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Preconcentration of Co, Ni, Cd and Zn on naphthalene–2,4,6-trimorpholino-1,3,5-triazin adsorbent and flame atomic absorption determination

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Abstract: A preconcentration method was developed for the determination of trace amounts of Co, Ni, Cd and Zn by atomic absorption spectrometry. The method is based on the retention of the metal cations by naphthalene–2,4,6-trimorpholino-1,3,5-triazin adsorbent in a column. The adsorbed metals were then eluted from the column with hydrochloric acid and the Co, Ni, Cd and Zn were determined by flame atomic absorption spectrometry. The optimal extraction and elution conditions were studied. The effects of diverse ions on the preconcentration were also investigated. A preconcentration factor of 250 for Co(II), Ni(II) and Zn(II), and 400 for Cd(II) can easily be achieved. Calibration graphs were obtained and the detection limits of the method for Co(II), Ni(II), Cd(II) and Zn(II) were 0.51, 0.49, 0.17 and 0.10 ng mL^{-1}, respectively. The relative standard deviations (*RSD*) of 0.37–2.31 % for Co, 0.37–3.73 % for Ni, 2.20–2.40 % for Cd and 1.50–2.56 % for Zn were obtained. The method was also used for the simultaneous preconcentration of these elements and the method was successfully applied to their preconcentration and determination. The method was applied to the determination of Co, Ni, Cd and Zn in several real samples.

Keywords: 2,4,6-trimorpholino-1,3,5-triazin; solid–liquid extraction; environmental samples; naphthalene.

INTRODUCTION

The determination of metal ions in natural samples such as waters, soils and biological fluids is a very important part of environmental and public health studies. However, the direct determination of metal ions at trace level is limited due to their low concentration and matrix interferences. Flame atomic absorption spectrometry (FAAS), which is often used for the determination of trace metal ions, suffers from insufficient sensitivity for the direct determination of metal

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ions in environmental samples. Therefore, a preconcentration or separation step is frequently necessary to improve the detection limit and sensitivity. For this purpose, several separation and preconcentration procedures have been developed for trace metal ion determination involving different analytical strategies. To accomplish this task, solvent extraction, co-precipitation or solid phase preconcentration technique can be applied.

Solid phase extraction is a sensitive, fast and economic preconcentration method for traces of analyte ions in various materials, including natural waters, ores, biological samples, *etc*. Of all separation-enrichment separation procedures, solid phase extraction possesses several advantages: large preconcentration factors, simplicity of phase separation and suitability for automation.[1–3]

A variety of solid materials, such as modified ion exchange resins,[4–6] zeolites,[7] silica gel,[8] activated carbon,[9] C60–C70 fullerene[10] and microcrystalline naphthalene,[11–13] have been used for preconcentration of trace metals. It was shown that the type of employed support material is a critical factor in the performance of the resulting supported reagent or catalyst. Two main factors should be considered when employing a material as a support. First, the material needs to be stable both thermally and chemically during the reaction process. Secondly, the structure of the support needs to be such that the active sites are well dispersed on its surface and that these sites are easily accessible.

Solid–liquid extraction of metals with microcrystalline naphthalene is a very rapid and convenient method, which can be used for many types of metal complexes.[14–16] Under selected experimental conditions, the analyte can be adsorbed on the adsorbent and subsequently washed off using an inorganic acid.

In this study, a simultaneous solid-phase preconcentration method for the determination of cadmium, cobalt, nickel and zinc by atomic absorption is described. The method is based on the adsorption of these ions on 2,4,6-trimorpholino-1,3,5-triazin supported on naphthalene, used as an adsorbent in a column. The metal ions adsorbed on the adsorbent are then eluted with hydrochloric acid solution and determined by FAAS. The method was applied to the determination of Ni, Co, Zn and Cd in tap water, spring water, apple leaves, multi-vitamin tablets and B_{12} vitamin samples.

EXPERIMENTAL

Apparatus

A Shimadzu model 670 atomic absorption spectrometer was used for the determination of the preconcentrated metal ions. The employed conditions are given in Table I. The flow rates of air and acetylene were set as recommended by the manufacturer.

