components are mixed in a Tygon coil 500 mm long, 1.0 mm i.d. A three-way solenoid valve is placed after the reaction coil, which is used to bring the reagent for elution and column washing and is followed by the silica gel column.

Once the sample is quantitatively aspirated, valve 1 is switched so that redistilled water washes the reaction column for 10 s. During elution, the elution solution is pumped through the second channel for 30 s (5 ml min^{-1}) and the elution peak is simultaneously recorded by AAS. Solenoid valve 2 directs the eluate stream from the column into the AAS nebulizer capillary during the elution step. The column is finally washed with methanol for 10 s at a rate of 5 ml min^{-1} and the whole cycle is repeated. The length of tubing from the valve to the nebulizer orifice is 50 mm. The time sequence of the peristaltic pump operation and the solenoid valve switching are shown in Fig. 2. The relatively large volume of the sample (aspiration time 300 s, corresponding to 50 ml sample) was selected in order to attain better determination limits.

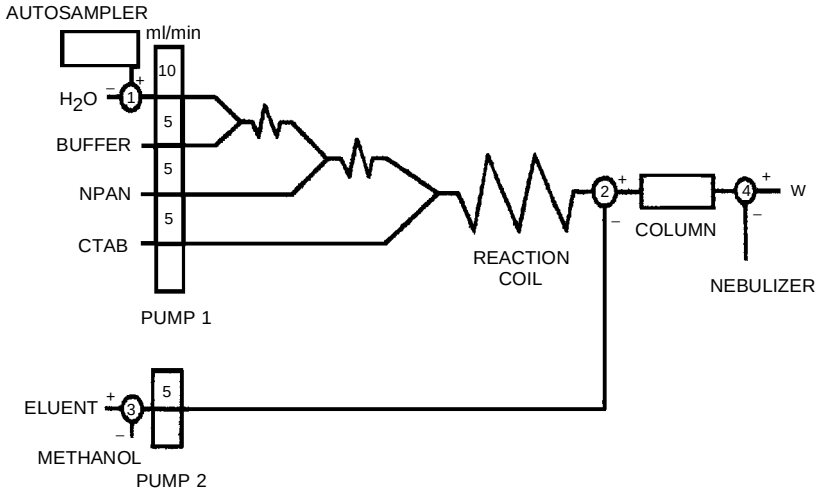

FIG. 1
The manifold for the on-line preconcentration system. 1 – 4 three-way solenoid valves, W waste

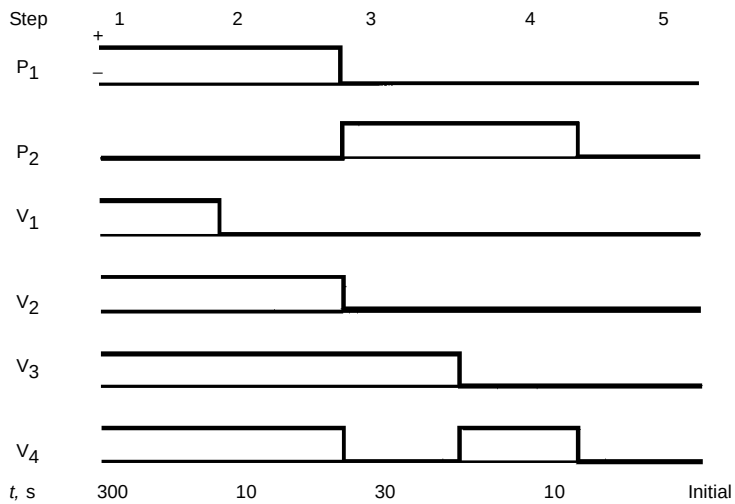

FIG. 2
Operation of the solenoid valves (V) and pumps (P) for the on-line column preconcentration. Steps: 1 sampling, 2 cleaning of coil, 3 elution, 4 removal of the elution agent, 5 return to initial state

RESULTS AND DISCUSSION

Optimal Sorption Conditions

The effect of pH was followed within the range of 6 to 12. The effect of the pH on the Cd and Pb sorption is depicted in Fig. 3, from which it follows that the sorption begins at pH ca 8.5 for Pb (9.0 for Cd) and is quantitative at pH ca 10.5.

