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Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations

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Abstract

A method for separation–preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions by membrane filtration has been described. The method based on the collection of analyte metal ions on a cellulose nitrate membrane filter and determination of analytes by flame atomic absorption spectrometry (FAAS). The method was optimized for several parameters including of pH, matrix effects and sample volume. The recoveries of analytes were generally in the range of 93–100%. The detection limits by 3 sigma for analyte ions were $0.02 \, \mu g \, L^{-1}$ for Pb(II), $0.3 \, \mu g \, L^{-1}$ for Cr(III), $3.1 \, \mu g \, L^{-1}$ for Cu(II), $7.8 \, \mu g \, L^{-1}$ for Ni(II) and $0.9 \, \mu g \, L^{-1}$ for Cd(II). The proposed method was applied to the determination of lead, chromium, copper, nickel and cadmium in tap waters and RM 8704 Buffalo River Sediment standard reference material with satisfactory results. The relative standard deviations of the determinations were below 10%.

1. Introduction

Flame atomic absorption spectrometry (FAAS) with its relative low cost and good analytical performance, is the main instrument in the research laboratories for determining a variety of heavy metals. Accurate determination of traces heavy metals by flame atomic absorption spectroscopy is the one of the important problem for the analytical chemist because of their low concentrations. Also other important problem in FAAS determinations of heavy metals is influences of the matrix of the analyzed samples. In order to overcome, these problem analytical chemists generally use separation–preconcentration techniques including liquid–liquid extraction, coprecipitation, cloud point extraction, electrodeposition, solid phase extraction, etc. [1–5].

Membrane filtration is one of the important enrichment techniques for trace heavy metal ions [6–8]. The formation of hydrophobic species is necessary for the quantitative extraction of the desired trace element on a membrane filter. In the membrane filtration, the collection of traces metal ions is performed very quickly by filtration under suction with the aid of a vacuum aspirator. The collected analyte species on the membrane filter are dissolved together with the membrane in a small amount of mineral acids. The traces species in the final solution is determined by an instrumental method including spectrophotometry, flame or graphite furnace atomic absorption spectrometry. The most attractive features of membrane filtration technique are the simplicity and rapidity of the procedure, an easily attainable high concentration factor and determination with high-precision [9,10]. Various application of the membrane filtration for the preconcentration of traces heavy metal ions were performed by the researchers [11–14].

In the present study, an enrichment/separation system based on the collection of analytes on cellulose nitrate membrane filter was investigated prior to the atomic absorption spectrometric determinations of lead, chromium, copper, nickel and cadmium in environmental samples. The optimum experimental conditions such as pH, matrix effects and sample volume were investigated for the quantitative recoveries of the analytes on cellulose nitrate membrane filter.

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2. Experimental

2.1. Instruments

The instrumental detection system used was a Perkin-Elmer Analyst 700 flame atomic absorption spectrometer. The operating parameters for working elements were set as recommended by the manufacturer. The nebulizer uptake rate was adjusted to give the optimum response for conventional sample introduction, the resulting rate being $6.0\,mL\,min^{-1}$. An acetylene flow rate of $2.5\,L\,min^{-1}$ was used with an air flow rate of $8.0\,L\,min^{-1}$. The atomic absorption signal was measured as a peak height mode against an analytical curve. All measurements were carried out deuterium background correction.

A pH meter, Hanna pH 211 Model with a glass-electrode was employed for measuring pH values in the aqueous phase. A home made filter-holder with a glass filter base was used for filtration of the solutions.

2.2. Reagents and solutions

All reagents used were of analytical reagent grade and double-distilled water was used throughout. Solutions of metal ions were prepared from their nitrates or chlorides working solutions were prepared by appropriate dilution with double-distilled water as needed. The calibration curves for analyte ions were established using the standard solutions prepared in $1\,mol\,L^{-1}$ HNO_3 by dilution from stock solutions. The calibration standards were not submitted to the preconcentration procedure. The pH of the samples was adjusted using $0.1\,mol\,L^{-1}$ hydrochloric acid or $0.1\,mol\,L^{-1}$ sodium hydroxide.

Membrane filters made of cellulose nitrate (Sartarous, No.: 11406, pore size, $0.45\,\mu m$, 47 mm in diameter) were used for the collection of analyte ions. Ammonium chloride buffer solution ($0.1\,mol\,L^{-1}$) were prepared by adding an appropriate amount of ammonia to ammonium chloride solution (Merck and Fluka) to result in solutions of pH 9.