Reagents

Triply distilled water was used and analytical reagent grade chemicals were purchased from Merck and Aldrich Chemical Companies. 2,4,6-Trimorpholino-1,3,5-triazin was prepared and purified according to a literature method.[17]

TABLE I. Operating parameters for the flame atomic absorption spectroscopic determination of cations

Element	Current, mA	Wavelength, nm	Slit, nm
Ni	4.0	232.0	0.15
Co	6.0	240.7	0.20
Zn	4.0	213.9	0.50
Cd	4.0	228.8	0.30

Preparation of the adsorbent

A 0.010 g of synthesized ligand was dissolved in acetone at 40 °C under vigorous stirring. After dissolving 0.20 g naphthalene in the above solution, 20 mL triply distilled water was added slowly to obtain adsorbent particles with suitable sizes. Then, the mixture was stirred for 1 h, at 40 °C. The product was filtered and the adsorbent was dried to use.

Analytical procedure

An accurately weighed amount of adsorbent was transferred into a glass column of 4 cm length and 0.8 cm diameter. The column was washed with triply distilled water. The pH of an optimized volume of metal ion solution was adjusted by the drop wise addition of dilute HNO_3. The solution was then passed through the column at a flow rate of 5 mL min^{-1}. Metal ion adsorbed on the column was then eluted with 2.0 mL of 1.0 mol L^{-1} HCl solution at an elution rate of 1 mL min^{-1}. The metal concentration in the eluted solution was determined by FAAS.

Determination of nickel and zinc in apple leaves

A 1.0 g sample was taken in a beaker and dissolved in 20 mL concentrated nitric acid with heating. The solution was cooled, diluted and filtered. The pH of the final solution was adjusted to 5 by suitable addition of an NH_3 solution and the solution was finally diluted to 250 mL with distilled water in a volumetric flask.[18] The nickel and zinc content of the solution was then determined after preconcentration as described above.

Determination of cobalt in pharmaceutical samples

The contents of vitamin B_{12} in four ampoules for injection were determined as cobalt. The contents of the ampoules were decomposed in a 50 mL round-bottom flask by heating with 5.0 mL of a mixture containing concentrated nitric and sulfuric acid (10:1) on a hot plate until near dryness.[19] The drop-wise addition of concentrated nitric acid was required to obtain a colorless residue. The residue was neutralized with a dilute sodium hydroxide solution and was then diluted to an appropriate volume (50 mL). The cobalt contents were analyzed by the recommended procedure.

Determination of zinc in a milk sample

A sample of powdered milk (1.0 g) was heated in a beaker containing a mixture of concentrated sulfuric acid (10 mL) and nitric acid (4.0 mL) until a clear solution was obtained. This was allowed to cool and most of the acid was neutralized with sodium hydroxide. The pH was adjusted to the optimum value and the volume was made up to 500 mL.[20] The concentration of zinc was estimated by passing the solution through the column. The metal ion was eluted from the column using 2.0 mL of 1.0 mol L^{-1} HCl and determined using FAAS.

Determination of zinc in multivitamin tablets

Ten multivitamin tablets were weighed, ground, placed in a conical flask and treated with 20 mL of 0.10 mol L^{-1} HCl. The solution was shaken mechanically and filtered, the precipitate was thoroughly washed with deionized water and then the combined filtrates were transferred into a 100 mL volumetric flask and diluted to the mark with deionized water.[21] The zinc content of the solution was then determined after preconcentration as described above.

RESULTS AND DISCUSSION

Adsorption of each ion was investigated separately. Ions from solutions with different concentrations of cations were adsorbed on the sorbent. Different parameters were optimized. The pH of the sample solution, the type and concentration of the eluent, the effect of sample and eluent flow rates on the extraction efficiency, the interference effect of foreign species and the capacity factor of the sorbent for metal ions recovery were studied. The optimization procedure was performed by varying one parameter while keeping the others constant.

Effect of variables on the preconcentration

The effect of pH on the preconcentration of the cations was examined in the range 3.0–7.0, and the results are shown in Fig. 1. The results show that in the pH range of 4.0–5.5, the analytes were quantitatively adsorbed on microcrystalline naphthalene and the recovery was more than 90 %. In order to obtain the best conditions for the determination after preconcentration, pH 4.5 was chosen.

