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Enrichment and determinations of nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions in natural waters, table salts, tea and urine samples as pyrrolydine dithiocarbamate chelates by membrane filtration–flame atomic absorption spectrometry combination

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Abstract

A membrane filtration procedure for the preconcentration of nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions has been established. The analytes were adsorbed on cellulose nitrate membrane filter as their ammonium pyrrolydine dithiocarbamate (APDC) complexes. Then membrane filter was dissolved by using nitric acid. The levels of the analytes in the final solutions were determined by flame atomic absorption spectrometry (FAAS). The analytical parameters including pH, amounts of APDC, sample volume, matrix effects, etc. have been optimized. The present method has been successfully applied for the FAAS determinations of analyte ions in a stream sediment reference material (GBW 07309), table salts and natural water samples with good results, e.g. recoveries greater than 95%, relative standard deviations generally lower than 9%. The analyte ion levels of the microwave digested urine and black tea samples were also analyzed by using proposed preconcentration procedure.
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Keywords: Preconcentration; Cellulose nitrate membrane; APDC; Flame atomic absorption spectrometry

1. Introduction

Sensitive and accurate determination of heavy metal ions at trace levels in the natural samples including waters, biological fluids, soils and sediments are very important part of environmental and public health studies [1–3]. For this purpose, flame atomic absorption spectrometry (FAAS) has been continuously used. However the relatively lower element concentrations than detection limits of atomic absorption spectrometry and the interferic effects sourced from the matrix of the real samples are two main difficulties in these determinations. These difficulties could generally be prevented by using preconcentration and separation methods [4,5]. The preconcentration techniques including solid phase extraction

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based on adsorption [6–9], liquid–liquid extraction [10,11], cloud point extraction [12,13], adsorption on microcrystalline naphthalene or benzophenone [14], coprecipitation [15,16], flotation [17], etc. have been used for the preconcentration and separation of traces heavy metal ions.

Membrane filtration is also the one of the preconcentration/separation methodology for the traces heavy metal ions in environmental samples including highly saline media [18,19]. The metal ions were collected on the membrane as a suitable form including metal chelates. The collection of traces metal ions is performed very quickly by filtration under suction with the aid of an aspirator. The adsorbed analyte species as metal chelates on the membrane filter are dissolved together with the membrane filter in a small amount of and suitable solvent including mineral acids or organic solvents. The trace species in the final solution is determined by an instrumental method such as AAS, inductively coupled plasma atomic emission spectrometry (ICP–AES), spectrophotometry, etc. The materials of membrane filters with a strong affinity for hydrophobic species in water are generally useful to retain the species by filtration. Membrane filters including cellulose nitrate, cellulose acetate, etc. have been used for enrichment and separation of trace heavy metal ions in various media like natural waters [20–23].

Ammonium pyrrolydine dithiocarbamate (APDC) is a chelating agent that reacts with metal ions to form very stable complexes that has an advantage for separation/preconcentration studies that is differences in formation constants between the transition metals and alkaline and alkaline earth metals to effect, separations of trace metals from saline solutions using APDC [24].

In the present work, a simple, rapid and cheap preconcentration/separation methodology based on the membrane filtration of traces heavy metal ions in table salts, natural water samples and a sediment reference material have been established. The procedure was also applied to microwave digested urine and black tea samples. The influences of various analytical parameters including pH, sample volume, amounts of APDC, and influences of matrix, etc. on the retentions of analyte ions on cellulose nitrate membrane filter were investigated.

2. Experimental

2.1. Reagents and solution

Doubly distilled water and high purity reagents were used for all preparations of the standard and sample solution. Standard stock solutions containing 1000 mg/l analyte were prepared from nitrate salts of investigated analyte ions in 1% of HNO_3 into 1 l calibrated flasks. Diluted standard solutions and model solutions were daily prepared from the stock standard solutions.

Stock solutions of diverse elements were prepared from high purity compounds. The calibration standards were not submitted to the separation/preconcentration procedure. Membrane filters used in the present study were purchased from Osmonics (Westborough, MA, USA).

A 1.0×10^{-3} M solution of APDC (Sigma, St. Louis, MO, USA) was prepared by dissolving the required amount of APDC in a water/ethanol (75/25 (v/v)) mixture. The APDC solution was prepared daily. The pH of the model solution was adjusted to pH 2–3 with phosphate buffer, pH 4–6 with CH_3COO^-/CH_3COOH buffers and pH 8–10 with NH_3/NH_4^+ buffers. The stream sediment standard reference material (GBW 07309) was obtained from National Research Centre for Certified Reference Materials (NRCCRM), China.