2.3. Recommended procedure

In the recovery experiments, a 30 mL portion of an aqueous solution containing an appropriate amount of metal ion, $5\,\mu g$ for Cd, $10\,\mu g$ for Ni and Cu, $20\,\mu g$ for Pb and Cr was placed in a glass beaker. This solution pH was adjusted to relevant pH with addition of $0.1\,mol\,L^{-1}$ NaOH or $0.1\,mol\,L^{-1}$ HCl. The solution together with analyte ions was collected on a cellulose nitrate membrane filter ($0.45\,\mu m$ pore size and 47 mm diameter). The cellulose membrane filter was dissolved in 0.5 mL of concentrated nitric acid at $80\,°C$, and the solution was diluted to 5 mL or 10 mL with water. The metal concentrations in the final solution were determined by flame AAS.

2.4. Application to real samples

In order to apply the method, drinking water samples taken from a tap in our laboratory and stuff accommodation for the preconcentration and separation of analyte ions. Three hundred milliliters of drinking water sample was placed in a beaker; the pH of the sample was then adjusted to pH with $1\,mol\,L^{-1}$ NaOH. The separation/preconcentration method given above was then applied. The concentration of the analyte ions in the final solution was determined by flame atomic absorption spectrometry.

The water samples were also analyzed using a reference method based on solid phase extraction on Amberlite XAD-7 adsorption resin [15]. For this analysis, 2 mL of $1.2 \times 10^{-3}\,mol\,L^{-1}$ p-xylenol blue solution was added to 250 mL of the sample buffered to pH 9. Metal chelates solution was passed through the Amberlite XAD-7 resin column at a flow rate of $5\,mL\,min^{-1}$. The sample solution was permitted to flow through the column under gravity. The adsorbed p-xylenol blue chelates on the column were eluted by using 5 mL of $1\,mol\,L^{-1}$ HCl at a flow rate $5\,mL\,min^{-1}$. The eluent was analyzed for the determination of analytes by flame atomic absorption spectrometry.

For sediment analysis, 100 mg amount of stream sediment standard reference material (Buffalo River RM 8704) sample was digested with 10 mL of aqua regia at room temperature, and then heated to $95\,°C$. After the evaluation of NO_2 fumes had ceased, the mixture was evaporated almost to dryness on a sand-bath and mixed with 10 mL of aqua regia. The mixture was again evaporated to dryness. Ten milliliters of distilled water was added to the residue. The suspension was filtered through a blue band filter paper (Whatman 41) and the insoluble part was washed with distilled water. The subsequent procedures were the same those described in Section 2.3. The final solution was diluted to 2 mL.

3. Results and discussion

To obtain quantitative recoveries of analyte ions on cellulose nitrate membrane filter, the enrichment/separation procedure was optimized for various analytical parameters. The percent of metal adsorbed on cellulose nitrate filter was calculated from the amounts of metal in the starting sample and the amounts of metal in the final solution.

3.1. Optimum conditions for recoveries of analytes

In the membrane filtration studies for preconcentration and separation of heavy metals at trace levels, generally heavy metal ions were converted to metal chelates by the using a suitable organic chelating agent [14,16–18]. The presented preconcentration work was performed by using cellulose nitrate membrane filter (pore size, $0.45\,\mu m$, and 47 mm in diameter) with the adjustment of the pH of solutions by using diluted NaOH or HCl without ligand.

In the preconcentration studies, the pH of the aqueous phases is the main factor for the quantitative recoveries of the analytes [19–21]. Due to this point, the effects of the pH on the retention of Cu(II), Pb(II), Cd(II), Cr(III) and Ni(II) ions on the cellulose nitrate membrane filter were studied in the pH range of 4–10. The results are depicted in Fig. 1. The recovery values for analyte
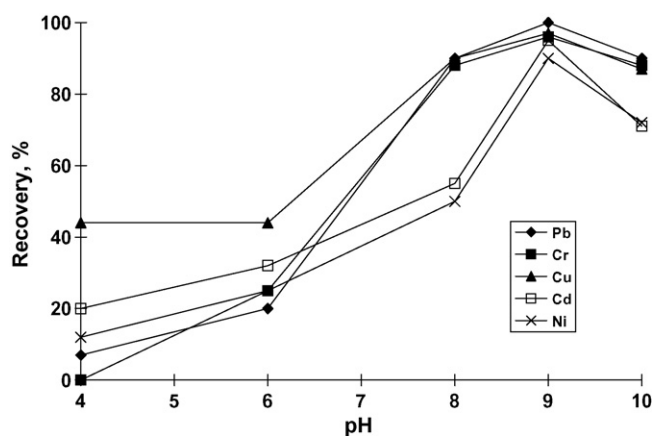
Fig. 1. The influences of the pH on the recoveries of trace metal ions ($N=4$, pH 9, amounts of analytes: 5 µg Cd, 10 µg Ni, 10 µg Cu, 20 µg Pb, 20 µg Cr).

ions at the acidic pHs were not quantitative. The recoveries of Cu(II), Pb(II), Cd(II), Cr(III) and Ni(II) were quantitative at pH 9 when the pH of the solutions was adjusted with NaOH. All further works were performed at pH 9.