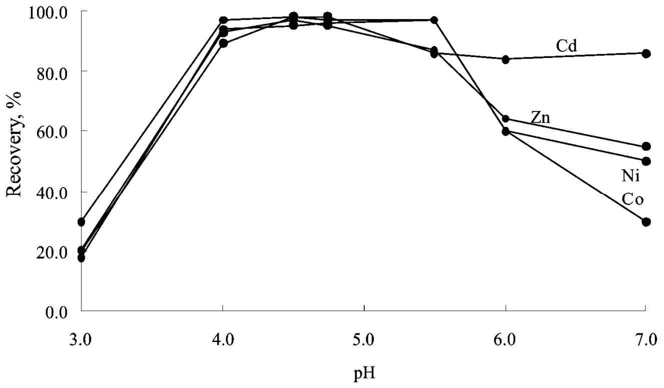

Fig. 1. Effect of pH of the metal ions solution on the percent of retention on sorbent. Experimental conditions: 10.0 mL 5.0 ng mL^{-1} metal ion solution at different pH, 0.21 g sorbent.

The percent sorption of 10.0 mL of 5.0 μg mL^{-1} of the solutions of the cations at pH 4.5 on the sorbent surface as a function of the flow rate of the sample solution was examined in the range of 0.5–15.0 mL min^{-1}. The results indicated that at flow rates lower than 10 mL min^{-1}, complete sorption of each cation on sorbent was achieved. However at flow rates greater than 10 mL min^{-1}, there was a decrease in the percentage sorption. This may be due to insufficient equilibration of the sample solution with the sorbent. Thus a flow rate of 10 mL min^{-1} was chosen for further studies.

In order to choose an appropriate eluent for desorbing the cations from the sorbent surface, a series of selected mineral acids, *i.e.*, hydrochloric nitric and sulfuric acid were used. Aliquots of 10.0 mL of 2.0 μg mL^{-1} of each cation solution were passed through a series of columns containing 0.21 g of adsorbent. A total of 2.0 mL of 1.0 mol L^{-1} of the above-mentioned eluents was used for desorption of the adsorbed cations. The amount of cation back-extracted into the liquid phase by each eluent was measured using FAAS. Percent recoveries of cations were calculated for each sample. The results show that the recovery was the best when hydrochloric acid solution was used as the eluent. Therefore, hydrochloric acid was selected as the eluent.

For desorbing metal ions already adsorbed on the adsorbent, different concentrations of the eluent, in the range 0.05–2.00 mol L^{-1} HCl, were used. As is shown in Fig. 2, at concentrations greater than 1.00 mol L^{-1}, HCl completely desorbed the metal ions from the sorbent surface. Therefore, a concentration of 1.0 mol L^{-1} of HCl was selected for further studies.

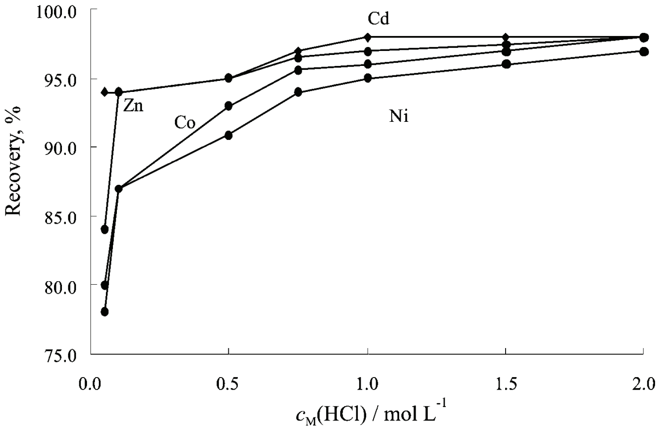

Fig. 2. Effect of eluent concentration on percent recovery of metal ions. Experimental conditions: 10.0 mL 5.0 ng mL^{-1} metal ions solution at pH 4.5, 0.21 g sorbent with different concentration of eluent.

The effect of the volume of the eluent solution was also studied. The results are shown in Fig. 3. The percent of recovery of cations increased with increasing volume of HCl up to 2.0 mL and thereafter remained constant. Therefore, the optimum volume of the eluent was chosen as 2.0 mL. The flow rate of eluent was 1.0 mL min^{-1}.

The prepared sorbent was subjected to several loadings with the sample solution and subsequent elution with the eluent. The capacity of the adsorbent had not changed after 5 cycles of sorption and desorption.