2.2. Instruments

A Perkin-Elmer Model 3110 atomic absorption spectrophotometer equipped with Perkin-Elmer single-element hollow cathode lamps and a 10 cm air–acetylene burner were used for the determination of the metal ions. All instrumental settings were those recommended in the manufacturer's manual book.

A pH meter, Nel pH-900 Model glass-electrode was employed for measuring pH values in the aqueous phase. An erlenmayer flask with ground stopper was used for filtration the solutions. Bosch HMT 812 C and Milestone Ethos D microwave ovens were used for the microwave assisted heating sample digestion of black tea and urine.

The samples were introduced to the nebulizer of the AAS by using micro injection method [25]. In this system, 100 μl of the samples were injected to a mini home-made Teflon funnel with a Eppendorf

Pipette. The Teflon funnel was connected to the nebulizer with capillary tubing. The peak height signals were recorded.

2.3. Preconcentration procedure

Fifty milliliters of an aqueous solution containing 10–20 µg of analyte ions was placed in a glass beaker. Ten milliliters of buffer solution (to give the desired pH between 2 and 10) and APDC solution were added. After 10 min, metal–APDC solution was collected through a cellulose nitrate membrane filter of 0.45 µm size and 47 mm diameter. The adsorption of the metal chelates is performed very quickly by filtration under suction with an aspirator. Then the membrane was completely dissolved in 0.5 ml of concentrated nitric acid at 80 °C on a hot plate. The solution was evaporated to dryness. The residue was diluted to 2–5 ml with 1 M HNO_3. The metal concentrations in the final solution were determined by FAAS.

2.4. Analysis of real samples

2.4.1. Procedure for the stream sediment SRM sample

A 50 mg amount of a stream sediment reference material (GBW 07309) sample was decomposed with 15 ml of aqua regia and the solution was evaporated to dryness. This process was repeated twice. Ten milliliters of distilled water was added to the residue. The suspension was filtered through a blue band filter paper, and the insoluble part was washed with distilled water. Then the preconcentration procedure given above was applied to the final solutions. The same procedure was applied to the blank solution.

2.4.2. Analysis of the water samples

To application of the method, 250 ml of water sample was taken a beaker, and then the pH of the sample was adjusted to pH 2 with phosphate buffer. Then the separation/preconcentration method given above was applied. The concentrations of the analyte ions in the final solution were determined by FAAS.

2.4.3. Analysis of salt samples

For the determination of metal ions in salt samples, 2.000 g of table salt was dissolved in distilled water and diluted to 25 ml with distilled water. The pH of the solution was adjusted to pH 2, preconcentration procedure then was applied to this solution. The metal concentrations in the final solution were determined by flame AAS.

2.4.4. Procedure for urine

For urine digestion, the digestion program procedure given by da Silva et al. [26] was modified with little change. Twenty-five milliliters of urine was mixed with 10 ml of concentrated HNO_3 in a Teflon beaker and the mixture was submitted to a four-step program: 360 W (5 min), 0 W (2 min), 400 W (5 min) and 600 W (10 min). After digestion, the volume was made up to 50 ml with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples. The final volume was 2 ml.

2.4.5. Analysis of black tea sample

For the digestion of black tea samples, 1 g of tea was mixed with the mixture of 9 ml of concentrated HNO_3 and 3 ml of concentrated hydrochloric acid in a Teflon beaker and the mixture was submitted to a three-step program: 180 W (3 min), 360 W (5 min) and 180 W (3 min). After digestion, the volume was made up to 25 ml with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples. The final volume was 2 ml.

To determine the analytes in the concentrated solutions for the samples, an aliquot 100 µl of the solution was introduced to the nebulizer of the flame atomic absorption spectrometer by micro injection method.