To obtain a high concentration factor, the recoveries of Cu, Pb, Cd, Cr and Ni from different sample volumes were examined in the concentration range of 0.2–0.7 µg mL^{-1}, depending on the analyte. The results were depicted in Fig. 2. The recoveries of

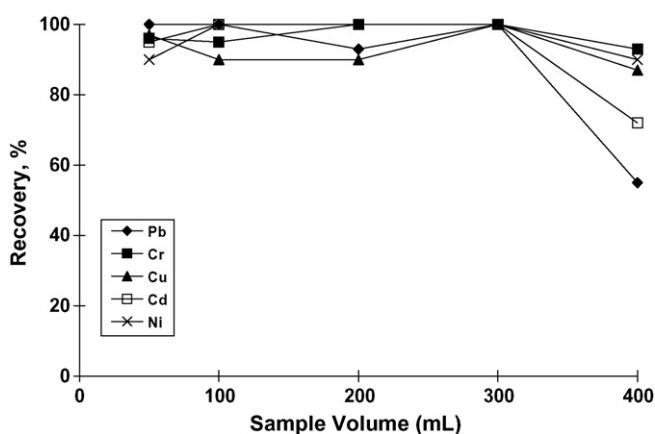Fig. 2. Effect of the sample volume on the recoveries of analyte ions ($N=4$, pH 9, amounts of analytes: 5 µg Cd, 10 µg Ni, 10 µg Cu, 20 µg Pb, 20 µg Cr).

Table 2
Recovery of analyte spikes from drinking water

Analyte	Added (µg)	Found (µg)[a]	Recovery (%)
Pb	0.0	BDL	–
	10.0	9.5	95
	20.0	18.8	94
	30.0	28.8	96
Cr	0.0	BDL	–
	10.0	10.0	100
	20.0	19.6	98
	30.0	30.0	100
Cu	0.0	BDL	–
	5.0	5.0	100
	10.0	9.6	96
	15.0	14.6	97
Ni	0.0	BDL	–
	5.0	4.8	96
	10.0	9.4	94
	15.0	14.4	96
Cd	0.0	BDL	–
	2.5	2.4	96
	5.0	4.8	96
	10.0	9.5	95

BDL: below the detection limit.
[a] Mean of three results.

the analyte ions on cellulose nitrate membrane filter were quantitative from up to 300 mL of the solution. As the concentrated final solution has a volume of 5 mL, the highest preconcentration factor is 60.

One of the main problems in the atomic spectroscopic techniques is interference effect of the matrix of the analyzed samples. Various amounts of NaCl, KCl, CaCl$_2$, MgCl$_2$, Na$_2$CO$_3$ and NaHCO$_3$ as the major components of water samples were added to a solution containing fixed amounts of analytes and the procedure was followed. The results are given in Table 1. The recovery of the investigated trace metal ions was not affected from the solution containing the high concentrations of these matrix ions. The ions normally present in drinking water do not interfere under the experimental conditions used [22]. This results show that the proposed preconcentration/separation method could be also applied to the saline samples at mg L^{-1} levels.

Table 1
Influences of the sample volume on the recovery of investigated trace metal ions ($N=4$)

Ion	Added as	Concentration (mg L^{-1})	Recovery (%)				
			Cu	Pb	Cr	Cd	Ni
Na$^+$	NaCl	20,000	100	100	100	100	92
K$^+$	KCl	2,500	100	100	100	100	100
Ca^{2+}	CaCl$_2$	1,000	100	100	100	92	100
Mg^{2+}	MgCl$_2$	2,500	100	93	100	93	90
SO$_4$$^{2-}$	Na$_2$SO$_4$	2,500	96	100	100	95	100
Cl$^-$	NaCl	12,000	100	100	100	100	92
HCO$_3$$^-$	NaHCO$_3$	250	100	93	100	100	90
CO$_3$$^{2-}$	Na$_2$CO$_3$	250	98	95	100	100	100

Table 3
Determination of analytes in drinking water samples

Analytes	Concentration, $x \pm ts/\sqrt{N}$ (μg L^{-1})			
	Tap of laboratory		Tap of stuff accommodation	
	Present method	Reference method [15]	Present method	Reference method [15]
Cu	0.53 ± 0.05 (3)	BDL	0.61 ± 0.04 (3)	BDL
Cr	2.89 ± 0.29 (8)	3.17 ± 0.35 (10)	2.71 ± 0.52 (8)	2.22 ± 0.59 (10)
Pb	3.56 ± 1.00 (10)	3.21 ± 0.07 (9)	3.23 ± 0.65 (10)	2.65 ± 0.51 (9)
Ni	1.19 ± 0.24 (3)	BDL	1.12 ± 0.15 (3)	BDL
Cd	0.37 ± 0.06 (4)	BDL	0.14 ± 0.04 (4)	BDL

BDL: below the detection limit. The values in parenthesis are number of replicate analysis.