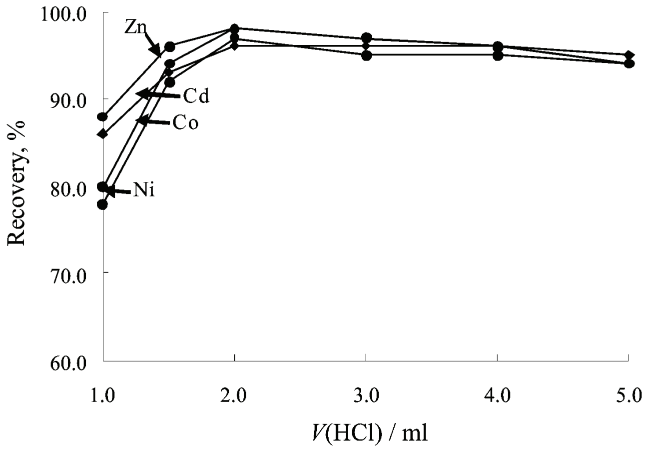

Fig. 3. Effect of the volume of eluent on percent of recovery of metal ions. Experimental conditions: 10.0 mL 5.0 ng mL^{-1} metal ions solution at pH 4.5, 0.21 g sorbent with different volumes.

The effect of the sample volume on the adsorption of cations on 0.21 g of sorbent was studied by passing sample volumes of 10–1000 mL containing the same amount of cation (10 µg) through the column and the signal of each eluted solution was compared with calibration curve data, which was achieved from the determination method. The obtained signals of concentrated cation solutions showed that a preconcentration factor of 250 for Ni(II), Co(II) and Zn(II), and 400 for Cd(II) can be achieved by this method.

Retention capacity of the adsorbent

The retention capacity of adsorbent was determined by the batch method. A 20 mL solution of 0.10 µg mL^{-1} of each cation at pH 4.5 was transferred into a separating funnel and 0.12 g adsorbent was added. The separating funnel was shaken vigorously for 30 min. The concentration of the cations in the filtrate was determined according to the calibration curves and then the adsorbed amount of each cation was calculated. The retention capacity (µg adsorbed cation/g adsorbent) was obtained and the results showed that the capacity factors were 102, 51.5, 7305, and 100 µg g^{-1} for Cd(II), Co(II), Ni(II) and Zn(II), respectively.

Effect of foreign ions

The effects of different cations and anions were investigated from the percentage recovery of 0.20 µg mL^{-1} of each metal ion in 10 mL of solution by the proposed method. The following ions did not interfere at a concentration of 1000 µg mL^{-1} with the preconcentration and determination of 0.20 µg mL^{-1} of the studied metal ions: K^+, SO_4^{2-}, NO_3^-, Br^-, CrO_4^{2-}, PO_4^{3-}, $S_2O_3^{2-}$, CH_3COO^-, F^-, SCN^-, $NH_4^+$and Cl^-. Hg^{2+}, MoO_4^- and Na^+ interfered at a concentration of 300 μg mL^{-1}, Sr^{2+} interfered at 20 μg mL^{-1}, Ca^{2+} interfered at 10.0 μg mL^{-1} with the determination of the studied cations but the presence of fluoride ion did not interfere up to 100 μg mL^{-1}. Mg^{2+}, Pb^{2+} and Mn^{2+} interfered at 10 μg mL^{-1} with the determination of the cations. The results indicate that high concentrations of all the tested ions did not interfere with separation and determination of the studied cations.

Analytical characteristics

Calibration graphs were constructed from measurements made under the optimum conditions described above. The calibration equations are given in Table II. The limit of detection and limit of quantification are defined as $c_{\rm LOD} = 3S_{\rm B}/m$ and $c_{\rm LOQ} = 10S_{\rm B}/m$, where $S_{\rm B}$ and m are the standard deviation of the blank and the slope of the calibration graph, respectively. To evaluate the accuracy and precision of the method, two different concentrations of each of the standard samples were repeated several times. The results are given in Table III, which shows that the relative standard deviation (*RSD*) for the determination of different concentrations of the cations was in the range 0.37–3.73 %.