3. Results and discussion

3.1. Effect of pH on the retentions of analytes

Because of the pH of the test solutions is the one of the important parameter on the recoveries of traces heavy metal ions as their metal chelates on membrane filters, firstly the effects of the pH of the aqueous solutions on the recoveries of the analytes on cellulose nitrate membrane filter were investigated in the pH range of 2–10. The results were given in Fig. 1. The quantitative recovery values (>95%) were obtained for nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions as APDC chelates at the pH range of 2–4.
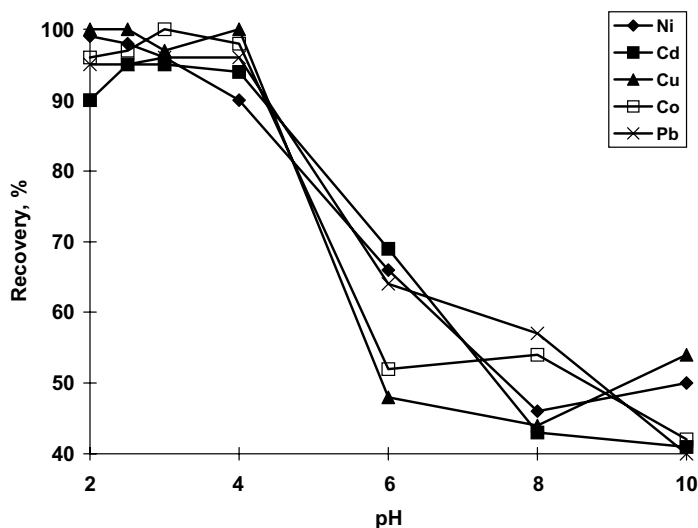
Fig. 1. The influences of the pH on the recoveries of nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions ($N = 4$, ligand: APDC).

After pH 4, the recoveries were decreased. In the light of the results in Fig. 1, all the further studies were carried out at pH 2 by using phosphate buffer solution.

3.2. Amounts of APDC

To determine the concentration of the ammonium pyrrolydine dithiocarbamate required for quantitative recoveries, the proposed method was applied, changing the APDC amounts concentration from 0 to 10 mg at pH 2. It was found that, the recovery of the nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions increased with increasing amounts of APDC added and reached a constant value with at 5.0 mg of APDC. The addition of 5.0 mg of APDC is recommended.

3.3. Effects of membrane type and size

The effects of the membrane type and membrane size on the recovery values of the analyte ions as APDC chelates were also examined by using various membrane filters. The recoveries of analytes were quantitative when cellulose nitrate and cellulose acetate membrane filters (0.22 and 0.45 μm). The recovery values for analytes were not quantitative with polysulfone (PES) and polytetrafluoroethylene (PTFE) membrane filter. In all further studies cel-

lulose nitrate membrane filter (47 mm and 0.45 μm) was used.

Some concentrated mineral acids including sulfuric acid, hydrochloric acid and nitric acid have been used for the dissolution of the membrane filter. Quantitative recovery values were obtained for the analyte ions by using only nitric acid.

3.4. Effect of sample volume

In order to study with high sample volumes, the effect of the sample volume on the recoveries of the analyte ions was also investigated in the sample volume range of 20–350 ml. The results are depicted in Fig. 2. The recoveries of nickel(II) ions were quantitative in the all-working range. Cobalt was recovered quantitatively in the range of 20–250 ml. Lead, copper and cadmium ions were quantitatively recovered on cellulose nitrate membrane till 300 ml of sample volume. The low recovery values for the analyte ions especially for lead may cause to the excess analytes loaded over the membrane capacity with increasing sample volume above 300 ml.

3.5. Interferences

The interferic effects of the some alkaline, earth alkaline and transition metal ions, and some anions were
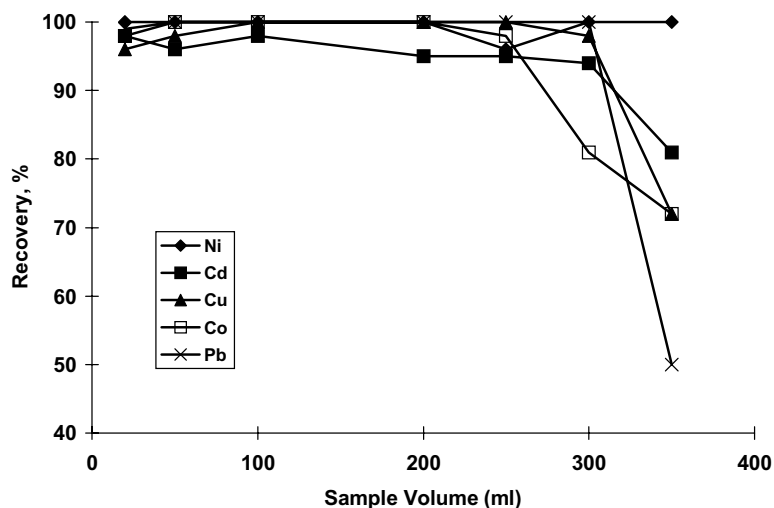
Fig. 2. Effects of sample volume on the recoveries of nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions ($N = 4$).