The effect of the complexing agent concentration within the range of 0 to $5.0 \cdot 10^{-1}$ mol l^{-1} for the optimum pH 10.5, can be seen in Fig. 4. The measuring procedure was as above. It is evident that quantitative sorption of the two metals requires NPAN in a concentration of $2.5 \cdot 10^{-5}$ mol l^{-1} at least (200-fold excess of the complexing agent over the metal). The influence of the surfactant concentration was studied analogously, within the CTAB concentration range of 0 to $3.0 \cdot 10^{-4}$ mol l^{-1} (Fig. 5). It follows that the concentration of CTAB must not be lower than $1.25 \cdot 10^{-4}$ mol l^{-1} (1 000-fold excess over the metal).

The effect of the sorption rate (F_s), within the range of 1 to 30 ml min^{-1}, on the Cd and Pb recovery is not very pronounced: the recovery does not decrease below 95 per cent within this range. To limit the pressure in the tubing and the column, the flow rate was held at 20 ml min^{-1} further on.

The break-through curve was only measured for cadmium, using a solution of 100 μg l^{-1} (7.5 l) cadmium in the above optimum conditions and collecting 50 ml fractions (see Fig. 6). The relative absorbance A_r is the fraction-to-put solution absorbance ratio. The capacity of the sorbent (for the optimal sorption conditions) was estimated from the projection of the inflexion point of the break-through curve on the *x*-axis, obtaining 325 μg

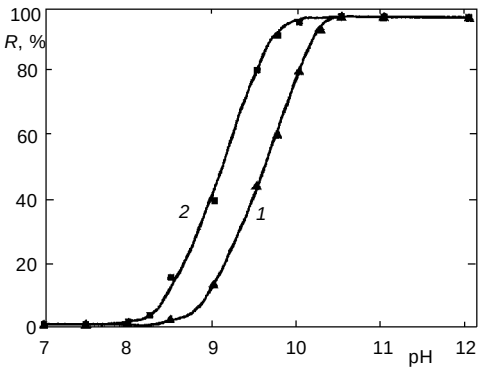

FIG. 3

The effect of pH on the recovery (*R*) of Cd (*1*) and Pb (*2*). *c*(NPAN) = $2.5 \cdot 10^{-5}$ mol l^{-1}, *c*(CTAB) = $1.25 \cdot 10^{-4}$ mol l^{-1}, ρ(Cd) = 10 μg l^{-1}, ρ(Pb) = 100 μg l^{-1}, F_s = 20 ml min^{-1}, F_e = 5 ml min^{-1}, eluent: 2.5 mol l^{-1} HNO_3

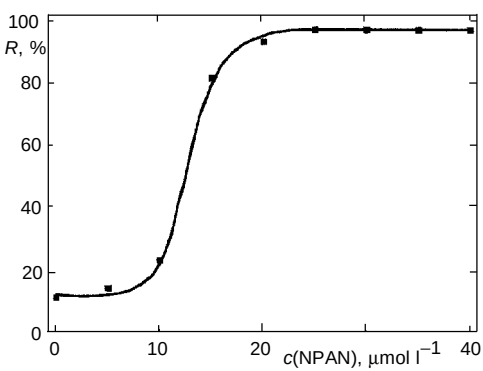

FIG. 4

The dependence of the recovery of Cd on the concentration of NPAN. pH 10.5, *c*(CTAB) = $1.25 \cdot 10^{-4}$ mol l^{-1}, ρ(Cd) = 10 μg l^{-1}, F_s = 20 ml min^{-1}, F_e = 5 ml min^{-1}, eluent: 2.5 mol l^{-1} HNO_3

of cadmium per g of sorbent. This sorption capacity is sufficient not only for obtaining a sufficiently high preconcentration factor but also for a possible competitive sorption of other metals. The shape of the break-through curve also suggests that the sorption process does not consists of simple sorption equilibria.

Optimal Desorption Conditions

Preliminary experiments showed that the metals are best eluted with a mineral acid. Nitric, hydrochloric and perchloric acids at a concentration of 1 mol l^{-1} were tested and nitric acid was found most suitable. The acid concentration was varied from 0.5 to 5.0 mol l^{-1} and the concentration of 2.5 mol l^{-1} was found sufficient for quantitative desorption. The complexing agent was then washed from the column with methanol. If the complexing agent is not removed, the column capacity decreases. Acetone can also serve as a suitable washing agent.