TABLE II. Analytical features of the proposed method

Cation	Equation	Linear range ng mL^{-1}	*LOD*^{a} ng mL^{-1}	*LOQ*^{b} ng mL^{-1}	R^2 (n = 8)
Cd(II)	$A = 0.0094c + 0.0023$	1.00–8.00	0.17	0.56	0.9995
Co(II)	$A = 0.0031c + 0.0007$	3.00–60.00	0.51	1.70	0.9993
Ni(II)	$A = 0.0032c + 0.0009$	4.00–100.00	0.49	1.63	0.9986
Zn(II)	$A = 0.0084c + 0.0105$	0.40–50.00	0.10	0.33	0.9983

[a] Limit of detection, [b] limit of quantification

TABLE III. Accuracy and precision of the proposed method

Cation	c / ng mL^{-1}	Relative error, %	*RSD* / % (n = 5)
Cd(II)	5.00	–1.86	2.40
	50.00	0.62	2.20
Co(II)	5.00	–0.54	2.31
	50.00	–0.19	0.37
Ni(II)	5.00	2.16	3.73
	50.00	0.16	0.37
Zn(II)	1.00	1.64	2.56
	25.00	1.27	1.50

Simultaneous preconcentration

A solution (500 mL) containing 30.0, 35.0, 25.0 and 10.0 ng mL^{-1} of Cd, Co, Ni and Zn ions, respectively, was prepared and passed through the column. The metal ions were eluted with 4.0 mL of HCl solution (1.0 mol L^{-1}) and Cd, Co, Ni and Zn were determined by FAAS. The results are given in Table IV and indicate the proposed method is suitable for the simultaneous preconcentration and separation of Cd, Co, Ni and Zn and allows the determination of trace amounts of these elements by FAAS, which is a technique available in almost every laboratory.

TABLE IV. Simultaneous preconcentration of the studied cations by the proposed method

Cation	c / ng mL^{-1}	Recovery, %
Cd(II)	30.0	93.4
Co(II)	35.0	99.2
Ni(II)	25.0	92.6
Zn(II)	10.0	94.8

Analytical application

The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples of spring water and tap water with different concentrations of cations. The results are given in Table V. The accuracy and applicability of the proposed method were tested by its application to the determination of Zn and Cd in tap and spring water samples, Zn in powdered milk, Zn in multi-vitamin tablets, Ni and Zn in apple leaves, and Co in vitamin B_{12}. The results are given in Table VI and they indicate the successful applicability of the proposed method for the determination of these cations in real samples.

TABLE V. Determination of the studied cations in natural water samples by the proposed method (n = 5)

Cation	Amount of cation, µg L^{-1}				Recovery, %	
	Added		Found			
	Tap water	Spring water	Tap water	Spring water	Tap water	Spring water
Ni(II)	0.0	0.00	4.36 ± 0.21	5.54 ± 0.27	–	–
	10.00	10.00	14.60 ± 0.22	15.45 ± 0.45	102.4	99.1
	20.00	20.00	24.40 ± 0.47	25.50 ± 0.48.	100.2	99.8
Cd(II)	0.00	0.00	n.d[a]	n.d	–	–
	10.00	10.00	9.50 ± 0.46	10.73 ± 49	95.0	107.3
	20.00	20.00	19.83 ± 0.91	20.50 ± 0.66	99.2	102.5
Co(II)	0.00	0.00	n.d	n.d	–	–
	10.00	10.00	9.64 ± 0.25	10.47 ± 0.38	96.4	104.7
	20.00	20.00	19.45 ± 0.61	20.36 ± 0.47	97.3	101.8
Zn(II)	0.00	0.00	28.43 ± 0.39	10.50 ± 0.36	–	–
	10.00	10.00	38.30 ± 0.64	20.34 ± 0.45	98.7	98.4
	20.00	20.00	48.20 ± 0.57.	30.61 ± 0.81	98.9	100.5

[a] Not detected

TABLE VI. Application of the proposed method to real samples (*n* = 5)

Cation	Added, μg L^{-1}	Found, μg L^{-1}	Recovery, %
Co(II) in orange juice	0.00	7.36 ± 0.32	–
	10.00	17.09 ± 0.76	97.3
	20.00	27.43 ± 0.84	100.3
Zn(II) in apple leaves	0.00	18.30 ± 0.46	–
	10.00	28.14 ± 0.48	98.4
	20.00	37.83 ± 0.59	97.7
Zn(II) in powdered milk	0.00	25.20 ± 0.96	–
	10.00	35.05 ± 1.00	98.5
Zn(II) in multi vitamin tablets	0.00	36.80 ± 1.21	–
	10.00	46.90 ± 1.49	101.0
Ni(II) in apple leaves	0.00	4.69 ± 0.19	–
	10.00	14.28 ± 0.26	95.9
	20.00	24.27 ± 0.57	97.9
Ni(II) in orange juice	0.00	14.30 ± 0.38	–
	10.00	24.24 ± 0.55	99.4
	20.00	34.25 ± 0.49	99.8
Co(II) in vitamin B_{12}	0.00	46.22 ± 1.03	–
	10.00	55.92 ± 1.73	97.0