investigated. The results are given in Table 1. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the preconcentration and determination of analytes. The ions normally present in water and table salt samples and some metal ions including Al^{3+}, Mn^{2+}, Zn^{2+}, Fe^{3+} and Fe^{2+} at the levels given in Table 1 do not interfere under the experimental conditions used. The alkaline and earth alkaline metal ions were not retained on the column because of their very low stability constants of APDC complexes. The tolerable levels of the some

Table 1
Effects of the matrix ions for recoveries of Cu(II), Ni(II), Cd(II), Pb(II) and Co(II); (N=4)

Ion	Added as	Concentration (mg/l)	Recovery (%)				
			Cu	Ni	Cd	Pb	Co
Na^+	NaCl	10000	98	103	93	94	98
K^+	KCl	5000	103	100	101	98	94
Ca^{2+}	$CaCl_2$	2000	102	98	96	96	98
Mg^{2+}	$MgCl_2$	2000	103	98	95	95	98
Fe^{3+}	$FeCl_3$	25	95	96	95	97	95
Fe^{2+}	$FeCl_2$	10	96	97	94	96	95
Mn^{2+}	$MnSO_4$	25	95	95	96	97	94
Zn^{2+}	$ZnSO_4$	25	95	95	95	98	96
Al^{3+}	$Al_2(SO_4)_3$	25	96	96	96	95	96
Cr^{3+}	$Cr(NO_3)_3$	100	95	98	95	96	99
Cl^-	NH_4Cl	15000	98	103	93	94	96
SO_4^{2-}	$(NH_4)_2SO_4$	1000	98	96	96	96	96

heavy metal ions are suitable for the separation and preconcentration of the analyte ions in the real samples examined present study, because of the levels of transition metals in these samples are lower than their interferic level.

3.6. Detection limits

The detection limits for analytes were calculated after presented preconcentration procedure applied to the blank solutions. The detection limits of the investigated elements based on three times the standard deviations of the blank ($k = 3$, $N = 21$) on a sample volume 100 ml for nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) were 55, 1.1, 33, 10 and 31 μg/l, respectively. The detection limits can be decreased by one order of magnitude by increasing the sample volume.

The preconcentration factors that were calculated from the ratio of highest sample volume obtained quantitative recoveries to 2 ml final volume. The preconcentration factors for nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) were 175, 150, 150, 125 and 150, respectively.

3.7. Recovery studies

For recovery studies, various amounts of analyte ions were spiked to a table salt and a water sample.

Table 2
Analysis of a table salt and a water spiked analyte ions (final volume: 5 ml, $N = 4$)

Element	Added (µg)	Water		Salt	
		Found $x \pm$ S.D.[a] (µg)	Recovery (%)	Found $x \pm$ S.D.[a] (µg)	Recovery (%)
Cd	0	N.D.	–	N.D.	–
	1.5	1.4 ± 0.1	93	1.5 ± 0.1	100
	2.5	2.6 ± 0.3	104	2.4 ± 0.1	96
Pb	0	N.D.	–	N.D.	–
	15	15.6 ± 1.2	104	15.6 ± 1.3	104
	25	25.7 ± 1.2	103	23.8 ± 0.5	95
Ni	0	1.5 ± 0.2	–	1.2 ± 0.2	–
	2.5	4.2 ± 0.4	108	3.8 ± 0.6	104
	4.0	5.2 ± 0.2	92	5.1 ± 0.4	98
Co	0	N.D.	–	N.D.	–
	2.5	2.4 ± 0.1	96	2.4 ± 0.2	96
	4.0	3.9 ± 0.3	98	3.8 ± 0.2	95
Cu	0	N.D.	–	N.D.	–
	2.5	2.6 ± 0.3	104	2.5 ± 0.3	100
	4.0	3.7 ± 0.2	92	3.9 ± 0.2	98

Not detected (N.D.).