3.2. Method validation and analytical performance

The analytical performance of cellulose nitrate enrichment/separation system for the preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) was also considered. To validate the present method, the recovery of analytes ions spiked into analyzing drinking water was studied; satisfactory results were obtained as shown in Table 2. The recovery values calculated for the added standards were always quantitative (>95), thus confirming the accuracy of the procedure and the absence of matrix effects.

The precision of the cellulose nitrate membrane filter method were evaluated as the relative standard deviations obtained after replicate analyses of water samples. The relative standard deviations for analyte ions were generally below 10%. The detection limits for analytes were calculated after presented preconcentration procedure applied to the blank solutions. The 3 sigma detection limits for Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) estimate from results on the blank solution, were found to be as 0.02 μg L^{-1}, 0.3 μg L^{-1}, 3.1 μg L^{-1}, 7.8 μg L^{-1} and 0.9 μg L^{-1}, respectively.

Table 4
The levels of analyte ions in sediment reference material (RM 8704 Buffalo River Sediment, $N = 5$)

Element	Concentration (mg kg^{-1})		
	Certified value	Observed value	R.S.D. (%)
Cu	98.6	95.9 ± 5.5	3.6
Pb	161	143.1 ± 4.5	2.5
Ni	44.1	41.9 ± 2.0	4.6
Cd	3.5	3.3 ± 0.1	0.8
Cr	135	148.5 ± 0.4	0.3

Mean expressed as 95% tolerance limit.

3.3. Analysis of real samples

The presented cellulose nitrate membrane filtration method was applied to drinking water samples taken from a tap in our laboratory and stuff accommodation for the preconcentration and separation of analyte ions. The results are given in Table 3. The accuracy of the method was also checked by analysis of drinking water samples by the reference method based on solid phase extraction on XAD-7 resin [15] (Table 3). There are no

Table 5
Comparative data from some recent studies on preconcentration

Technique	Analytes	System	Eluent	PF	Detection limit (μg L^{-1})	R.S.D. (%)	Refs.
SPE	Cd, Hg, Ni, Co, Cu, Zn	2-(Methylthio)aniline/ functionalized Amberlite XAD-2	1 mol L^{-1} HCl	400	0.02–0.08	<10	[23]
SPE	Fe	Fe-methylthymol complex/naphthalene-tetraoctylammonium bromide	1.5 mol L^{-1} HNO$_3$	36	12	<1.8	[24]
SPE	Cd, Cu, Ni, Zn	Ammonium pyrro-lidinedithiocarbamate impregnated activated carbon	1 mol L^{-1} HNO$_3$ in acetone	20	0.019–0.028	<0.6	[25]
Coprecipitation	Hg, Pb, Cd	Aluminum hydroxide	HNO$_3$	–	3–16	<2	[26]
On-line SPE	Pb, Cd	Polyurethane foam/2-(6′-methyl-2′-benzo thiazolylazo) chromotropic acid	1 mol L^{-1} HCl	37	0.1–3.8	<3.1	[27]
CPE	Cr	Triton X-100/Cr(VI)/ dibromophenylfluorone	1 mol L^{-1} HNO$_3$	50	0.01	2.6	[28]
MF	Pb, Cr, Cu, Ni, Cd	Cellulose nitrate	HNO$_3$	60	0.02–7.8	<10	Present work

MF: membrane filtration; SPE: solid phase extraction; CPE: cloud point exraction; PF: preconcentration factor.

significant differences at the 95% confidence level between the results obtained with two methods.

The method was applied to a sediment standard reference material (RM 8704 Buffalo River) for the determination of copper, lead, nickel, cadmium and chromium levels. The results were given in Table 4. The results found with presented method are in good agreement with the certified values for the investigated analyte ions. If the concentration levels of the most common matrix constituents of reference standard materials analyzed and the accuracy of the presented method are considered together, it can be concluded that the proposed method is free from interferences of the various constituents.

4. Conclusions

The proposed preconcentration/separation procedure a fast and simple method for the enrichment of copper(II), lead(II), nickel(II), cadmium(II) and chromium(III) on cellulose nitrate membrane filtrate. Comparative information from some studies on preconcentration of heavy metals by various techniques for the figure of the merits is given in Table 5. The detection limits and preconcentration factor of analyte ions are superior to those of preconcentration technique for analyses [23–27]. The matrix effects with the method were reasonably tolerable by the comparison some other preconcentration techniques in literature [28–35]. The recoveries were quantitative (93–100%). Also the presented method relatively rapid as compared with previously reported procedures for the enrichment of trace metal ions.

Acknowledgement

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