The influence of the elution rate (F_e) on the desorption efficiency was examined within the range of 1 to 10 ml min^{-1}; the metal recovery is apparently unaffected by the rate up to 7 ml min^{-1}. The rate of 5.0 ml min^{-1} was chosen for subsequent measurements. A typical absorption peak for 5 μg l^{-1} Cd is shown in Fig. 7. Since the pH for the sorption process and the acid concentration during desorption are high, the life-time of the preconcentration column is not very long, corresponding to some 20 preconcentration cycles after which the column capacity decreases.

In the preconcentration and determination of Cd and Pb in potable and other waters, additional ions that may be adsorbed on silica gel as complexes or affect the sorption

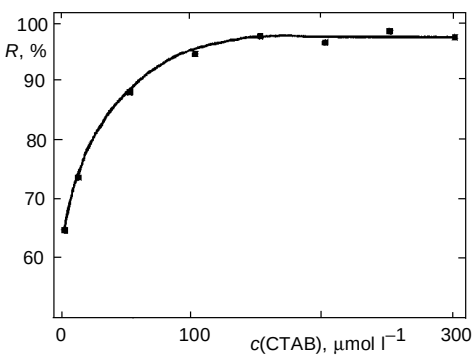

FIG. 5

The effect of CTAB concentration on the recovery of Cd. c(NPAN) = 2.5 . 10^{-5} mol l^{-1}, pH 10.5, ρ(Cd) = 10 μg l^{-1}, F_s = 20 ml min^{-1}, F_e = 5 ml min^{-1}, eluent: 2.5 mol l^{-1} HNO_3

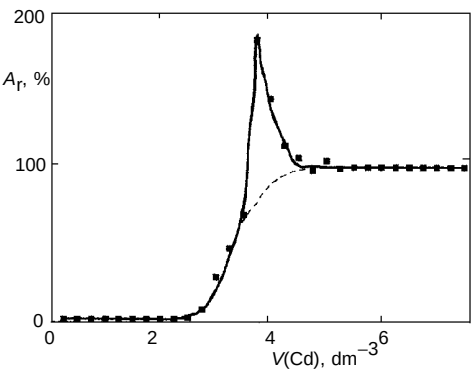

FIG. 6

The break-through curve (A_r relative absorbance, V(Cd) volume of passed Cd solution). c(NPAN) = 2.5 . 10^{-5} mol l^{-1}, c(CTAB) = 1.25 . 10^{-4} mol l^{-1}, pH 10.5, ρ(Cd) = 100 μg l^{-1}, F_s = 20 ml min^{-1}

of the analytes in other ways must be taken into account. The most probable interferents include magnesium, calcium, zinc, ferric, manganous and cupric ions. A thousandfold excess of these ions over the analytes (10 μg l^{-1} Cd) was tested and no interference was found, except for magnesium where the recovery of cadmium decreased to 95 per cent. The effect of sulfate and phosphate anions was also examined at an excess of 8 orders of magnitude over the analyte and no interference was found.

Under the optimum conditions discussed above, linear calibration dependences on the basis of peak areas were obtained within ranges of 0 to 20 μg l^{-1} and 0 to 200 μg l^{-1} for Cd and Pb, respectively. The correlation coefficients of calibration lines for the two metals were 0.9994 and 0.9997, respectively. A set of 10 samples (10 μg l^{-1} and 100 μg l^{-1} for Cd and Pb, respectively) was used and relative standard deviations of 0.8 and 0.5 were obtained for Cd and Pb, respectively. The detection limit (3*s*) (0.15 μg l^{-1} and 0.61 μg l^{-1} for Cd and Pb, respectively) and limit of determination (10*s*) (0.50 μg l^{-1} and 2.0 μg l^{-1} for Cd and Pb, respectively) were obtained from 10 blank measurements.

The method was employed to analyze 10 samples of potable water and 5 samples of surface waters, taken from the Prague water mains and from the Botic brook in Prague. The results are summarized in Table I.

No reference samples were available but the results were compared with those obtained by differential pulse anodic stripping voltammetry (DPASV) and a very good agreement was obtained.

The parallel slope technique was applied to surface water samples in order to verify the validity of the calibration curves. The slopes of the two straight lines for the two metals were in a very good agreement and the slope differences amounted to mere 0.5 and 0.8 per cent for cadmium and lead, respectively, whereas a difference of 5 per cent would still be regarded as a good agreement. Therefore, the effect of interferences in this determination can be considered negligible.