CONCLUSIONS

Solid–liquid extraction with microcrystalline naphthalene is an effective separation and preconcentration technique for trace elements. This proposed preconcentration method has a high enrichment factor, which opens the possibility of determining concentration levels of cations as low as sub-micro amounts. In it is suitable for the simple and accurate determination of these elements in a variety of real samples giving satisfactory results. A comparison between the proposed method and some existing methods reported for preconcentration of metal ions by the solid phase extraction method[20,22–26] is given in Table VII. As Table VII shows, the proposed method exhibits a comparable capacity level, a lower detection limit and a wider linear range, as well as being a convenient, safe, simple, rapid and inexpensive method for the determination of trace quantities of the studied cations in real samples giving satisfactory results.

TABLE VII. Comparison of the proposed method with some other SPE methods

Matrix	Detection limit, μg L^{-1}	Application	Ref.
Modified silica gel with aminothioamidoanthraquinone	Ni = 2.90 Co = 0.95 Cd = 1.95	Natural waters	22
Cellulose functionalized with 8-hydroxyquinoline	Zn = 0.84 Ni = 1.61 Co = 1.09 Cd = 2.59	Natural waters and Co in drugs	23

TABLE VII. Continued

Matrix	Detection limit, μg L^{-1}	Application	Ref.
o-Aminobenzoic acid-functionalized XAD-4 copolymer resin	Zn = 2.50 Ni = 5.00 Co = 6.50 Cd = 2.50	Natural waters	24
4,6-Dihydroxy-2-mercaptopyrimidine (DHMP) loaded on activated carbon	Ni = 3.80 Co = 3.40	Natural waters and spinach	25
Glycerol–silica gel	Co = 1.00	Natural waters	26
2-{[1-(2-Hydroxynaphthyl)-methylidene]amino}-benzoic acid (HNMABA)	Zn = 5.00 Ni = 20.00 Co = 8.00 Cd = 10.00	Natural waters, Co in B_{12} vitamin, Zn in powdered milk	20
Modified microcrystal naphthalene with 2,4,6-trimorpholino-1,3,5-triazin	Zn = 0.10 Ni = 0.49 Co = 0.51 Cd = 0.17	Natural waters, Co in B_{12} vitamin, Zn in powdered milk, Zn and Ni in apple leaves	Proposed method

ИЗВОД

ПРЕКОНЦЕНТРАЦИЈА Co, Ni, Cd И Zn НА АДСОРБЕНТУ НАФТАЛЕН–2,4,6-ТРИМОРФОЛИНО-1,3,5-ТРИАЗИНА И ОДРЕЂИВАЊЕ ПЛАМЕНОМ АТОМСКОМ АПСОРПЦИОНОМ СПЕКТРОМЕТРИЈОМ

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За одређивање трагова Co, Ni, Cd и Zn пламеном атомском апсорпционом спектрометријом развијена је метода преконцентрисања, која се заснива на ретенцији катјона на стубу адсорбенса нафтален–2,4,6-триморфолино-1,3,5-триазина. Адсорбовани катјони се потом елуирају са колоне помоћу хлороводоничне киселине, а Co, Ni, Cd и Zn одређују пламеном атомском апсорпционом спектрометријом. Испитивани су оптимални услови екстракције и елуције. Испитиван је такође и ефекат страних јона на преконцентрацију. Постигнут је фактор преконцентрисања од 250 за Co(II), Ni(II), Zn(II) и 400 за Cd(II). Детекционе границе методе за Co(II), Ni(II), Cd(II) и Zn(II) износе: 0.51, 0.49, 0.17 и 0.10 ng mL^{-1}, а добијена је релативна стандардна девијација (*RSD*) за Co, 0,37–2,31 %, за Ni, 0,37–3,73 %, за Cd, 2,20–2,40 % и Zn, 1,50–2,56 %. Метода је успешно примењена за одређивање Co, Ni, Cd и Zn у неколико различитих реалних узорака.

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