[a] Standard deviation (S.D.).

Table 3
Results of the analysis a stream sediment standard reference material (GBW 07309) ($N = 5$)

Element	Certified value (µg/g)	Our value (µg/g)
Cu	32	32.9 ± 2.6
Ni	32	30.7 ± 2.6
Cd	0.26	0.40 ± 0.03
Pb	23	24.1 ± 2.6
Co	14	15.0 ± 0.7

The results are given in Table 2. The results obtained in these experiments demonstrate that the presence of table salt and natural waters have no significant effect on the recovery of analyte ions.

3.8. Application of the proposed method

The method was applied to a stream sediment standard reference material (GBW 07309) for the determination of Cu(II), Ni(II), Cd(II), Pb(II) and Co(II). The results in Table 3 are based on the average of five replicates. The results are in good agreement with the certified values. If the concentration levels of the most common matrix constituents of the stream sediment reference sample, including 1.07% Na, 1.65% K, 3.04% Fe, 5.60% Al, 3.82% Ca, 1.44% Mg 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.

Table 4
Concentration of Cu(II), Ni(II), Cd(II), Pb(II) and Co(II) in natural water samples (final volume: 2 ml, $N = 5$)

Sample	Concentration (µg/l)[a]				
	Cu	Ni	Cd	Pb	Co
Drinking water-1	6.2 ± 0.4	3.4 ± 0.1	1.4 ± 0.4	8.3 ± 0.1	3.3 ± 1.1
Drinking water-2	7.6 ± 0.1	10.6 ± 1.4	2.2 ± 0.4	5.3 ± 3.9	6.0 ± 2.0
Bottled mineral water-1	17.7 ± 0.4	5.0 ± 0.6	1.3 ± 0.2	10.6 ± 1.8	8.5 ± 1.0
Bottled mineral water-2	8.5 ± 0.1	6.6 ± 0.2	1.0 ± 0.2	10.6 ± 1.8	2.5 ± 0.1
Bottled mineral water-3	10.4 ± 0.1	7.3 ± 1.2	0.8 ± 0.2	13.3 ± 4.1	2.8 ± 0.4
Bottled mineral water-4	10.1 ± 0.8	5.0 ± 1.8	0.9 ± 0.02	15.0 ± 3.9	3.3 ± 1.1

[a] $x \pm t \cdot s / \sqrt{N}$, $P = 0.05$.

Table 5
Concentration of analyte ions in table salts, urine and black tea samples (final volume: 2 ml, $N = 5$)

Sample	Concentration (μg/g)[a]				
	Cu	Ni	Cd	Pb	Co
Table salt-1	0.8 ± 0.1	0.6 ± 0.1	0.12 ± 0.02	0.9 ± 0.1	0.24 ± 0.03
Table salt-3	0.8 ± 0.1	0.5 ± 0.1	0.10 ± 0.01	0.9 ± 0.1	0.40 ± 0.06
Table salt-3	0.7 ± 0.1	0.4 ± 0.1	0.11 ± 0.03	0.6 ± 0.1	0.36 ± 0.11
Urine[b]	6.2 ± 0.5	0.4 ± 0.1	0.14 ± 0.01	9.6 ± 0.1	7.1 ± 0.9
Black tea	0.5 ± 0.1	0.6 ± 0.1	BDL	1.0 ± 0.1	0.65 ± 0.01

Below detection limit (BDL).

[a] $x \pm t \cdot s/\sqrt{N}$, $P = 0.05$.

[b] Concentration in μg/l.

The proposed membrane filtration procedure has been also applied to natural water samples for the preconcentration and separation of analyte ions. The results are given in Table 4. The preconcentration method proposed was applied to the flame atomic absorption spectrometric determination of analyte ions some table salt samples purchased from a local market. The results are given in Table 5.

The microwave digested black tea and urine samples were also analyzed for the determination of Cu(II), Ni(II), Cd(II), Pb(II) and Co(II) ions by using proposed method/flame atomic absorption spectrometry combination. The results of these studied were also given in Table 5.

4. Conclusion

The present preconcentration method is simple, economic and fast. The proposed procedure is very important and fortunate for analytical problem of the determination of metal traces in presence of alkali and alkaline earth salts. The precision, based on replicate analysis, is around 5% for the analytes, and recovery is quantitative, based on analysis of spiked samples and solutions including matrix components.

Acknowledgements

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