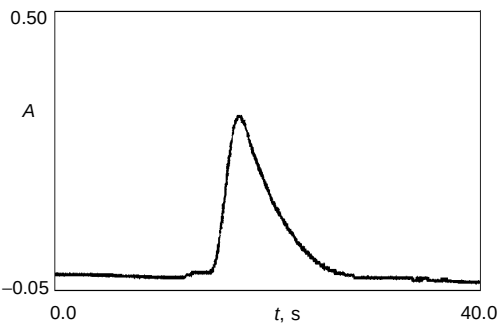

FIG. 7
The signal shape of Cd after the elution. c(NPAN) = 2.5 . 10^{-5} mol l^{-1}, c(CTAB) = 1.25 . 10^{-4} mol l^{-1}, ρ(Cd) = 5 μg l^{-1}, pH 10.5, F_s = 20 ml min^{-1}, F_e = 5 ml min^{-1}, eluent: 2.5 mol l^{-1} HNO_3, integration time 30 s, sorption time 300 s

TABLE I
Analysis of practical samples[a]

Sample	ρ(Cd), μg l^{-1}		ρ(Pb), μg l^{-1}	
	FAAS	DPASV	FAAS	DPASV
		Potable water		
I	0.80	0.87	$<x_D$	0.97
II	1.15	1.07	$<x_D$	0.56
III	1.07	1.05	$<x_D$	1.01
IV	$<x_D$	0.19	$<x_D$	0.08
V	0.83	0.80	$<x_D$	0.34
VI	0.94	1.02	$<x_D$	0.19
VII	1.22	1.18	2.25	2.09
VIII	1.39	1.35	2.78	2.88
IX	1.33	1.36	$<x_D$	0.15
X	1.14	1.07	3.01	2.94
		Surface water		
Botic I	8.10	7.52	4.06	3.90
Botic II	12.10	12.85	3.55	3.78
Botic III	10.72	13.32	4.14	4.28
Botic IV	33.15	31.79	5.35	5.61
Botic V	22.92	24.03	6.04	5.89

[a] x_D Detection limit.

REFERENCES

1. Fang Z. L.: Spectrochim. Acta Rev. *14*, 235 (1991).
2. Tyson J. F.: Anal. Chim. Acta *234*, 3 (1990).
3. Carbonell V., Salvador A., Delaguardia M.: Fresenius Z. Anal. Chem. *342*, 529 (1992).
4. Shabani M. B., Akagi T., Shimizu H.: Anal. Chem. *62*, 2709 (1990).
5. Shijo Y., Shimizu T., Tsunoda T.: Anal. Chim. Acta *242*, 209 (1991).
6. Iwata Y., Imura H., Suzuki N.: Anal. Chim. Acta *239*, 115 (1990).
7. Frigge C., Jackwerth E.: Anal. Chim. Acta *242*, 99 (1991).
8. Fang Z. L., Sperling M., Welz B.: J. Anal. Atom. Spectrom. *6*, 301 (1991).
9. Atsuya I., Itoh K., Ariu K.: Pure Appl. Chem. *63*, 1221 (1991).
10. Dominguez M. D. P., Escribana M. T. S., Macias J. M. P.: Microchem. J. *42*, 323 (1990).
11. Tikhomirova T. I., Fadeeva V. I., Kudryatsev G. V.: Talanta *38*, 267 (1991).

12. Singh D. K., Mishra N. K.: Chromatographia *31*, 300 (1991).
13. Terada K.: Anal. Sci. *7*, 187 (1991).
14. Akman S., Ince H., Koklu V.: Anal. Sci. *7*, 799 (1991).
15. Satake M., Lee J. R., Puri B. K., Katyal M.: Analusis *20*, 49 (1992).
16. Miura J., Sugita N., Satake M.: Microchem. J. *42*, 306 (1990).
17. Miura J., Arima S., Satake M.: Anal. Chim. Acta *237*, 201 (1990).
18. Porta V., Abollino D., Mentasti E.: J. Anal. Atom. Spectrom. *6*, 119 (1991).
19. Sperling M., Yin X. F., Welz B.: J. Anal. Atom. Spectrom. *6*, 295 (1991).
20. Fang Z. L., Guo T. Z., Welz B.: Talanta *38*, 613 (1991).
21. Purohit R., Devi S.: Analyst *116*, 825 (1991).
22. Fang Z., Sperling M., Welz B.: J. Anal. Atom. Spectrom. *5*, 639 (1990).